2D Materials Technical Group
Room 303 - Session 2D+EM-MoM

2D Materials: Electronic, Mechanical, and Optical Properties

Moderator: Sarah Haigh, University of Manchester, UK

8:20am **2D+EM-MoM-1 Scanning Tunneling Spectroscopy of 2d Electronic Materials – from Monolayers to Complex Heterostructures***, Chih-Kang (Ken) Shih,* Department of Physics, The University of Texas at Austin **INVITED**

Atomically thin, single-crystalline 2D electronic materials have recently emerged, offering a remarkably wide range of building blocks of nanostructures, ranging from metals (e.g. graphene), large gap insulators (BN), to semiconductors (transition metal dichalcogenides and black phosphorous). One key advantage of these van der Waals materials lies in the flexibility of stacking different types of materials to form heterostructures, providing a design platform for achieving novel device functionality.With the ability to probe electronic structures with atomic resolution, scanning tunneling microscopy/spectroscopy (STM/S) has played a crucial role in advancing our understanding of the electronic structures of 2D electronic materials and their heterostructures.

In this talk, I will present a comprehensive combination of different modes of scanning tunneling spectroscopy beyond the conventional constant height tunneling spectroscopy.I will use a few examples to show how such comprehensive investigations provide an in-depth understanding of the electronic structure evolutions from monolayer to complex heterostructures (including moire superlattices and beyond).

9:00am **2D+EM-MoM-3 Strain and Charge-Transfer at the Device Relevant Interface Between Single Layer MoS$_2$ and Gold: In-Situ Raman Study***, **Stephanie Lough**, J. Thompson,* University of Central Florida*; R. Rao,* Air Force Research Laboratory*; M. Ishigami,* University of Central Florida

Next-generation technology nodes will reach the sub-nanometer range via the introduction of ultra-thin and short-channel devices. Traditional semiconductors such as silicon (Si) suffer from device-degrading effects such as roughness-induced scattering or short-channel effects at this size scale. Two-dimensional transition metal dichalcogenides (2D TMDs) do not suffer from these effects. Therefore, they could be candidate materials for the next-generation nodes. Single-layer molybdenum disulfide (SL-MoS$_2$) devices exhibit carrier mobilities exceeding that of Si-based devices with similar thicknesses, but suffer from high contact resistance, reducing their utility in device technologies. Our previous results show that the physics at the interface between SL-MoS$_2$ and gold (Au) is complex and that thermal annealing (TA) under certain conditions could lead to lowered contact resistance by direct chemical hybridization and/or doping.

We performed detailed *in situ* Raman spectroscopy of exfoliated SL-MoS$_2$ on Au during and after annealing at temperatures ranging from room temperature (RT) to 300 °C in Ar. This revealed doping and mechanical strain induced in the SL-MoS$_2$ by the underlying Au layer. Using peak deconvolution, we identify the presence of two sub-peaks comprising each of the well-known MoS$_2$ fingerprint peaks (A$_{1g}$ and E$_{2g}$), consistent with previous studies. The ratio of intensities and relative shifting of the sub-peaks indicates a strong interaction between the MoS$_2$ and the Au layer, which could be due to hybridization between the MoS$_2$/Au. The well-known Si peak at 520 cm^{-1} diminished as the temperature was increased. As such, we conclude that the MoS$_2$ delaminated from the Au layer at elevated temperatures. The coupling between the Au and MoS$_2$ was reestablished upon cooling to RT after annealing as indicated by the reappearance of the Si peak. Further, as the MoS$_2$ was annealed at progressively higher temperatures, it became increasingly electron-doped by the Au with the strain remaining constant at 1% in tension.

Our data shows that TA and cooling of the interface between SL-MoS$_2$ and Au produces stronger coupling, suggesting an increased level of hybridization between the MoS$_2$/Au. The hybridization results in a nearly charge-neutral MoS$_2$-Au heterostructure, indicating that TA could be a path toward achieving intrinsic contacts for device applications. Finally, the strain between these surfaces remains unchanged upon annealing, implying that annealing promotes stronger coupling between SL-MoS$_2$/Au, without increasing strain. Thus, annealing presents an ideal route towards generating charge-neutral MoS$_2$/Au contacts with minimal interfacial strain.

9:40am **2D+EM-MoM-5 Optical and Electrical Investigation into HfS$_2$ Oxidation Mechanisms***, I. Chirca, A. Almutairi, **Stephan Hofmann**,* University of Cambridge, UK

2D layered materials are emerging as potential candidates for energy-efficient conventional devices, as well as new memristive and neuromorphic device architectures. The focus to date has been on new semiconductor materials, particularly transition metal dichalcogenides (TMDs). Yet, feasible technology, especially in the optoelectronics field, relies on clean interfacing, particularly to a suitable dielectric. HfS$_2$ is one of the few materials that offer a native oxide conversion pathway, previously demonstrated in various experimental set-ups. Here we explore the oxide formation kinetics on HfS$_2$ layers and the achievable interface quality in HfS$_2$/HfO$_x$ devices.

To accomplish this, we employ several HfS$_2$ oxidation methods, from thermal to plasma and pulsed water vapour exposure, and compare the electrical switching behaviour of MIM and MIS device structures while characterizing their dielectric properties via spectroscopic ellipsometry. The oxidative behaviour of HfS$_2$ and the buried HfS$_2$/HfO$_x$ interface are observed optically using a combination of reflectance spectra and ellipsometric modelling. In order to determine the viability of such an approach for device fabrication, the natively grown HfOx is benchmarked against ALD grown hafnia.

Thus, our study is a step towards finer control of interface quality in HfS$_2$/HfO$_2$ devices through calibration of the native oxidation pathway.

10:40am **2D+EM-MoM-8 Electrical Characterization of β-In$_2$Se$_3$ Thin Films Synthesized via Molecular Beam Epitaxy***, **Cooper Voigt**,* Georgia Institute of Technology, USA*; B. Wagner,* Georgia Tech Research Institute*; E. Vogel,* Georgia Institute of Technology, USA

β-In$_2$Se$_3$ is a two-dimensional semiconductor that has long been believed to have a centrosymmetric crystal structure. α-In$_2$Se$_{3-}$ is a closely related, two-dimensional, ferroelectric semiconductor [1,2] and has shown promise in low-power, neuromorphic electronic devices [3,4] and transistors [5]. Much work has been devoted to exploring the performance of α-In$_2$Se$_3$ in electronic devices due its unique combination of properties; however large-area thin-film synthesis of α-In$_2$Se$_3$ has not been established. Since 2018 there have been reports of polarization in a β'-In$_2$Se$_3$ phase arising from displacements of the center layer selenium atoms [6–8]; however, these studies have not included any fabrication and characterization of electronic devices. One study from 2018 claims deposition of large-area, ferroelectric In$_2$Se$_{3-\,-}$thin-films via MBE; however, it is difficult to distinguish the α from β phase by the Raman spectra and TEM micrographs provided. Earlier this year, ferroelectric behavior was reported in transistors fabricated from metal-organic chemical vapor deposition (MOCVD) β-In$_2$Se$_3$ [9]. If β-In$_2$Se$_3$ does truly exhibit ferroelectric ordering, it would be a very promising material for low-power transistors and neuromorphic electronic devices.

In this study, we demonstrate molecular beam epitaxy (MBE) synthesis of β-In$_2$Se$_3$ thin-films and electrical characterization of β-In$_2$Se$_3$ transistors. We link processing parameters such as synthesis substrate temperature, and Se/ In flux ratio to resulting β-In$_2$Se$_3$ electrical properties and device performance.

[1]M. Küpers, et. al., Inorg. Chem. **57**, 11775 (2018).

[2]J. Xiao, et. al.,Phys. Rev. Lett. **120**, 227601 (2018).

[3]B. Tang, et. al., ACS Appl. Mater. Interfaces **12**, 24920 (2020).

[4]L. Wang, et. al., Adv. Funct. Mater. **29**, 1 (2019).

[5]M. Si, et. al., Nat. Electron. **2**, 580 (2019).

[6]S. Li, et. al., Sci. Adv. **4**, eaar7720 (2018).

[7]F. Zhang, et. al., ACS Nano **13**, 7, 8004–8011 (2019).

[8]Z. Zhang, et. al., Adv. Mater. **34**, (2022).

[9]S. Lee, et. al., 2D Mater. **9**, 025023 (2022).

[9]S. M. Poh, et. al., Nano Lett. **18**, 6340 (2018).

[10]S. Lee, et. al., 2D Mater. **9**, 025023 (2022).

11:00am **2D+EM-MoM-9 Mechanics of Pristine and Pyrolysed Carbon Nanomembranes (CNMs)*, André Beyer*,** *F. Paneff, X. Zhang, A. Gölzhäuser,* Bielefeld University, Germany

The discovery of graphene has triggered a great interest in inorganic as well as molecular two-dimensional (2D) materials. Over the last years, a remarkable progress in the mechanical characterization of free-standing 2D materials was achieved [1]. In this contribution, we compare mechanical characterization of membranes by means of bulge tests and nanoindentation experiments. The bulge test was found to be a reliable method, which is suited for any kind of membrane. Nanoindentation was found to be suited for a number of membrane types while others entail a high risk of rupturing. With these two methods, a number of different pristine and pyrolysed carbon nanomembranes (CNMs) were examined. CNMs form by irradiation induced cross-linking of molecular layers e.g. self-assembled monolayers of terphenylthiol (TPT) molecules. Cross-linking between adjacent molecules was induced by low energy electron exposure. Pyrolysis of CNMs is known to yield nanocrystalline graphene, which is in agreement with the observed stiffening of the membranes. Part of this contribution will be devoted to a comparison of different approaches to analyse pressure-deflection measurement data of bulge tests. A sum of the limits approach is suggested as most precise method that employs an analytic pressure-deflection expression for determining the mechanical properties.

[1] X. Zhang and A. Beyer, Nanoscale 13, 1443 (2021).

11:20am **2D+EM-MoM-10 Interplay between Electronic, Magnetic and Mechanical Properties in 2D Crystals*, Young-Woo Son*,** Korea Institute for Advanced Study, Republic of Korea **INVITED**

In this talk, I will discuss unique aspects of two-dimensional crystals that show intertwined nature between electronic, magnetic, optical properties and structural distortions. First, when a transition metal dichalcogenide (TMD) overlay another TMD forming moire superlattices, the softer one deforms itself to conform the mismatched lattices between them so that the unique whirlpool shaped lattice distortions occur [1]. I will show our recent theoretical and computational study shown that the pair of torsional distortions with the opposite chirality introduce characteristic fuzziness in Raman spectroscopy and interesting excitonic signatures irrespective twist angles. agreeing with experiments very well [1]. Second, a newly synthesized 2D carbon allotrope by linking biphenylene molecules is shown to host interesting type II Weyl fermions together with a possible magnetic orderings [2]. With external mechanical perturbations, our first-principles calculations including self-consistent extended Hubbard interactions reveal the anomalous Lifshitz transition of pair annihilations with merging onto zone-center saddle point.

[1] J. Kim, E. Ko *et al.*, *Nat. Mater.* (2022). https://doi.org/10.1038/s41563-022-01240-2

[2] Y.-W. Son *et al.*, *Nano Lett.***22**, 3112 (2022).

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)

---

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

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

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

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**[1],* 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. 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 NS2+AS+EM+SS-MoM

Quantum Based Sensors and Metrology

Moderator: Nikolai Klimov, National Institute of Standards and Technology

10:40am **NS2+AS+EM+SS-MoM-8 Interfacing Biomolecules with Coherent Quantum Sensors***, **Peter Maurer**,* University of Chicago **INVITED**

Quantum optics has had a profound impact on precision measurements, and recently enabled probing various physical quantities, such as magnetic fields and temperature, with nanoscale spatial resolution. In my talk, I will discuss the development and application of novel quantum metrological techniques that enable the study of biological systems in a new regime. I will start with a general introduction to quantum sensing and its applications to nanoscale nuclear magnetic resonance (NMR) spectroscopy. In this context, I will discuss how we can utilize tools from single-molecule biophysics to interface a coherent quantum sensor with individual intact biomolecules, and how this could eventually pave the way towards a new generation of biophysical and diagnostic devices.

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.

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

---

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

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. Fe_2MnGe, layered $Fe_{1.5}TiSb$, $Co_{1.5}TiSn$). 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 $L2_1$ and $C1_b$ 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.

Applied Surface Science Division
Room 320 - Session AS+CA+EL+EM+LS+SE+SS-MoA

Quantitative Surface Analysis

Moderators: Jordan Lerach, PPG Industries, **Hong Piao**, FUJIFILM Electronic Materials USA., Inc.

1:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-1 Hard Targets: Developing Tools for Quantitative HAXPES***, **David Cant**,* National Physical Laboratory, UK **INVITED**

'Soft' x-ray based XPS, using aluminium or magnesium anodes, has been a workhorse of surface analysis labs for decades. Over this time, substantial efforts have been made in the development of tools such as sensitivity factors, transmission function corrections, physical parameter databases, simulation software, interpretation methods, and more. Thanks to the existence of such tools, the data obtained from 'soft' XPS, with careful analysis, can provide a strong, quantitative understanding of samples in terms of the relative concentration of elements and their chemistry within the topmost ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, XPS of materials beyond this topmost region of the surface would require either destructive depth profiling of the sample or the use of synchrotron light sources; the former carries its own metrological challenges, as well as ruining a sample, while the latter introduces a plethora of complexities which render calibration difficult. However, recent developments in the design of instruments utilising higher-energy x-ray anodes have begun to make HAXPES instruments more readily available in the lab. This allows far more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples with overlayers beyond the ~10 nm limit of 'soft' XPS. Yet with new instruments come new issues; transmission function calibrations that work for the 0 - 1400 eV energy range are not much use for spectra that stretch some KeV beyond, and relative sensitivity factors for each new photon energy and instrument geometry are needed, particularly given the cornucopia of new core levels made available, and the breadth of sensitivity at higher photon energies.

Here we discuss progress towards more quantifiable XPS and HAXPES measurements. A method for the calculation of theoretical sensitivity factors is described, applicable to instruments of any geometry for x-ray sources in the energy range 1.5 - 10 keV, and their validity for depth-profiling of samples well beyond the depths achieved by aluminium sources is demonstrated. We discuss developments in straightforward transmission-function calibrations of standard aluminium sources by the use of a mathematically-defined reference spectrum, as well as progress towards transmission calibration of higher energy sources for which reference spectra do not yet exist. From these developments, the possibility of a 'universal' calibration and sensitivity scheme for both lab- and synchrotron-based HAXPES systems at a range of energies is proposed.

2:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-3 Process-Induced Reactions in Interfaces of High-K/Metal Gate Stacks Studied Using HAXPES***, **Thierry Conard**, A. Vanleenhove, F. Mascarenhas, I. Hoflijk, I. Vaesen,* IMEC, Belgium

While high-energy photoemission has been in use for decades, it has remained mostly confined to synchrotron radiation facilities. Synchrotron beamlines allow a large flexibility regarding measurement conditions and set-up but are inconvenient in the framework of technological developments, where routine analysis of material systems is needed. The recent availability of performant lab-scale high-energy photoemission spectrometers [1,2,3] alleviate these beamline limitations and thus allow to investigate technological relevant models.

In this presentation, we will demonstrate the potential of HAXPES lab-scale systems regarding application in the semiconductor industry, and more specifically regarding the chemical analysis of interfaces. We will demonstrate the investigation of modifications in layer chemistry of buried layers in multi-layer high-k/metal gate stacks upon thermal treatments. Annealing is one of the critical stages during manufacturing of gate stacks and chemical modification at interfaces play a major role in device performance. With this presentation we will present results on simple stacks such as TiN/HfO$_2$/SiO$_2$/Si as well as more complex stacks such as TaN/TiAl/TiN/HfO$_2$/SiO$_2$/Si or W/TiN/HfO$_2$/SiO$_2$/Si. Results will be presented obtained both with Cr Kα (5.4 keV) and Ga Kα (9.25 keV) HAXPES. The respective advantages of these two energies will be discussed in terms of chemical identification, sensitivity and quantification.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the HAXPES Lab instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

References

[1]https://www.ulvac-phi.com/en/products/xps/quantes/

[2]https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument

[3]https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab

2:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-4 Quantification and Reporting of XPS Data Taken Under Near Ambient Pressure Conditions – Chances and Challenges in Acquision Speed, Beam Damage, Sensitivity, Reliability, Reproducibility and Repeatability***, P. Dietrich, **Andreas Thissen**,* SPECS Surface Nano Analysis GmbH, Germany

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.

3:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-5 The Modern Spectrometer – Reliable, Repeatable and Relatable***, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*; **Christopher Moffitt**,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Limited, UK

The outlook of the XPS community has changed significantly in the last decade. The technique has seen constant steady growth due to the rise in surface-based material research – energy storage and harvesting are two such disciplines. This growth of new first-time users needs to be considered, as does the way in which faculties manage centralised analytical facilities. This has led to a change in the philosophy of the workflow of an XPS spectrometer and how the user interacts with the "tool". In this modern era of devolved data and non-expert users the spectrometer itself needs to be reliable, repeatable and relatable. Reliable

– delivers on the promise, Repeatable – consistency with data acquisition and processing, Relatable – simple, easy-to-use, non-expert. This new philosophy creates new challenges for manufacturers who need to deliver the best spectrometer for this new market whilst at the same time maintaining the expectations and beliefs of the traditional analyst.

The discussion will focus on defining the issues of the current XPS outlook and providing practical, workable solutions. The following topics, when combined together, will illustrate the holistic design principles of a modern spectrometer: Simplified workflow, standard methods, automated routines, parameter logging, calibrated and up-to-date sensitivity factors, processing operators, data output and report generation.

3:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-6 Modulation with Atomic Number of the Shirley Background of the Photoemission Spectra of Transition Metals***, **Alberto Herrera-Gomez**, D. Guzman-Bucio,* CINVESTAV-Queretaro, Mexico*; D. Cabrera-German, M. Mayorga-Garay, O. Cortazar-Martinez, J. Torres-Ochoa, A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico*; M. Gonzalez Reyna ,* UNAM-Mexico*; V. Crist,* XPS Library*; C. Ospina-Ocampo,* Cinvestav-Unidad Queretaro, Mexico

The 2*p* photoemission spectra of the first-row pure transition metals are similar enough to each other to display a meaningful progression, through the row, of the characteristics of the peaks and background [1]. The same goes for the 3*d* spectra of the second-row pure transition metals [2]. In addition, there are similarities between the behavior of the peak and background parameters of these two rows, such as the dependence of the intensity of the Shirley background with atomic number. The Shirley background is largest for the first column (3B column of the periodic table), decreases to a local minimum to then rise again to a local maximum on the seventh column (8B). The large value of the Shirley background for the first column elements is correlated with the large asymmetry of the main peak and the presence of strong intrinsic plasmons. This correlation might be due to a similar physical origin [3] The local maximum in the 8B column coincides with the maximum of permutations of the valence band, as previously pointed out by Castle and Salvi [4]. The physical mechanism of these phenomena will be discussed.

[1] D. Cabrera-German, G.-B. Dulce-Maria, M. Mayorga-Garay, O. Cortazar-Martinez, J.-A. Torres-Ochoa, A. Carmona-Carmona, A. Herrera-Gomez, Peak and background parameters of the 2p core level of the pure first row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[2] D.-M. Guzman-Bucio, A. Carmona-Carmona, M.A. Gonzalez-Reyna, A. Herrera-Gomez, Peak and background parameters of the 3d core level of the pure second row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[3] A. Herrera-Gomez, D. Cabrera-German, A.D.A.D. Dutoi, M. Vazquez-Lepe, S. Aguirre-Tostado, P. Pianetta, D. Nordlund, O. Cortazar-Martinez, A. Torres-Ochoa, O. Ceballos-Sanchez, L. Gomez-Muñoz, L.G.M. Herrera-Gomez, Alberto., Dagoberto Cabrera-German., Anthony D. Dutoi., Milton Vazquez Lepe., Servando Aguirre-Tostado., Piero Pianetta., Dennis Nordlund., Orlando Cortazar-Martinez., Alejandro Torres-Ochoa., Oscar Ceballos-Sanchez., Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge, Surf. Interface Anal. 50 (2018) 246–252. https://doi.org/10.1002/sia.6364.

[4] J.E. Castle, a. M. Salvi, Interpretation of the Shirley background in x-ray photoelectron spectroscopy analysis, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 19 (2001) 1170. https://doi.org/10.1116/1.1378074.

4:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-8 Thin Film Analysis by XPS: Quantitative Modeling of Sputtering and Depth Profile Data***, **Lev Gelb**, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both compositional profiles and sputtering parameters from XPS depth-profiles of multilayer films. Depth-profile data are routinely processed to provide "fractional composition vs ion dose" profiles, but such profiles suffer from significant drawbacks: they are constructed assuming that the sample is homogeneous in the probed region, which is not true near interfaces, and it is not normally possible to precisely convert between units of ion dose and depth.

Our approach is to first construct analytical models for both the sample structure and for the erosion process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) most consistent with the observed apparent fractional composition profiles. This is done numerically, by comparing simulated and observed apparent composition profiles in a maximum-likelihood framework using an evolutionary optimization algorithm. The only required inputs to the calculation are the "fractional composition" profiles (above) and models for the inelastic mean free paths (IMFPs) for each tracked peak.

We demonstrate the basic idea by analysis of using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. Small deficiencies in the structure or sputter model do not strongly affect the extracted compositional profiles, while errors in the IMFPs used have much larger effects. We then discuss promising results obtained from the analysis of experimental data from some well-characterized samples. Finally, we discuss improvements and extensions of this modeling/analysis framework. The sputtering model can be extended to include in-sample mixing and chemical reactions. The scheme can also be extended to use complete spectra as input.

4:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-9 Understanding and Controlling Sample Degradation on Modern XPS Spectrometers***, **David Morgan**,* Cardiff University, UK

As XPS systems become ever more user-friendly, with "load-point-click-report" type automated analysis possible, the expertise in understanding samples, their handling and ultimately identifying and dealing with experimental artefacts is slowly eroding.

It has been previously shown that developments in the charge compensation methodology employed, especially the use of dual electron-ion compensation systems, can cause significant damage to a range of inorganic and organic materials [1,2] and in some cases a synergistic effect from the x-rays on the degradation rates can be observed.

Herein, the degradation effect using x-rays and a dual beam neutraliser are explored and discussed, and a delineation of the effects from both neutraliser and the x-rays on a series of polymeric, organic and inorganic materials are presented, together with methodologies to mitigate, or at the very least minimise, such analysis induced damage and propose that which we believe to be a better way of estimating sample damage on a per-system basis than those previously published [3].

[1] L. Edwards, P. Mack and D. J. Morgan, "Recent advances in dual mode charge compensation for XPS analysis". Surface and Interface Analysis, 51 (2019) 925-933
[2] R. McLaren, G. Owen and D. J. Morgan, "Analysis Induced Reduction of a Polyelectrolyte", Results in Surfaces and Interfaces, (2021) 100032
[3] G. Beamson and D. Briggs, "High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database," Wiley, Chichester, 1992.

4:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-10 XPS Intensity Calibration and Validation Using Polyethylene and Ionic Liquids***, **Benjamen Reed**,* National Physical Laboratory (NPL), UK*; J. Radnik,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Shard,* National Physical Laboratory (NPL), UK

For quantitative X-ray photoelectron spectroscopy (XPS) analysis, it is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument. There is a huge variability of transmission functions between different laboratories and instruments, as well as different acquisition parameters for the same instrument. For comparable and reproducible analyses, there is a necessity for a standardised method of intensity calibration and validation.

For intensity calibration, the simplicity of polyethylene's inelastic background can be described by a mathematical function that can be easily reproduced, is continuous, and noise-free. Instrument geometry must be considered due to the anisotropic emission of photoelectrons and the polarization of monochromated x-rays in many commercial XPS instruments. We therefore present geometry-corrected reference spectra of polyethylene for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Polyethylene does not require in-situ sample preparation needing only to be scraped with a scalpel before measurement, making it a suitable method for instruments without an ion-sputtering source. VAMAS study A27 determined that over a kinetic energy range of 180 eV to 1500 eV, intensity calibration with polyethylene deviates by ±6.5% compared to previous NPL method using precious metals. Deviations less than 5%, and as low as 1%, are attainable with careful data acquisition from well-maintained instruments. This intensity calibration method is now being developed as an international standard under the auspices of ISO TC201 "Surface Chemical Analysis".

Once an instrument has been intensity corrected, it is good practice to validate the calibration by measuring a homogeneous sample of known composition. Ionic liquids have several notable properties that make them an ideal material for XPS analysis. Ionic liquids exhibit a high degree of lateral and depth homogeneity, are UHV compatible, and have well-defined stoichiometries. When deposited in recessed sample holder, the meniscus of an IL will be perfectly flat meaning that there are no contributions from sample topographic effects. 1-propyl-3-methyl-imidazolium-bis(trifluoromethyl sulfonyl)imide (Solapur®) is one such IL candidate, with core levels up to ~800 eV binding energy, making it apt for verifying the quantification of light elements, especially for organic materials. Here we present spectra for Solapur® ionic liquid and discuss how they may be used to validate an XPS intensity calibration.

Nanoscale Science and Technology Division
Room 304 - Session NS1+AS+EM-MoA

Correlative Microscopy for Nanoscale Characterization

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, **Georg Fantner**, EPFL, Switzerland

1:40pm **NS1+AS+EM-MoA-1 Large Volume 3D Biological Imaging with Electron and Cryo-Super-Resolution Microscopy***, **Harald Hess**,* HHMI, Janelia **INVITED**

Volume or 3D electron microscopy continues to expand its potential for imaging ever larger biological entities while preserving a best compromise step edge isotropic resolution of 5-10 nm. This was driven by the challenge of imaging the entire fly brain in sufficient detail for extracting the circuitry of connectome. While the resolution is not of the standards of TEM's, such resolution is of unique value when it encompasses whole cells and complete tissues.We will review the capabilities of FIB-SEM, with ~100 micron sized volumes. Numerous examples can be browsed on openorganelle.com . A cryogenic protocol involving sample vitrification, cryogenic imaging by structured illumination or by photoactivated localization microscopy then followed by staining and resin embedding can then produce the sample suitable for further FIBSEM imaging. This effectively adds protein location information as a color to the 3D EM image. Likewise, several examples correlating specific proteins in the nucleus, on membranes, on and defining organelles and vesicles. Prospects of future challenges are discussed. We will also describe a system capable of imaging volumes approaching 1 mm^3 It is based on Ion Beam Etching and Milling with a Multi beam Scanning Electron MicroscopeIBEaM MSEM.

2:20pm **NS1+AS+EM-MoA-3 The Role of SnO$_2$ Processing on Ionic Migration in Multi-Halide Perovskites***, **Holland Hysmith**,* University of Tennessee Knoxville*; S. Park,* National Renewable Energy Laboratory*; A. Ievlev, Y. Liu,* Oak Ridge National Laboratory*; K. Zhu,* National Renewable Energy Laboratory*; M. Ahmadi,* University of Tennessee Knoxville*; J. Berry,* National Renewable Energy Laboratory*; O. Ovchinnikova,* Oak Ridge National Laboratory

Moving towards a future of efficient, accessible, and less carbon reliant energy devices has been at the forefront of energy research innovations for the past 30 years. Multi-halide perovskite (MHP) thin films have gained significant attention due to their flexibility of device applications and tunable capabilities for improving power conversion efficiency.[1] Many behavioral aspects to MHP's are thoroughly investigated: functionality of grain boundaries, recombination effects, ionic migration patterns, and hysteresis.[2-4]

Chemical Vapor Deposition (CVD) is a widely used technique for thin film coatings due to its ability for producing high volume batches of MHP's with larger grain sizes, fewer defects, and fewer grain boundary formations.[5-6] Additionally, nanoparticle processing has been applied to induce enlargement of grain boundaries, showcasing larger current signals than its MHP counterparts.[7] Therefore, how does common substrate processing techniques (i.e. CVD, nanoparticles, hybrid) influence the behavior of MHP phenomenon such as ion migration and grain boundary formation? Speculated as inducing ionic recombination and driving I-V hysteresis in MHP's, understanding how chemistry can be tuned to reduce such effects would be optimal.[8-9]

We demonstrate how a hybrid approach of CVD and nanoparticle SnO$_2$ substrate processing significantly improves the performance of (FAPbI$_3$)$_{0.97}$(MAPbBr$_3$)$_{0.03}$ perovskites in comparison to each technique utilized on its own. As shown in **Figure 1**, higher performing hybrid devices exhibit fused grain boundary formations, not seen in exclusive CVD or nanoparticle devices. Conductive Atomic Force Microscopy (c-AFM) was used to track fused boundary locations and differentiate them from topographic features. Such fusing behavior has been previously observed to showcase higher counts of current and reduce defects such has halide vacancies.[7]

In summary, to understand the chemistry behavior with respect to each device interface, Time of Flight Secondary Ionization Mass Spectrometry (ToF-SIMS) depth profiling was applied. Demonstrated in **Figure 2**, migration of K$^+$, Na$^+$, Ca$^+$, FA$^+$, MA$^+$ was found in hybrid devices, in addition to Ca$^+$ and Na$^+$ clustering on the perovskite/air layer. Salt clustering could be correlated to the fusing effect demonstrated in the surface morphology imaged in c-AFM. Presence of K$^+$ has shown to reduce defects driven by alkali iodides like NaI$^-$ and Ca$^+$ can help with enlarging the bandgap layer in studies where Ca+ was used to replace Pb$^+$.[10-11] Furthermore, reduced separation between positive ion such as MA$^+$ and FA$^+$ from negative ions can decrease the potential responsible for I-V hysteresis.[12]

2:40pm **NS1+AS+EM-MoA-4 Nanoplastic Arrays – from Chaotic Measurements to New Order***, A. Madison, D. Westly, R. Ilic, C. Copeland, A. Pintar, C. Camp, J. Liddle, **Samuel M. Stavis**,* National Institute of Standards and Technology (NIST)

Nanoplastic particles are ubiquitous contaminants of the environment, and their unknown hazards are of deepening concern. Optical microspectroscopy is essential to elucidate the structure–property relationships of nanoplastic particles. However, a lack of standards that are fit for purpose limits the reliability of such measurements, resulting in a growing spate of chaotic reports. In particular, the default standard of a colloidal suspension has disadvantages, with sample preparation typically resulting in disordered arrays of nanoparticles with uncontrolled sizes on imaging substrates. Moreover, existing nanoplastic standards can have broad and asymmetric distributions of optical properties. This issue confounds inference of dimensional properties and requires further study.

Optical microspectroscopy often involves contrast from Rayleigh scattering, fluorescence emission, and Raman scattering to detect, quantify, and identify nanoplastic particles. Numerous issues limit accuracy, including optical responses that vary with nanoparticle dimensions and imaging systems that present aberration effects. These issues require standards that provide reference values of dimensional, optical, and positional properties. The latter issue is unexplored, motivating a new order of microscopy standards.

We introduce the concept of the nanoplastic array, addressing these issues. This prototype standard enables calibration, correction, and correlation of image data from multiple instruments, improving the accuracy of microspectroscopy measurements. To prove the concept, we fabricate nanoplastic arrays in nanoscale films of phenolic resin by electron-beam lithography, including both fluorescent dopants and sorbents to study optical properties that are indicators of chemical sorption and resulting hazards.

Our nanoplastic arrays feature three types of nanostructures. The simplest is a uniform film, enabling correction of non-uniform irradiance for the accurate analysis of fluorescence intensity, and providing reference spectra for Raman measurements. Building in complexity, arrays of uniform pillars provide reference dimensions and positions to correlate and calibrate multiple imaging modes. Finally, and most complex, variable pillar arrays facilitate measurements of optical properties as a function of dimensional properties, with fine gradations of pillar diameter enabling quantification of the limits of detection.

Nanoplastic arrays will enable new accuracy and reliability in optical microspectroscopy, advancing the quantitative study of nanoplastic contaminants to transform unknown hazards into known quantities.

3:00pm **NS1+AS+EM-MoA-5 Development of Nanoendoscopy-AFM for Visualizing Intracellular Nanostructures of Living Cells***, **Keisuke Miyazawa**,* Kanazawa University, Japan*; M. Penedo,* EPFL, Switzerland*; N. Okano, H. Furusho, T. Ichikawa, M. Shahidul Alam, K. Miyata,* Kanazawa University, Japan*; C. Nakamura,* AIST, Japan*; T. Fukuma,* Kanazawa University, Japan

Atomic force microscopy (AFM) is the only technique that allows label-free imaging of nanoscale biomolecular dynamics, playing a crucial role in solving biological questions that cannot be addressed by other major bioimaging tools (fluorescence or electron microscopy). However, such imaging is possible only for systems either extracted from cells or reconstructed on solid substrates. Thus, nanodynamics inside living cells largely remain inaccessible with the current nanoimaging techniques. Here, we overcome this limitation by the nanoendoscopy-AFM, where we fabricate a needle-like nanoprobe (diameter < 200 nm, length > 500 nm) made of Sillicon or Carbon, and insert it into a living cell directly in order to measure a force curve, and visualize 2D or 3D internal structures of living cells by the measured 3D force applied to the tip during three-dimensional tip scanning. By using this method, we measured the 3D force image of a human cancer cell (HeLa). The result clearly shows the nucleus in the living cell. In addition, our results using the developed nanoendoscopy-AFM showed undetectable changes by the previous methods such as actin fiber three-dimensional (3D) maps, and 2D nanodynamics of the membrane inner scaffold in the living cells. Unlike previous AFM methods, the nanoprobe directly accesses the target intracellular components, exploiting all the AFM capabilities, such as high-resolution imaging, nanomechanical mapping, and molecular recognition. These features of the nanoendoscopy-AFM should greatly expand the range of intracellular structures observable in living cells, and contribute to the various life science research fields.

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

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL+AS+EM-TuM

Optical Characterization of Thin Films and Nanostructures

Moderators: Tino Hofmann, University of North Carolina at Charlotte, **Mathias Schubert**, University of Nebraska - Lincoln

8:00am **EL+AS+EM-TuM-1 Femtosecond Time Resolved Pump-Probe Spectroscopic Ellipsometry – Applications and Challenges*, Rüdiger Schmidt-Grund,*** TU Ilmenau, Germany **INVITED**

I will introduce the method fs-time resolved pump-probe spectroscopic ellipsometry (TSE), recently developed by us [1], as a mighty instrument to investigate the electronic structure and lattice properties of materials in great detail, going beyond many established experimental methods. TSE measures the transient complex dielectric function after optical excitation of charge carriers, which gives us a powerful tool to probe band structure, joint-density of states and transition matrix elements in various regions of the Brillouin zone as well as dynamic phenomena like carrier-carrier scattering, carrier-phonon scattering, excitation, and relaxation. As all this properties and effects in general also depend on the transient carrier density, analysis of TSE data provides vast knowledge about the electronic structure dynamics of materials, in particular valuable for fundamental theory approaches.

After excitation with an intense pump-laser, electrons and holes are created in the conduction and valence bands, respectively. These excited carriers then can scatter within the Brillion zone and interact with the lattice. This leads to dynamic carrier distribution changes in energy and momentum within time scales of fs up to ns or longer. The ellipsometry probe pulse then feels the actual energetic charge carrier distribution at a given delay time step, as expressed in changes of the dielectric function due to Pauli blocking or enabling of new transitions, energy shifts, as well as Drude response induced by these excess carriers in the respective band states. When modelling the experimentally found transient dielectric function with appropriate line shape model functions under mutual comparison with theoretically obtained data for the band structure and joint density of states, we can identify the positions of the charge carriers within the band structure in time, energy, and momentum.

Modelling TSE data is a very complex task: The spatial distribution of the excited carriers must be considered in transfer-matrix analysis, many time-delay steps have to be analysed simultaneously in model function approximation to identify positive and negative contributions as well as to obtain physically meaningful time-evolution of the parameters, and many more challenges. To circumvent the problems, we apply machine-learning based algorithm to find the best modelling of the data.

In my presentation I will introduce technical details of the method TSE, discuss modelling strategies, and give examples of processes observed in various material systems.

[1] S. Richter, M. Rebarz, O. Herrfurth, S. Espinoza, R. Schmidt-Grund, and J. Andreasson, Rev. Sci. Instrum. 92, 033104 (2021)

8:40am **EL+AS+EM-TuM-3 Evolution of Anisotropy and Order of Band-to-Band Transitions, Excitons, Phonons, Static and High Frequency Dielectric Constants Including Strain Dependencies in Alpha and Beta Phase ($Al_XGa_{1-X})_2O_3$*, Megan Stokey*,** *R. Korlacki, M. Hilfiker, T. Gramer, J. Knudtson,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight,* Linkoping University, Sweden*; A. Mock,* Weber State University*; A. Mauze, Y. Zhang, J. Speck,* University of California Santa Barbara*; R. Jinno, Y. Cho, H. Xing, D. Jena,* Cornell University*; E. Ahmadi,* University of Michigan*; V. Darakchieva,* Lund University, Sweden*; M. Schubert,* University of Nebraska-Lincoln

The rhombohedral alpha and monoclinic beta phases of gallium oxide both make promising candidates for ultra-wide bandgap semiconductor technology. Of particular interest are alloyed films and the evolution of anisotropic optical properties with respect to both alloy composition and strain induced effects. Here, we study alpha and beta phase $(Al_xGa_{1-x})_2O_3$ via a combined density functional theory and generalized spectroscopic ellipsometry approach across a range of alloying. Infrared-active phonon properties, static dielectric constants and midband gap indices of refraction are quantified.[1,2,3] Strain and alloying effects are shown and compared to previous theoretical works.[4] Bandgaps, excitons, and high-frequency dielectric constants are also investigated in the visible to vacuum-ultra-violet (VUV) spectral range.[5,6,7,8] We identify a switch in band order where the lowest band-to-band transition occurs with polarization along the ordinary plane in α-Ga--$_2$O-$_3$ whereas for α-Al-$_2$O$_3$ the lowest transition occurs with polarization in the extraordinary direction. With this, we present the most comprehensive picture of optical properties' evolution along composition and strain currently available.

[1] M. Stokey, R. Korlacki, *et al.,* Phys. Rev. Materials 6, 014601 (2022)

[2] M. Stokey, T. Gramer, *et al.,* Appl. Phys. Lett. 120, 112202 (2022)

[3] M. Stokey, R. Korlacki, *et al.*, "The influence of strain and composition on the infrared active phonons in epitaxial β-(AlxGa1-x)2O3 deposited onto (010) β-Ga2O3", *In Preparation*

[4] R. Korlacki, M. Stokey, A. Mock, *et al*., Rev. B 102, 180101(R) (2020)

[5] M. Hilfiker, R. Korlacki, *et al.,* Appl. Phys. Lett. 118, 062103 (2021)

[6]M. Hilfiker, R. Korlacki, *et al.,* Appl. Phys. Lett. XX, XX (2022)

[7] M. Hilfiker, U. Kilic, M. Stokey, *et al.,* Appl. Phys. Lett. 119, 092103 (2021)

[8] M. Hilfiker, U. Kilic, *et al.,* Phys. Lett. 114, 231901 (2019)

9:00am **EL+AS+EM-TuM-4 Engineering the Bi-Signate Broadband Enhanced Chirality Revealed by All Dielectric *Nanoboomerang* Structure*, Ufuk Kilic*,** *M. Hilfiker, A. Ruder, S. Wimer, S. G. Kilic, E. Schubert, C. Argyropoulos, M. Schubert,* University of Nebraska-Lincoln

Chirality phenomenon has recently aroused remarkable interest because of its promising potential applications in optics, catalysis and sensing. However, the large-scale mismatch between the wavelength of incident circular polarized (chiral) light and the size of natural chiral crystals (such as quartz or benzyl) or small size of chiral molecules (such as DNA or proteins) led the chiral light-matter interactions to be extremely weak in nature and cannot be made tunable [1]. The recent studies showed that one can obtain strong and tunable chiral response using subwavelength scale structures so-called metamaterials. As a promising large-scale area, bottom-up 3D nanomorphology fabrication method with precise sample stage manipulation ability, the glancing angle deposition (GLAD), is envisioned as a promising route to the experimental realization of strong and tunable chiroptical responses [1].

Here, we propose a simplistic chiral-nano-platform: all-dielectric spatially coherent, superlattice type, distorted L-shape metamaterials so-called chiral *nanoboomerangs* which were fabricated using custom-built, ultra-high-vacuum electron beam evaporated GLAD instrument. The structure consists of two achiral silicon nano-columnar segments, but the sample stage is rotated prior to the fabrication of second segment. Using a Mueller matrix spectroscopic ellipsometry based chiroptical characterization method, we found that our proposed large-scale nanophotonic metamaterial platform exhibits extremely broadband, large, tunable, and bi-signate chiroptical response within the near infrared to vacuum ultraviolet spectral range. We believe that this new material platform is a strong candidate for a myriad of next generation photonic integrated technological applications including but not limited to chiral sensors, drug-delivery systems, and chiral-topological insulators.

Reference:

1. Kilic, U. *et al.*, Advanced Functional Materials, 31(20), 2010329, (2021).

9:20am **EL+AS+EM-TuM-5 Structural Properties and Optical Constants of CaF_2 at 300 K from 0.03 to 6.5 eV*, Jaden R. Love,*** *N. Samarasingha, C. Armenta, S. Zollner,* New Mexico State University*; H. Kim,* National Institute of Aerospace (NIA)

In this undergraduate student presentation, we describe the structural and optical properties of calcium fluoride (CaF_2) an insulator with an ultrawide band gap of 12 eV and a large exciton binding energy of 1 eV. CaF_2 has a wide range of transparency from 125 meV in the infrared to 10 eV in the ultraviolet making it an ideal substrate for optical devices. Such optical devices include actively tunable transmission filters utilizing certain phase change memory materials (PCM's) which can be used for higher resolution imaging on satellites. Most studies of the optical constants of CaF_2 were performed in the 1960's and are discussed in [1]. Revisiting these optical constants using modern ellipsometry equipment and specimens from different manufacturers with (100) and (111) orientation seems timely. CaF_2 crystallizes in the fluorite structure with space group Fm-3m and has a lattice constant of 5.4626 Å. The Ca-$^{2+}$ atoms are located in the Wyckoff

(4a) position at the origin. The F^- atoms are at the (8c) positions (¼,¼,¼) and (¼,¼,3/4). There is a three-fold degenerate Raman-active T_{2g} mode and a three-fold degenerate infrared active T_{2u} mode, which splits into a transverse optical (TO) doublet and a longitudinal optical (LO) singlet. The T_{2u} mode can be observed with Fourier-transform infrared ellipsometry and described with a Lorentzian. The TO and LO energies are 261 and 477 cm^{1-}, respectively, with an amplitude A=4.1, a broadening of 4 cm^{1-}, and a high-frequency dielectric constant of 1.98[1]. A dip in the reststrahlen band is due to two-phonon absorption described with an anharmonically broadened Lorentzian. In the visible and near ultraviolet approaching 6.5 eV, normal dispersion can be described with a pole located at 7.48 eV and a Tauc-Lorentz oscillator at 20 eV. The imaginary part of the pseudo dielectric function, $<\varepsilon_2>$ is negative above 3 eV. This indicates a surface layer of 2 to 5 nm thickness with a larger refractive index than that of the bulk substrate. We apply the CaF_2 optical constants to determine the thickness of an SiO_2layer on the CaF_2 substrate.

[1] D. F. Bezuidenhout in Handbook of Optical Constants of Solids II, edited by E. D. Palik

(Academic, San Diego, 1998).

9:40am **EL+AS+EM-TuM-6 Optical Dielectric Function of a Solution-Processable Thiazolothiazole Thin Films Determined by Spectroscopic Ellipsometry***, **Nuren Shuchi**, J. Mower, V. Stinson, M. McLamb, G. Boreman, M. Walter, T. Hofmann,* University of North Carolina at Charlotte

Fluorescent molecules are ubiquitous in contemporary technologies and can be found for instance in energy-conversion devices [1], sensors [2], and are used for biological imaging techniques [3]. Recently, families of fluorescent molecules which combine multiple functionalities have gained considerable attention [4]. Significant progress has been made in the field of molecular electronics due to the advent of unique oligothiophenes [5] and thiadiazolobithienyl dyes [6]. We have synthesized solution-processable, 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole (TTz) dyes for thin film organic electronics applications. The TTz dyes were synthesized by refluxing 4-pyridinecarboxaldehyde, 4-(dibutylamino)benzaldehyde, and dithiooxamide in 40 mL of anhydrous dimethylformamide for 6 hours at 120 °C. The reaction solution was chilled overnight and crude precipitate was collected using vacuum filtration and rinsed with dimethyl sulfoxide and water. The isolated product was purified using silica gel column chromatography (Silica Flash M60) with a 1:1 hexanes/chloroform mixture. <1,0,0> Si wafers were cut to approximately 20 mm x 15 mm and sonicated in acetone, deionized water, and isopropyl alcohol for 15 minutes. The wafers were dried with compressed nitrogen gas and treated with UV / ozone for 15 minutes. The Si wafers and a 16.1 g/L 1,2-dichlorobenzene solution of the thiazolothiazole dye were heated to 55 °C in a nitrogen glove box. While in the glove box, 90 µL of the TTz solution was spin coated onto each Si wafer at 2000 RPM for 30 seconds. The wafers were heated to 110 °C for 20 minutes and stored in the glove box away from light. In this presentation, we will discuss spectroscopic ellipsometry data obtained from a 2,5-bis(N,N-dibutyl-4-aminophenyl)thiazolo[5,4-d]thiazole thin films deposited by spin coating on a silicon substrate in the spectral range from 354 nm to 1907 nm. The ellipsometric data were analyzed using a stratified layer model composed of thiazolothiazole thin film, native SiO_2 oxide, and Si substrate. The model dielectric function of the thiazolothiazole thin film was composed of a series of Tauc-Lorentz and Gaussian oscillators. The best-model calculated data are rendering the experimental data very well. Obtained transition energies will be reported and compared with those of related thiazolothiazole dyes. **References:** [1] J. Am. Chem. Soc. **133**, 20009 (2011). [2] Chem. Soc. Rev. **40**, 2222 (2011). [3] BMC Systems Biology **2**, 1(2008). [4] CHEM-EUR J. **19**, 2582 (2013). [5] J. Phys. Chem. Lett. **9**, 1958 (2018). [6] Sci. Rep. 6, 18870 (2016).

11:00am **EL+AS+EM-TuM-10 Bandgap Engineering of Polycrystalline Ge-doped Sb_2Se_3 Thin-Film: Surface and Optical Properties***, **Sanghyun (Philip) Lee**,* University of Kentucky*; M. McInenery,* Rose-Hulman Institute of Technology

Antimony Chalcogenide, $Sb_2(S_x,Se_{1-x})_3$ is a third-generation thin-film photovoltaic device. $Sb_2(S_x,Se_{1-x})_3$ solar cells have received growing attention due to their favored properties with <9.2 % efficiency. In particular, $Sb_2(S,Se)_3$ has a high absorption coefficient at visible light (>10^5 cm^{-1}), tunable bandgap (1.0 eV – 1.7 eV), stable upon exposure to sunlight under ambient conditions.

For the optimization of bandgap of Sb_2Se_3 alloy films, Ge-doped Sb_2Se_3 thin-film for solar cells applications have been studied with various compositions and doping concentrations, showing different crystallization, surface, and optical characteristics. Sb_2Se_3 thin-films are crystalline as deposited and on heating with orthorhombic structures. As a few molar percent of Ge doped into Sb_2Se_3 (<15 %) films (GeSbSe), polycrystalline films are formed upon annealing above 200 - 250 C, demonstrating no significant dependence of lattice constant on the Ge doping level. However, most GeSbSe studies are focused on amorphous Sb_2Se_3 films doped with higher Ge concentration (> 15 %).

In this contribution, we have fabricated and studied the bandgap energy and surface properties of polycrystalline GeSbSe thin-films (<15 %) for the application to the photovoltaic absorber. We investigated critical optical properties of absorption coefficient and engineered optical bandgap of films grown at different temperatures. Optical responses are explored with UV-Vis spectrometer. Moreover, scanning electron microscopy and Energy-dispersive X-ray spectroscopy are used to confirm optical bandgap, surface structures, and chemical composition of GeSbSe thin-films grown by Vapor Transport Deposition at different film growth temperatures. The optimum optical characteristics of thin-film absorber materials depend on film surface microstructure, which in turn affects the overall optical behaviors of GeSbSe films.

Ge-doped Sb_2Se_3 thin-films (<15 %) are polycrystalline with thickness around 1 um grown at 500 C and 520 C. As the deposition temperature increases from 500 C to 520 C, uniform grains of approximately 0.9 um at 500 C become mixed grains of larger (~6 um) and smaller grains (~0.9 um), revealed by Scanning Electron Microscopy characterization. The surface morphology becomes smooth (500 C) to irregularly rougher (520 C). For the characterization of optical properties, the absorption coefficient is >10^5/cm near 600 nm for both films. Based on the widely used Tauc's relation, the optical bandgap of Ge-doped Sb_2Se_3 thin-film absorbers is extracted as 1.15 eV and 1.23 eV for samples grown at 500 C and 520 C, respectively.

11:20am **EL+AS+EM-TuM-11 Optical Properties of Orthorhombic $LiGa0_2$ from Far-Infrared to Vacuum Ultraviolet***, **Teresa Gramer**, E. Williams, M. Stokey, R. Korlacki, U. Kilic, M. Hilfiker, M. Schubert,* University of Nebraska - Lincoln

Within the Li_2O-Ga_2O_3 oxide system, $LiGaO_2$ (LGO) and multiple phases of Ga_2O_3 (GO) are prospective ultra-wide bandgap metal oxides for electronic and optoelectronic applications [1]. While both GO and LGO have recently been identified to most likely trap holes and which makes achievement of sufficient p-type conductivity difficult [2], LGO is particularly promising as a substrate for heteroepitaxial growth of GaN due to very small lattice mismatch (<1%), and a composite LGO/β-GO substrate has also been demonstrated [3]. Here, we provide a comprehensive study of the fundamental optical and phonon mode properties of high-quality single-crystals of LGO using generalized spectroscopic ellipsometry in combination with hybrid-level density functional theory calculations that covers the optical properties in the far-infrared to vacuum ultraviolet spectral range. In the mid- to far-infrared range, we identify all 33 infrared-active pairs of transverse and longitudinal optical phonon modes. We derive the anisotropic mid-band gap indices of refraction and static dielectric constants. In the visible to vacuum ultraviolet spectral range we identify band-to-band transitions and discuss near band-gap excitonic contributions. We compare the obtained results with the previous experimental and theoretical studies. [4,5,6]

[1] A review of band structure and material properties of transparent conducting and semiconducting oxides: Ga_2O3 , Al_2O3 , In_2O3 , ZnO, SnO_2, CdO, NiO, CuO, and Sc_2O3 , Joseph A. Spencer, Alyssa L. Mock, Alan G. Jacobs, Mathias Schubert, Yuhao Zhang, and Marko J. Tadjer , Applied Physics Reviews 9, 011315 (2022)

[2] Self-trapped holes and polaronic acceptors in ultrawide-bandgap oxides, John L. Lyons, Journal of Applied Physics 131, 025701 (2022)

[3] Composite substrate $LiGaO_2$ (0 0 1) β-Ga_2O3 (1 0 0) fabricated by vapor transport equilibration, Zhang, Jungang & Xia, Changtai & Li, Shuzhi & Xu, Xiaodong & Wu, Feng & Pei, Guangqing & Xu, Jun & Zhou, Shengming & Deng, Qun & Xu, Wusheng & Shi, Hongsheng. Mater. Lett. 60. 3073-3075. (2006)

[4] Optical properties of lithium gallium oxide, S. Tumenas, P. Mackonis, R. Nedzinskas, L. Trinkler, B. Berzina, V. Korsaks, L. Changc, M.M.C. Chou , Applied Surface Science, Volume 421, Part B. (2017)

[5] Quasiparticle self-consistent GW band structures and high-pressure phase transitions of $LiGaO_2$ and $NaGaO_2$, Santosh Kumar Radha, Amol

Ratnaparkhe, and Walter R. L. Lambrecht, Physical Review B 103, 045201 (2021)

[6] Piezoelectric, Elastic and Dielectric Properties of $LiGaO_2$, Satoshi Nanamatsu et al, Jpn. J. Appl. Phys. 11 816 (1972)

11:40am **EL+AS+EM-TuM-12 Optical and X-ray Characterization of Ge-Sn Alloys on GaAs**, ***Haley Woolf***, *C. Emminger, C. Armenta,* New Mexico State University; *M. Kim,* QuantTera; *S. Zollner,* New Mexico State University

In this undergraduate student presentation, we describe the optical and x-ray characterization of a thick $Ge_{1-y}Sn_y$ alloy grown on GaAs by chemical vapor deposition. From (224) x-ray reciprocal space maps we find that the alloy layer is grown pseudomorphically on the GaAs substrate. Therefore, we can use (004) rocking curves and reciprocal space maps to determine the alloy composition based on Vegard's Law. We find y=0.012.

For ellipsometry measurements, we first cleaned the surface ultrasonically with water and isopropanol to remove adsorbed organic overlayers and a portion of the native oxide. The remaining native oxide was found to be 2.6 nm thick. We then acquired the ellipsometric angles ψ and Δ from 0.5 to 6.5 eV photon energy and 60 to 75° incidence angle using a vertical variable angle of incidence ellipsometer (VASE) equipped with a computer-controlled Berek wave plate compensator. Due to the low tin content, these ellipsometric angles and the resulting pseudo-dielectric function could be described very well using a four-layer model, consisting of a GaAs substrate, a pure Ge layer, GeO_2 oxide, and air as the ambient. This results in an epilayer thickness of 1600 nm.

After fixing the thickness, we also obtained the dielectric function ε of the epitaxial $Ge_{1-y}Sn_y$ layer from a point-by-point fit. This is very similar to that of bulk Ge. The second derivative $d^2\varepsilon/dE^2$ was fitted with analytical line shapes to determine the critical point parameters of the alloy (amplitude, energy, broadening, and phase angle). The energy was compared with predictions from continuum elasticity theory based on established deformation potentials for Ge.

12:00pm **EL+AS+EM-TuM-13 Zinc Gallate ($ZnGa_2O_4$) Epitaxial Thin Films: Determination of Optical Properties and Bandgap Estimation Using Spectroscopic Ellipsometry**, *S. Bairagi, J. Chang, C. Hsiao, R. Magnusson, J. Birch,* Linköping University, Sweden; ***Jinn P Chu,*** National Taiwan University of Science and Technology, Taiwan; *F. Tarntair,* National Yang Ming Chiao Tung University, Taiwan; *R. Horng,* National Yang Ming Chiao Tung University, Taiwan; *K. Järrendahl,* Linköping University, Sweden

Very high quality Zinc gallate (ZGO) epitaxial thin films were grown on c-plane sapphire substrates by Metal-Organic Chemical Vapor Deposition and investigated using Spectroscopic Ellipsometry (SE). Two or more samples were grown with identical growth conditions but different growth times to obtain samples with similar crystallographic and optical properties but different thicknesses. Their thickness, roughness and optical properties were then determined using a Multiple Sample Analysis (MSA) based approach in tandem by the regression analysis of the optical model and measured data for all samples. Another set of ZGO samples were grown for the same growth time but etched using ion-bombardment for different time durations to achieve different thicknesses. These samples were also analyzed by SE using MSA and it was observed that etching times of 1 – 4 minutes had no discernible impact on the material's optical properties. It was also observed that both sets of samples exhibited identical optical properties and thus could be described using the same optical model, thereby showcasing the robustness of the MSA model. Line shape analysis of resulting absorption coefficient dispersion revealed that ZGO exhibited both direct and indirect interband transitions. A modified Cody formalism was employed to determine their optical bandgaps, resulting in a direct bandgap of 5.07 ± 0.015 eV and indirect bandgap of 4.72 ± 0.015 eV. These values were compared to values obtained using other popular bandgap extrapolation procedures to find which technique resulted in the most linear line shape. In a subsequent study, the first set of samples was annealed to different temperatures and their optical properties were analyzed using SE. It was observed that the onset of absorption and hence the optical bandgap blue-shifted to higher photon energies as the annealing temperature was increased from 800° C to 1100° C. This was a consequence of inter-diffusion between the ZGO thin film and sapphire substrate, resulting in the formation of an epitaxial β-(Al, Ga)O intermediate layer between the two, and modification of ZGO to Zn(Al, Ga)O due to diffusion of Al. Post analysis it was observed that the formation of β-(Al, Ga)O intermediate layer began already at 800° C and led to an increase in the overall film thickness with increasing annealing temperatures. The direct and indirect optical bandgaps for the Zn(Al, Ga)O thin film were determined to be 5.10, 5.19, 5.73 eV and 4.80, 4.87, 5.45 eV for 800, 950 and 1100° C, respectively and the increase is attributed to the diffusion of Al from the sapphire substrate.

Mini Symposium on 2D Materials Synthesis
Room 303 - Session MS-2DMS+2D+EM+NS-TuM

Direct Growth of 2D Materials, Including CVD and MBE

Moderators: Matthias Batzill, University of South Florida, **Erica Douglas**, Sandia National Laboratories, **Maryam Ebrahimi**, Lakehead University, Canada, **Kathleen McCreary**, Naval Research Laboratory

8:00am **MS-2DMS+2D+EM+NS-TuM-1 Efficient Control of 2D Magnetism**, ***Cheng Gong,*** University of Maryland **INVITED**

The recently discovered magnetic two-dimensional (2D) van der Waals materials [1, 2] provide ideal platforms to enable the atomic-thin, flexible, lightweight magneto-optical and magnetoelectric devices. Though many have hoped that the ultra-thinness of 2D magnets should allow an efficient control of magnetism, the state-of-the-art has not achieved notable breakthroughs to this end, with only proof-of-concept reports. There appear to be some fundamental obstacles for efficient control. In this talk, I will analyze the challenges and present our recent theoretical and experimental progress on efficient electrical and optical control of 2D magnetism [3-7]. We envision the efficient control of 2D magnets could open new avenues for the low-power spintronics and photonics.

1. C. Gong et al. Nature 546, 265-269 (2017).
2. C. Gong, X. Zhang. Science 363, eaav4450 (2019).
3. C. Gong, et al. Nature Communications 10, 2657 (2019).
4. S.-J. Gong, et al. PNAS 115, 8511-8516 (2018).
5. E.-W. Du, et al. Nano Letters 20, 7230-7236 (2020).
6. T. Xie, et al. under review (2022).
7. S. Liang, et al. under review (2022).

8:40am **MS-2DMS+2D+EM+NS-TuM-3 Epitaxial Growth of Transition Metal Dichalcogenide Monolayers for Large Area Device Applications**, *J. Redwing,* ***Thomas V. Mc Knight,*** The Pennsylvania State University **INVITED**

Wafer-scale epitaxial growth of semiconducting transition metal dichalcogenide (TMD) monolayers such as MoS_2, WS_2 and WSe_2 is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Epitaxy is required to achieve single crystal films over large areas via coalescence of TMD domains. Our research has focused on epitaxial growth of 2D semiconducting TMDs on c-plane sapphire substrates using metalorganic chemical vapor deposition (MOCVD).Steps on the miscut sapphire surface serve as preferential sites for nucleation and can be used to induce a preferred crystallographic direction to the TMD domains which enables a reduction in twin boundaries in coalesced films. The step-directed growth is dependent on the surface termination of the sapphire which can be altered through pre-growth annealing in H_2 and chalcogen-rich environments. Uniform growth of TMD monolayers with significantly reduced inversion domains is demonstrated on 2" diameter c-plane sapphire substrates enabling large area transfer of monolayers for characterization and device fabrication and testing.Applications for wafer-scale TMD monolayers in nanoelectronics, sensing and photonics will be discussed.

9:20am **MS-2DMS+2D+EM+NS-TuM-5 Formation of Transition Metal Dichalcogenide Janus Monolayers and 2D Alloys Through Non-Equilibrium Synthesis and Processing Approaches**, ***Kai Xiao***, *S. Harris, Y. Lin, C. Liu,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *G. Duscher,* University of Tennessee Knoxville; *M. Yoon,* Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA; *L. Liang, C. Rouleau, A. Puretzky, D. Geohegan,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Doping and alloying in 2D materials are efficient ways to tune the optical and electronic properties, induce new crystal structures and phases, and add new functionalities. In this talk, I will introduce how to precisely tailor the doping of 2D TMDs using non-equilibrium synthesis and processing techniques including chemical vapor deposition and hydrothermal laser implantation. By tailoring isoelectronic doping of chalcogens and metals in 2D TMDs (e.g., $MoSe_2$, WS_2) during CVD synthesis, the uniform alloys, gradient alloys, and lateral heterostructures are controlled grown on substrates which exhibit many novel properties including tunable bandgaps, enhanced photoluminescence, modulated charge carriers, etc. I will also describe a novel PLD approach with in situ diagnostics such as Raman and photoluminescence to sensitively tune the kinetic energies of Se clusters (3-5 eV/atom) to selectively implant Se atoms within monolayer WS_2 and MoS_2 crystals to form novel Janus WSSe and MoSSe monolayers. Synthesis science was supported by the U.S. Dept. of Energy, Office of Science, Materials Science and Engineering Division. This work was performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:40am **MS-2DMS+2D+EM+NS-TuM-6 Effects of Deposition Technique on Monolayer MoS_2 and WS_2*, Ama Agyapong*,** *S. Mohney,* Pennsylvania State University

It is important to understand how the deposition of metal contacts affects two-dimensional transition metal dichalcogenides (TMDs) so that we can successfully integrate TMDs into next-generation electronic and optoelectronic devices. This study employs Raman spectroscopy as a non-destructive method to probe structural changes induced by depositing metals on monolayer MoS_2 and WS_2. Differences between electron-beam evaporated and DC magnetron sputtered metal/MoS_2 and metal/WS_2 samples were observed in Raman spectra obtained through a transparent substrate using a backside geometry. The disappearance of characteristic Raman modes of the TMDs indicates structural disorder, as observed for sputtered In, Pd, and Pt films on both monolayer MoS_2 and WS_2. This disorder is introduced even though the metals are not reactive with the TMDs. On the other hand, Raman modes remain if the metals are e-beam evaporated. The mass of the metal atoms appears to impact the structural disorder caused by sputtering, as characteristic MoS_2 and WS_2 modes are preserved (albeit with some changes to the spectra) when lighter metal atoms (Cu and Al) are sputtered. The results of this work provide insight on structural changes at the metal/TMD interface that may not be easily detectable in bulk TMDs, and we conclude that e-beam evaporation is a less destructive deposition technique for forming metal contacts on 1L TMDs than sputtering.

11:40am **MS-2DMS+2D+EM+NS-TuM-12 The Growth of $Nb_{1+x}Se_2$ by Molecular Beam Epitaxy*, Peter Litwin,*** *S. Jaszewski, J. Ihlefeld, S. McDonnell,* University of Virginia

$NbSe_2$, a metallic transition metal dichalcogenide, has been the focus of numerous recent scientific studies due to the coexistence of superconductivity and charge density wave states it exhibits at low temperature. While less studied, this material also exists in a metal rich, Nb-intercalated (self-intercalated) phase in which additional Nb atoms populate the van der Waals gap. The self-intercalated phase, $Nb_{1+x}Se_2$, has been studied in the bulk form since the 1960's when it was synthesized by chemical vapor transport techniques; however, thin film synthesis of this material is rarely reported. Here we report on the growth of few layer $Nb_{1+x}Se_2$ by molecular beam epitaxy (MBE). We demonstrate that the degree of Nb-intercalation can be tuned through alteration of the Se to Nb flux ratio used during growth. Interestingly, we find that Nb-intercalation exists in all multilayer films, even under Se to Nb flux ratios as high as 45,000:1. The presence of Nb-intercalation results in an expansion of the material's c-axis lattice parameter which we measure using ex-situ x-ray diffraction (XRD). Chemical analysis of the grown thin films is carried out using in-situ x-ray photoelectron spectroscopy (XPS) and further confirms the Nb-rich nature of the grown thin films. The in-plane electrical conductivity is measured using a 4-point probe measurement tool and shows an inverse relationship with the Se to Nb flux ratio used during growth. Lastly, we also report on the thickness scaling of the material's electrical conductivity down to few-layer thick $Nb_{1+x}Se_2$ thin films.

12:00pm **MS-2DMS+2D+EM+NS-TuM-13 Formation of 1D and 2D Carbon-Based Nanomaterials on Surfaces*, Maryam Ebrahimi,*** Lakehead University, Canada

On-surface reactions offer a platform to design molecular-based low-dimensional nanomaterials whose chemical and electronic properties can be tailored by their chemical structure. The molecules' functional groups and the reactivity of the substrates control the molecule-molecule and molecule-substrate interactions, which steer the design of the obtained molecular structures.We present various surface reactions for creating 1D and 2D polymers, metal-organic networks, and organometallic structures on Au(111), Ag(111) and Cu(111).To identify their topography and chemical nature, we employ scanning tunnelling microscopy and non-contact atomic force microscopy, and other surface characterization techniques, such as X-ray photoelectron spectroscopy, complemented with density functional theory calculations.

The chemical and thermal stability and structural design of these molecular-based low-dimensional nanomaterials make them promising candidates for various applications. These materials are tailored to exhibit unique electronic properties, charge mobility and/or electron spin-based structure, suitable for carbon-based nanoelectronics, spintronics, and quantum technology applications.

References

[1] M. Ebrahimi, *Nat. Chem.* 14 (2022) 3-4

[2] M. Ebrahimi, F. Rosei, *Nature* 542 (2017) 423-424

[3] M. Ebrahimi, F. Rosei, *Nat. Photonics* 10 (2016) 434-436

[4] G. Galeotti et al., *Nat. Mater.* 19 (2020) 874-880

[5] G. Galeotti et al., *Faraday Discuss.* 204 (2017) 453-469

[6] F. De Marchi et al., *Nanoscale* 10 (2018) 16721-16729

[7] G. Galeotti et al., *Chem. Sci.* 10 (2019) 5167-5175

[8] C. Jing et al., *Angew. Chem. Int. Ed.* 58 (2019) 18948-18956

[9] P. Ji et al., *Small* 16 (2020) 2002393

[10] N. Cao et al., *Nanoscale* 13 (2021) 19884-19889

Applied Surface Science Division
Room 320 - Session AS+EM+SE-TuA

Surface Analysis Using Complementary Techniques

Moderators: Samantha Rosenberg, Sandia National Laboratory, **Carl A. Ventrice, Jr.**, SUNY Polytechnic Institute

2:20pm **AS+EM+SE-TuA-1 Origins of the Emergent Phenomena at Oxide Interfaces Studied with Complementary X-Ray Spectroscopic and Scattering Techniques***, **Alexander Gray**,* Temple University **INVITED**

Atomic-level design of complex-oxide heterostructures that exhibit functional electronic and magnetic phenomena has become a diverse and vibrant subfield of condensed matter physics and material science. Of particular interest are the material systems wherein rich physics and intricate interplay between various degrees of freedom at the interface give rise to functional properties not observed in the constituent materials. Detection and characterization of these interfacial properties present a unique practical challenge due to the lack of direct yet non-destructive techniques that are capable of probing minute changes in the electronic and magnetic states at a buried interface with element specificity and Ångstrom-level spatial resolution. In this talk, I will discuss several recent studies in which we utilized a combination of complementary x-ray spectroscopic and scattering techniques to understand the origins of the emergent low-dimensional ferromagnetic states in $LaNiO_3/CaMnO_3$ and $CaRuO_3/CaMnO_3$ superlattices. Depth-resolved standing-wave photoemission spectroscopy was used to probe the depth-dependent changes in the electronic states, while soft x-ray resonant magnetic scattering was used to extract the element-specific magnetic profile of the interface. The results of the experiments were compared to and interpreted using state-of-the-art first-principles theoretical calculations.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences, and Engineering Division under Award DE-SC0019297.

3:00pm **AS+EM+SE-TuA-3 Multi-Technique Forensic Analysis by Co-Incident XPS & Raman Imaging***, **Robin Simpson**, P. Mack,* Thermo Fisher Scientific, UK

For more than 100 years fingerprint analysis has been ubiquitous in the forensic sciences and is still a core method for identifying individuals in forensics. The techniques used to analyze fingerprints are either structural, for identifying the features of the fingerprints, or chemical, characterizing the composition of the deposited material. Many of these chemical characterization techniques are destructive to the sample preventing any further analysis from being performed or the sample from being preserved as evidence for a later date. Here we show the benefits of using XPS to analyze fingerprints, where the elemental and chemical state composition of a sample can be acquired non-destructively from the top 10 nm of the surface.

In this investigation, we build on our previous work investigating fingerprint analysis. In that study, XPS and XPS mapping techniques were utilized to identify and characterize the contamination of fingerprints. Fingerprints contaminated with TiO-$_2$, and PbO deposited on the silicon wafer can be chemically mapped and visualized using XPS using principal component analysis, PCA.

In this study, we also discuss other examples of forensic analysis including the identification of pharmaceutical substances using complementary XPS and Raman analysis. To achieve this an “over the counter” multi-component analgesic tabletwas crushed to a powder form and deposited onto the substrate. The powder is mapped rapidly using XPS imaging and the data is processed by PCA. This information was used to identify areas for further analysis by high-resolution XPS and Raman. Further Raman analysis was used to characterize the composition of the 3 areas of the sample and identify the compounds contained in them. These are shown to be aspirin, paracetamol, and caffeine through comparison with known sample spectra in the OMINC Raman spectral database.

In the final two examples of forensic analysis workflows in this presentation, we discuss the identification and differentiation between overlapping ink and paint samples deposited on paper or fabric substrates. Raman mapping is used to differentiate between two paint samples that have virtually identical chemistry when analyzed via XPS, and rapid XPS imaging is used to identify the order of events between the deposition of computer-printed ink and handwritten ink from a ballpoint pen.

3:20pm **AS+EM+SE-TuA-4 Comparison of Methods to Quantify Silicone on Hair***, **Michaeleen Pacholski**, B. Johnson, T. Case, T. Powell, D. Carsten, J. Stratton,* The Dow Chemical Company*; C. Ji,* The Dow Chemical Company, China*; M. McIvor, N. Goodman, S. Yusuf, M. Upshur,* The Dow Chemical Company

Silicone has been used as a conditioning agent on hair for a long time.Silicone deposition can produce numerous benefits in reducing the coefficient of friction, improving combability and decreasing frizz.It can be delivered in multiple ways such as conditioning shampoo, rinse off conditioners, leave in conditioners and detangling products.Regardless of how it is delivered to the hair surface, the quantification of silicone on hair is an important metric for R&D product development and marketing.In a large analytical group there are many techniques that can be used including XPS, XRF, ICP, GC and IR.Each has different limits of detection, amount of sample required, time involved to both acquire and analyze the data, etc.A set of samples was generated using both shampoo and rinse off conditioner on both brown and bleached hair for a comparison study.The amount of silicone varied from low to high levels.Comparison of the techniques showed general agreement between all techniques within expectations.These experiments can now guide internal work based on the needs of the specific project and what instrumentation is available within that region.

4:20pm **AS+EM+SE-TuA-7 Progress Towards Atomic Scale Analytical Tomography***, **Brian Gorman**,* Colorado School of Mines*; T. Kelly,* Steam Instruments, Inc*; M. Holtz,* Colorado School of Mines **INVITED**

Atomic-Scale Analytical Tomography (ASAT) has been recently defined as the ability to identify every atom in its place. Specifically, ASAT is the ability to determine the isotopic identity and sub-Angstrom position of 100% of the atoms in a specific volume. Taking this a step further, ASAT should also be able to determine the local electronic structure of these atoms, thus giving rise to true 3-D atomic structure / electronic property relationships. ASAT datasets of semiconductor nanostructures will reveal the 3-D position of individual dopant atoms with pm spatial resolution, the 3-D position of nuclear spin isotopes, nanometer scale changes in strain due to structural defects and lattice mismatch, the 3-D position of point defects such as vacancies, and any electronic band structure changes at all these atomic-scale features.

Undoubtedly, ASAT is a lofty metrology goal but is nearly within reach. Contemporary metrology techniques such as (Scanning) Transmission Electron Microscopy ((S)TEM) are not currently capable of ASAT. (S)TEM can image atomic positions with better than 0.01 nm resolution in some specimens and tilt-series tomographic imaging can give 3-D information, sometimes at atomic resolution. Analytical STEM can be performed at atomic resolution in some cases, although identifying a single atom in 3-D is only possible in limited specimens and with poor depth resolution. Atom Probe Tomography (APT) can provide mass spectral information on individual atoms, however, 3-D image reconstruction methods are constrained by multiple empirical assumptions and lack of information about the specimen that limit the spatial resolution.

Recently, it was demonstrated that correlative TEM and APT on the same specimen can approach ASAT. We used (S)TEM imaging of the specimen before and after APT to define the analyzed 3-D volume. 4-D STEM diffraction was used to define atom positions within that volume (a dataset known as the specimen function) using information about the crystal space group, orientation, and lattice parameters. Individual isotopic nuclear spins are accurately placed within a semiconductor quantum do to within 0.05 Anstroms.

More work needs to be done using correlative TEM and APT to achieve ASAT, including demonstrating the ability to capture structural features such as interfaces and defects as well as 100% efficiency ion detectors. In the near future, ASAT will be achieved through integration of 100% efficiency ion detectors, improved data handling algorithms, and integration of TEM and APT into a single instrument.

5:00pm **AS+EM+SE-TuA-9 Investigating 2d-Materials Using Correlative Spectroscopy & Microscopy***, **Tim Nunney**, R. Simpson, P. Mack, H. Tseng,* Thermo Fisher Scientific, UK

Across a wide range of application areas, understanding the chemistry and structure of surfaces and interfaces is crucial. In the last fifty years, X-ray photoelectron spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry, and advances in instrumentation have enabled it to keep pace with the requirements for both academia and industry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry, but the limit on spatial resolution for XPS can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using just XPS.

Other experimental techniques which are unable to match the surface selectivity of XPS are able to provide complementary information to extend the data from XPS. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This can be a perfect complement to XPS analysis, so long as the same points of interest can be identified. Molecular spectroscopy, such as FTIR or Raman, can also provide complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures using the wide range of spectral libraries available for those techniques.

In this presentation, we will describe how a correlative approach using both surface analysis instrumentation and scanning electron microscopy can be used to characterize 2D nanomaterials. Samples of MoS_2 grown on Si substrates have been investigated using XPS, Raman and SEM to determine their composition and structure. To facilitate co-alignment of the analysis positions when moving between the instruments, special sample carriers and software alignment routines have been developed.

5:20pm **AS+EM+SE-TuA-10 Surface Analysis in Fujifilm Electronic Materials Research & Development Laboratory: Applications on Chemical Mechanical Planarization***, **Hong Piao,*** FUJIFILM Electronic materials USA., Inc.*; Y. Liang, K. Huang, B. Duong, J. McDonough, Y. Zhang, H. Lee, B. Hu,* FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization (CMP) is a chemical reaction assisted polishing process in the semiconductor manufacturing industry. It has played a key role on integrated circuit (IC) manufacturing to anisotropically remove overburden material or specific layers in the film stacking and to planarize the topography at the wafer surface. Specific slurry formulations have been designed towards to the device structure and materials to be polished. The surface chemical processes at the interface of the wafer/slurry/pad have significant influence on the CMP performance. As device geometries are continuously shrinking as well as the introduction of new interconnect materials, the technological requirements on CMP performance have become more stringent. Thus, in-depth understanding of surface chemical processes which occur during polishing remains essential to the improvement of slurry design, the development of next-generation CMP processes and post-CMP cleaning applications.

Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of “nano-structured” materials in other fields.Surface analysis tools (XPS, Tof-SIMS and AFM) at FUJIFILM Electronic Materials U.S.A., Inc. combined with other complementary testing methods have already shown great promise as a means of achieving fundamental knowledge to the mechanisms involved in CMP processes [1].

This review continues to highlight the promising role that surface chemical analysis methods can and should play in understanding the complex interplay that drives design of CMP slurry formulation for contributions to the CMP technology. Examples describing the CMP characterization have been given in several aspects that are growing in importance: (1) Cu, Co and Ru CMP, (2) Defects (organic residues,metal contaminants and particles) removal in a post-CMP cleaning process and (3) CMP consumables: root cause analysis of pad stains.

[1]Hong Piao, Yannan Liang, James McDonough, Tawei Lin, Hyosang Lee, Carl Ballesteros, Eric Turner, Abhudaya Mishra and Richard Wen, “*Industrial Applications of Surface Science in Chemical mechanical Planarization*”, The AVS 65th International Symposium, Oct. 21-26, 2018, Long Beach, California.

5:40pm **AS+EM+SE-TuA-11 Investigating GeTe as an Ovonic Threshold Switch with Spectroscopic and Electronic Techniques***, **Melissa Meyerson**, M. Kalaswad, M. King, D. Adams, J. Custer, P. Kotula, M. Rodriguez, S. Rosenberg,* Sandia National Laboratories

Ovonic threshold switches (OTS) are a class of two or three terminal devices that exhibit a sharp transition between resistive and conductive operating regions. This transition is temporary, with the device reverting to a resistive state once bias is de-asserted from the device. The volatile resistive behavior makes OTS devices very attractive as select devices for phase change memory, voltage controlled tunable filters, and other applications. Metal telluride thin films show unique temperature dependent characteristics that may make them good materials for OTS devices. In this study, we examine the effect of annealing temperature on the chemical, physical, and electronic properties of GeTe thin films including exploring changes in crystallinity, chemical composition, and switching behavior. More specifically, X-ray photoelectron spectroscopy shows a chemical transition that occurs between 125 °C and 150 °C that results in an increase in metallic Ge and decrease in metallic Te relative to the concentration of GeTe present. Similarly, X-ray diffraction shows a transition from amorphous to crystalline GeTe around 160 °C. The films are further characterized with transmission electron microscopy, energy dispersive X-ray spectroscopy, and surface electronic measurements including ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy to determine the band gap.

Sandia National Laboratories is a multi-mission 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.

6:00pm **AS+EM+SE-TuA-12 Multi-Technique Analysis of Organic and Inorganic Semiconductors for Composition and Electronic Information***, **Paul Mack**,* Thermo Fisher Scientific, UK*; M. Modreanu,* Tyndall National Institute-University College Cork, Ireland

Photoelectron spectroscopy has been used for many years to analyse the elemental and chemical composition of a broad range of industrially relevant materials, from polymers to semiconductors.In recent years, with the development of novel organic and inorganic semiconductors, there has also been an increasing demand to measure electronic parameters alongside the elemental and chemical state information.

In this work, complementary electron spectroscopic techniques were used to comprehensively characterise organic and inorganic semiconductors for composition and electronic properties.X-ray photoelectron spectroscopy (XPS) was used to analyse the elemental and chemical composition of the organic semiconductor, P3HT, and a range of ferroelectric films with the general formula, $Hf_xZr_yO_z$.Ultraviolet photoelectron spectroscopy (UPS) and reflection electron energy loss spectroscopy (REELS) were then used together to measure the ionisation potential, band gap and electron affinities of those samples.

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL1+AS+EM-TuA

Emerging Technological Advances and Breakthroughs of Spectroscopic Ellipsometry

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Ruediger Schmidt-Grund**, Technical University Ilmenau, Germany

2:20pm **EL1+AS+EM-TuA-1 Terahertz to Vacuum Ultraviolet Ellipsometry Characterization of Spin, Lattice, Strain, Free Charge Carrier, Dielectric Constants, Exciton and Band-to-Band Transition Properties in Ultrawideband Gap Alpha and Beta Aluminum Gallium Oxide Semiconductor Alloys***, **Mathias Schubert**, R. Korlacki, M. Stokey,* University of Nebraska-Lincoln*; A. Mock,* Weber State University*; M. Hilfiker,* University of Nebraska-Lincoln*; J. Knudtson,* University of Nebraska-Lincoln, USA*; U. Kilic,* University of Nebraska-Lincoln*; S. Richter,* Lund University, Sweden*; S. Knight, P. Kuehne,* Linkoping University, Sweden*; V. Darakchieva,* Lund University, Sweden **INVITED**

Two phases of ultrawideband gap semiconductor gallium oxide emerge in composition with aluminum, the rhombohedral alpha and monoclinic beta phase of AlGaO. Progress in epitaxial deposition provides quality materials investigated currently with large efforts. Both phases permit access to ultrawideband gap properties reaching approximately 9 eV with sapphire. We employ a wide range of ellipsometry techniques covering 100 GHz to approximately 9.5 eV, including magnetic fields and density functional theory calculations. We provide an overview of current knowledge of properties for both compounds, discussing strain-stress relationships, evolution of phonon mode and band to band transition behaviors, dielectric constants, indices of refraction, anisotropy, and free charge carrier and defect properties [1-8]. We report on a new hyperbolic shear polariton formation in monoclinic Ga2O3 [9]. We also report on initial results of our newly developed instrumental approach for defect characterization in quantum materials, THz electron paramagnetic resonance ellipsometry for ultrahigh field and high resolution frequency spin detection and analysis in epitaxial semiconductor layer systems [10]. [1] M. Stokey et al., Phys. Rev. Materials 6, 014601 (2022). [2] M. Hilfiker et al., Appl. Phys. Lett. 118, 062103 (2021). [3] M. Hilfiker, U. Kilic, M. Stokey, R. Jinno, Y. Cho, H. Grace Xing, D. Jena, R. Korlacki, and M. Schubert, Appl. Phys. Lett. 119, 092103 (2021). [4] R. Korlacki, M. Stokey, A. Mock, S. Knight, A. Papamichail, V. Darakchieva, and M. Schubert, Phys. Rev. B 102, 180101(R) (2020). [5] P. Gopalan, S. Knight, A. Chanana, M. Stokey, P. Ranga, M. Scarpulla, S. Krishnamoorthy, V. Darakchieva, Z. Galazka, K. Irmscher, A. Fiedler, S. Blair, M. Schubert, and B. S. Rodriguez, Appl. Phys. Lett. 117, 252103 (2020). [6] M. Hilfiker, U. Kilic, A. Mock, V. Darakchieva, S. Knight, R. Korlacki, A. Mauze, Y. Zhang, J. Speck, and M. Schubert, Appl. Phys. Lett. 114, 231901 (2019). [7] J. A. Spencer, A. L. Mock, A. G. Jacobs, M. Schubert, Y. Zhang, and M. J. Tadjer, Appl. Phys. Rev. 9, 011315 (2022). [8] R. Korlacki, J. Knudtson, M. Stokey, M. J. Hilfiker, V. Darakchieva, and M. Schubert, Appl. Phys. Lett. 120, 042103 (2022). [9] N. Passler, X. Ni, G. Hu, J. R. Matson, M. Wolf, M. Schubert, A. Alù, J. D. Caldwell, T. G. Folland, and A. Paarmann, Nature 602, 595 (2022). [10] M. Schubert, S. Knight, S. Richter, P. Kuehne, V. Stanishev, A. Ruder, M. Stokey, R. Korlacki, K. Irmscher, P. Neugebauer, and V. Darakchieva, Appl. Phys. Lett. 120, 102101 (2022).

Spectroscopic Ellipsometry Focus Topic
Room 304 - Session EL2+EM-TuA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Ruediger Schmidt-Grund**, Technical University Ilmenau, Germany

4:20pm **EL2+EM-TuA-7 A Study of Wire Grid Polarizers with Mueller Matrix Ellipsometry**, *T. Gholian Avval, M. Linford,* Brigham Young University*; N. Keller,* ***G. Andrew Antonelli,*** Onto Innovation, Inc.

Wire grid polarizers are essential optical components used in a wide variety of optical systems, from AR/VR to medical imaging to optical measuring systems. Physical properties of the polarizer, such as groove height and width all impact the polarizer's efficiency. Here we show how a wire grid polarizer can be characterized non-destructively in the fabrication process with Mueller Matrix ellipsometry and RCWA-based analysis. Using this methodology, physical properties like grating profile, height, pitch, material thicknesses and even grating tilt can be measured non-destructively and inline to provide process control.

4:40pm **EL2+EM-TuA-8 Temperature Dependence of the Direct Band Gap of InSb from 80 to 700 K**, ***Melissa Rivero Arias,*** *N. S. Samarasingha, C. Emminger, S. Zollner,* New Mexico State University

In this undergraduate student presentation, we describe measurements of the dielectric function of bulk InSb near the direct band gap using Fourier-transform infrared (FTIR) spectroscopic ellipsometry from 80 to 800 K in an ultra-high vacuum (UHV) cryostat with diamond windows. Indium antimonide (InSb) is the zinc blende compound semiconductor with the smallest direct band gap (ε_0= 0.18 eV at room temperature) due to its heavy elements and the large resulting spin-orbit splitting and Darwin shifts. It also has a low melting point of 800 K. Previously, the bandgap of InSb has mostly been measured optically up to room temperature and estimated from Hall effect measurements of the effective mass up to 470 K. Ellipsometry measurements of the direct gap of InSb have been described at 300 K. Calculations indicate that InSb should undergo a topological phase transition from semiconductor to semi-metal (and topological insulator) at 600 K. It is interesting to see in the data if this transition occurs below the melting point of InSb.

5:00pm **EL2+EM-TuA-9 Coherent Acoustic Phonon Oscillations in Ge Using Pump-Pulse Time-Resolved Spectroscopic Ellipsometry**, ***Carlos Armenta,*** New Mexico State University*; M. Zahradnik,* ELI Beamlines, Czechia*; C. Emminger,* Humboldt University Berlin, Germany*; S. Espinoza, M. Rebarz, J. Andreasson,* ELI Beamlines, Czechia*; S. Zollner,* New Mexico State University

Photoexcitation of bulk materials can create hot charge carriers that relax by transferring energy to the lattice, hence exciting phonons in the process. By photoexciting the material through femtosecond laser pulses, coherent acoustic phonon (CAP) oscillations at picosecond time scales are generated via this method. These CAP oscillations are related to an increase in charge carrier density, as well as strain triggered by the laser pulse, however details of this relationship are scarce in the literature. CAP oscillations affect the pseudo-dielectric function (DF) of the material, which makes time-resolved spectroscopic ellipsometry ideal to understand the processes in hand.

The present work aims to describe the relationship between CAP oscillations and charge carrier density, as well as surface orientation dependence via femtosecond pump-probe ellipsometry of Ge. Photoexcitation is induced by 800 nm laser pump pulses at different intensities, generating a strain pulse that travels normal to the surface within the ~200 nm penetration depth in the semiconductor. Measurements in Ge at (100), (110), and (111) orientations and charge carrier concentrations ranging from ~7.5×10^{20} cm^{-3} to ~3.5×10^{21} cm^{-3} were performed. The behavior of these oscillations is characterized by analyzing the changes in the pseudo-DF of Ge as a function of the delay time between the pump and probe pulse. Analyzing the E1 and E1+Δ1 critical points (CP) and the variation of their parameters (energy, broadening, amplitude, and phase) with delay time, the behavior of phonon oscillations can be studied.

In order to determine these parameters, second derivatives of the pseudo-DF were calculated using a linear filter technique based on extended Gauss (EG) functions. The periods of these oscillations are deduced by tracking the energy of these CPs as a function of time

5:20pm **EL2+EM-TuA-10 Time-Resolved Spectroscopic Ellipsometry Helped by Imaging Spectroscopic Ellipsometry**, ***Shirly Espinoza,*** ELI Beamlines, Czechia

Thanks to femtosecond pulsed lasers, at ELI Beamlines in the Czech Republic, we developed a time-resolved femtosecond ellipsometry technique, where a pump beam from any wavelength between 200 nm and 2000 nm excites a material; and a second pulse, the probe beam, with a continuous spectrum from 350 nm to 750 nm measures the dielectric function of that material. The pump and the probe beam can be separated in time from femtoseconds to nanoseconds generating a time-scan of the relaxation processes that happens in the material when it returns to its original unexcited state.

This time-resolved pump-probe ellipsometry technique is available to the scientific community through a yearly call for user proposals. We then get the opportunity to measure different type of materials from thin films to crystals of semiconductors and metals including 2D materials and organic samples deposited on metal layers. By imaging ellipsometry, the sample inhomogeneity, roughness and optical properties prior and after the pump-probe measurement are diagnosed. A discussion about newly imaging-analyzed samples that were and will be study by pump-probe ellipsometry will be presented.

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room 318 - Session LS1+2D+AS+EM+QS+SS-TuA

Operando Catalysis and Energy Systems

Moderator: Jyoti Katoch, Carnegie Mellon University

2:20pm **LS1+2D+AS+EM+QS+SS-TuA-1 In-situ/Real-time XPS Study of Electrochemical Reactions in All-solid-state Thin-film Lithium-Ion Batteries**, ***Takuya Masuda,*** National Institute for Materials Science, Japan **INVITED**

All-solid-state lithium-ion batteries (ASSLIBs) are one of the most promising next generation rechargeable batteries because of their very high safety and reliability. Understanding of the mechanism of electrochemical reactions and related physicochemical phenomena is very important for improving cell performances and durability. Application of ex-situ techniques to multiple samples disassembled from cells after certain charge/discharge cycles often results in misinterpretation due to the variation of samples and undesired side effects during sample transfer between battery test environment and characterization apparatus. Thus, various in-situ techniques which can be applied to the same position of the same sample kept at a certain charge/discharge state have been developed for hierarchical understanding of a series of electrochemical events interplaying with each other. X-ray photoelectron spectroscopy (XPS) is a powerful tool for analyzing the composition of reaction products, chemical state, and electronic structure of sample surfaces. By tuning the energy of incident x-rays, it also enables us to conduct the depth-resolved analysis of surfaces and interfaces including those buried with solid thin films. Recently, we developed an in-situ XPS apparatus equipped with a bias application system and a vacuum suitcase for sample transfer,[1] and applied it to the electrochemical lithiation/delithiation reactions of an amorphous Si thin film electrode sputter-deposited on a solid electrolyte sheet.[2] The chemical state of Si electrode changing during lithiation/delithiation processes was successfully tracked by sequential XPS measurements in the regions of Li 1s, C 1s, O 1s, and Si 2p. Not only lithium silicide (Li_xSi) which reversibly responds to the lithiation/delithiation but also irreversible species such as lithium oxides, lithium silicates and lithium carbonates were formed due to the lithiation of the Si electrode. Moreover, a rapid spectral change attributable to the phase transition of a crystalline Li_xSi to an amorphous phase was observed in the successive delithiation after preceding lithiation up to certain level. Based on the state of charge, Li content x in Li_xSi, and positions of XPS peaks, we summarized the lithiation/delithiation mechanism in Si electrodes. Further details will be presented.

[1] R. Endo, T. Ohnishi, K. Takada, T. Masuda, Journal of Physics Communications, 2021, 5, 015001.

[2] R. Endo, T. Ohnishi, K. Takada, and T. Masuda, J. Phys. Chem. Lett. 2020, 11, 6649−6654.

3:00pm **LS1+2D+AS+EM+QS+SS-TuA-3 Interaction of Molecular Nitrogen with Vanadium Oxide in the Absence and Presence of Water Vapor at Room Temperature: Near-Ambient Pressure XPS***, S. Nemsak,* Lawrence Berkeley National Laboratory*; **Kabirat Balogun**, P. Chukwunenye, T. Cundari, P. Bagus, J. Kelber,* Department of Chemistry, University of North Texas

Interactions of N_2 and H_2O at transition metal oxide surfaces are of fundamental interest for gaining insight into electrocatalytic nitrogen reduction reaction (NRR) mechanisms. N_2/H_2O interactions at the polycrystalline vanadium oxide/vapor interface were monitored at room temperature and N_2 partial pressures between 10^{-9} Torr and 10^{-1} Torr using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). The oxide film was predominantly V(IV), with significant V(III) and V(V) components. Such films have been previously demonstrated to be NRR active at pH 7. There is little understanding, however, of the detailed nature of N_2-surface interactions. XPS measurements were acquired at room temperature in environments of both pure N_2 and equal pressures of N_2 and H_2O vapor, up to a N_2 partial pressure of 10^{-1} Torr. In the absence of H_2O, broad N 1s features were observed at binding energies of 401 eV and 398.7 eV with relative intensity ratios of ~ 3:1, respectively. These features remained upon subsequent pumpdown to 10^{-9} Torr, indicating that adsorbed nitrogen is stable at room temperature in the absence of equilibrium with gas phase N_2. In the presence of equal pressures of N_2 and H_2O vapor, the 401 eV N 1s feature was reduced in intensity by ~ 50% at 10^{-1} Torr N_2 partial pressure, with the feature at 398.7 eV binding energy barely observable. DFT calculations show that the above NAP-XPS data demonstrating stable N_2-surface binding in the absence of N_2 overpressure are consistent with N_2 binding at V(IV) or V(III) sites, but not at V(V) sites, and further show that N_2/H_2O binding is competitive. SCF-HF calculations suggest that the two N 1s XPS features correspond to "shake" and normal transitions at 401 eV and 398.7 eV, respectively, for N_2 bonded end-on to the surface. The shake feature involves a charge transfer from V 3d to N_2 pi* in addition to N 1s ionization. The difference in binding energies of the two features, ~ 2.3 eV, strongly suggests N_2 -V(III) binding. The data presented demonstrate the ability of NAP-XPS, in concert with theory, to provide atomic-level insight concerning interfacial reactions relevant to electrocatalysis.

Acknowledgement:
This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility, under Contract No. DE-AC02-05CH11231. Work at UNT was supported in part by the NSF through grants DMR-2112864 (JAK, TRC), and via NSF support for the UNT CASCaM HPC cluster via Grant CHE-1531468. PSB was supported by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE through its Geosciences program at PNNL.

3:20pm **LS1+2D+AS+EM+QS+SS-TuA-4 Catalysts Caught in the Act: an Operando Investigation of Copper during CO_2 Hydrogenation***, **Elizabeth Jones**,* University of Oxford, UK

Amongst the foremost challenges in mitigating global warming are replacing fossil fuels with renewable alternatives, and storing/using carbon captured from CO2-emitting processes. Methanol production by CO2 hydrogenation promises a possible solution to both of these issues, particularly if H2 can be obtained through water electrolysis. When the resulting methanol is used as a fuel an equivalent amount of CO2 is released making it a “net-zero” fuel alternative. CO2 hydrogenation is performed industrially using a CO2/H2 mix at 200-300oC, 50-100 bar with a Cu-based catalyst, and the addition of CO is known to increase the methanol yield. However, mechanistic understand of this reaction and the role played by CO remains limited. Soft X-ray spectroscopies can provide details on the chemical state of copper to uncover the chemistry behind this reaction, however the typical requirement for measurement under high vacuum constrains how realistic these studies can be. There has been much recent development on improving operando techniques to enable heterogeneous catalytic reactions to be studied under realistic pressure conditions (E. S. Jones et al., in Ambient Pressure Spectroscopy in Complex Chemical Environments, 2021, ACS Symposium Series, vol. 1396, ch. 8, 175-218). A promising approach is to use an environmental cell which encloses the desired gas and separates it from the high vacuum environment, using an X-ray transparent window (R. S. Weatherup, J. Phys. Chem. Lett., 2016, 7, 1622-1627).

Using a custom-designed high pressure environmental cell we have studied model Cu catalysts using operando NEXAFS in total electron yield mode up to pressures of 1 bar and temperatures of 200oC. A thin Cu film was deposited onto a Si3N-4 membrane which acted to seal the high pressure gas within the cell and as a transparent window for incident X-rays. The aim of the study was to investigate how the Cu oxidation states varied when exposed to H2 and CO2 in different sequential order and how the introduction of CO can further influence the chemical state of Cu. It was found that H2 can provide a protective barrier to oxidation from CO2 when dosed first, however if H2 was added after CO2 it is unable to return the surface to its metallic state where CO is then required for reduction. This offers an insight into why CO plays an important role in the industrial production of methanol. Additionally, advances in sealing of the environmental cell enabled high pressures to be achieved at elevated temperatures, allowing this approach to be extended to more industrially-relevant conditions.

2D Materials Technical Group
Room 303 - Session 2D+EM+MI+NS+QS-WeM

2D Materials: Quantum and Symmetry-Protected States

Moderators: Thomas Michely, University of Cologne, Germany, **Frances Ross**, Massachusetts Institute of Technology

8:00am **2D+EM+MI+NS+QS-WeM-1 Semi-High Throughput Investigation of 2d Materials: Anomalous Quantum Confinement Effect and Spectral Properties***, **Francesca Tavazza**, K. Choudhary,* National Institute of Standard and Technology **INVITED**

Materials with van der Waals-bonding exhibit quantum confinement effect, in which the electronic bandgap of the three-dimensional (3D) form is lower than that of its two-dimensional (2D) counterpart. However, the possibility of an anomalous quantum confinement effect (AQCE) exists, where the bandgap trend is reversed. In this work, we computationally identify materials with AQCE. Using density functional theory (DFT), we compute ≈1000 OptB88vdW (semi-local functional), ≈50 HSE06 and ≈50 PBE0 (hybrid functional) bandgaps for bulk and their corresponding monolayers, in the JARVIS-DFT database. OptB88vdW identifies 65 AQCE materials, but the hybrid functionals only confirm such finding in 14 cases. Electronic structure analysis shows that AQCE is often characterized by the lowering of the conduction band in the monolayer and related changes in the p_z electronic orbital contribution. In addition to AQCE, the JARVIS-DFT contains IR and Raman spectra for many 2D materials. Properties of such spectra will be discussed as well.

8:40am **2D+EM+MI+NS+QS-WeM-3 Dry Patterning Chemically Sensitive Quantum Materials***, **Joseph Benigno**, Q. Zou, C. Cen, L. Li,* West Virginia University

Accurate, repeatable patterning of quantum material-based electronic devices is desirable for electrical transport measurements. However, the most common method, photolithography, can degrade, or even damage, chemically sensitive quantum materials during fabrication. Here we introduce a new dry-patterning method for device fabrication with lateral etching resolution down to ~30 µm. The new method utilizes a tabletop computer numerical control (CNC) router machine to gently etch patterns into thin films, leaving behind the desired device or devices on the substrate. We create Hall bars with conductive channel widths of 30, 60, and 120 µm from ~20 layer FeTe-capped superconducting single layer $FeSe/SrTiO_3$ systems. Transport measurements show the same zero resistance T_c of 10 K for the Van der Pauw (vdP) geometry and all Hall bar structures. However, the onset temperature T_{onset} is the largest at 28K for the vdP geometry, and decreases with the width of the Hall bar to 13K for the 60 µm device. Our method provides a new time-saving, cost-effective, and chemical-free strategy for fabrication of devices from quantum materials.

This research is supported by DOE DE-SC0021393.

9:00am **2D+EM+MI+NS+QS-WeM-4 Electron Transport and Charge Sensing in Strongly Coupled Quantum Dot Array in Silicon***, **Fan Fei**, J. Wyrick, P. Namboodiri, J. Fox,* NIST*; E. Khatami,* SJSU*; R. Silver,* NIST

Atomically precise donor-based quantum devices in silicon are fabricated using STM lithography, which has become a promising platform for solid state quantum computation and analog quantum simulation. Lattices of dopant-based quantum dots have unique advantages in simulating strongly correlated Fermionic systems of real atomic lattice sites because of their naturally occurring ion-cores which make them the Fermi-Hubbard sites in the Silicon Vacuum. Understanding electron transport and charge configuration in a smaller array is critical to using these arrays to simulate larger systems and explore various condensed matter physics phenomena such as superconductivity in the future. This talk will focus on the electron transport in the strongly coupled regime where the electrons delocalize across small N x N dot arrays. Numerical simulations for charge stability diagrams and transport properties show qualitatively agreement with our experiments. We apply rf reflectometry on a SLQD and use it as charge sensor for probing the electron configuration within the array.

9:20am **2D+EM+MI+NS+QS-WeM-5 Observation of the Layer Hall Effect in Topological Axion Antiferromagnet $MnBi_2Te_4$***, **Suyang Xu**,* Harvard University **INVITED**

While ferromagnets have been known and exploited for millennia, antiferromagnets were only discovered in the 1930s. The elusive nature indicates antiferromagnets' unique properties: At large scale, due to the absence of global magnetization, antiferromagnets may appear to behave like any non-magnetic material; At the microscopic level, however, the opposite alignment of spins forms a rich internal structure. In topological antiferromagnets, such an internal structure leads to a new possibility, where topology and Berry phase can acquire distinct spatial textures. We study this exciting possibility in an antiferromagnetic Axion insulator, even-layered $MnBi_2Te_4$ flakes. We report the observation of a new type of Hall effect, the layer Hall effect,where electrons from the top and bottom layers spontaneously deflect in opposite directions.

Reference:

A. Gao, et al."Layer Hall effect in a 2D topological axion antiferromagnet." *Nature* 595, 521 (2021).

11:00am **2D+EM+MI+NS+QS-WeM-10 Phonon Limited Mobility and Phonon Drag in h-BN Encapsulated Monolayer and AB-stacked Bilayer Graphene***, **Vasili Perebeinos**,* University at Buffalo

We report the electrical transport in h-BN encapsulated AB-stacked bilayer graphene theoretically and experimentally. Using the perturbation theory within the tight-binding model approach, we identify the dominant role of the shear phonon mode scattering on the carrier mobility in AB-stacked graphene bilayer at room temperature. The shear phonon mode is absent in free-standing monolayer graphene, which explains high mobilities in monolayer devices fabricated under similar conditions resulting in minimal Coulomb impurity scattering. At temperatures above 200K, the surface polar phonon scattering from the boron-nitride substrate contributes significantly to the experimental mobilities of 15,000 -20,000 cm^2/Vs at room temperature and carrier concentration $n\sim10^{12}$ cm^2 reported here. A screened SPP potential for a dual gated bilayer and transferable tight-binding model allows us to predict mobility scaling with temperature and bandgap for both electrons and holes in agreement with the experiment Phys Rev. Lett. 128, 206602 (2022).

The resulting electron-SPP coupling is used to predict that, by exploiting the strong coupling of their electrons to surface polar phonons, van der Waals heterostructures can offer a suitable platform for phonon sensing, capable of resolving energy transfer at the single-phonon level. The geometry we consider is one in which a drag momentum is exerted on electrons in a graphene layer, by a single out-of-equilibrium phonon in a dielectric layer of hexagonal boron nitride, giving rise to a measurable induced voltage. Our numerical solution of the Boltzmann Transport Equation shows that this drag voltage can reach a level of a few hundred microvolts per phonon, well above experimental detection limits. Furthermore, we predict that drag voltage should be largely insensitive to the mobility of carriers in the graphene layer and increase the temperature up to at least 300 K, offering the potential of a versatile material platform for single-phonon sensing.

11:20am **2D+EM+MI+NS+QS-WeM-11 Exciton Physics at the Atomic Scale***, **Daniel Gunlycke**,* U.S. Naval Research Laboratory

Descriptions of excitons in pristine semiconducting crystals usually rely on the hydrogen model adopted for excitons. Owing to the weak screening in monolayer transition-metal dichalcogenides, however, the electron and hole separation in the strongest bound excitons is on the atomic scale, necessitating atomistic treatment. In this presentation, we present a minimalistic exciton model that accounts for the lattice and the spin-orbit and exchange interactions, thus making this model appropriate across the spectrum from Wannier to Frenkel excitons. Using this model, we show that the exciton lifetimes could be extended by transitioning the excitons into excitonic dark states. Longer exciton lifetimes could make these materials candidates for applications in energy management and quantum information processing.

11:40am **2D+EM+MI+NS+QS-WeM-12 Weyl Semimetals with Low-Symmetry Crystal Structure for Generating Out-of-Plane Oriented Spin Current***, **Simranjeet Singh**,* Carnegie Mellon University **INVITED**

Weyl semimetals (WSMs), such as WTe_2 and $MoTe_2$, host plethora of novel phenomena that are highly relevant for quantum spintronics, namely: Dirac type dispersion, strong spin-orbit coupling (SOC), Fermi arcs, and helical spin-momentum locked surface and bulk states. WSMsprovide a distinct opportunity to obtain highly efficient and unconventional charge to spin conversion owing to strong SOC, symmetry breaking, and these topology-based phenomena. On the other hand, spin-orbit torque (SOT) driven deterministic control of the magnetic state of a ferromagnet with perpendicular magnetic anisotropy is key to next generation spintronic applications including non-volatile, ultrafast, and energy efficient data storage devices. But field-free deterministic SOT switching of perpendicular magnetization remains a challenge because it requires an out-of-plane oriented spin current, which is not allowed in conventional spin source materials such as heavy metals and topological insulators due to the system's symmetry. The exploitation of low-crystal symmetries WTe_2 and $MoTe_2$ offers a unique approach to achieve SOTs with unconventional forms[1]. In this work, I will discuss our experiments to realize field-free deterministic magnetic switching of a perpendicularly polarized van der Waals magnet employing an out-of-plane spin current generated in layered WTe_2, which is a quantum material with low-symmetry crystal structure[2]. I will also discuss our experiments aimed at achieving field-free SOT switching of semiconducting and insulating FMs using spin current in WSMs. Our work establishes transition metal dichalcogenides, with lower symmetry crystal structure, as an appealing spin source material for future spin-orbit torque related magnetic memory technologies.

[1]. MacNeill, D. *et al.* Control of spin–orbit torques through crystal symmetry in WTe_2/ferromagnet bilayers. *Nature Physics***13**, 300-305, (2017).

[2]. Kao, I-H *et al.* Deterministic switching of a perpendicularly polarized magnet using unconventional spin–orbit torques in WTe_2. Nature Materials (2022). https://doi.org/10.1038/s41563-022-01275-5

2D Materials Technical Group
Room 303 - Session 2D+EM+MI-WeA

2D Materials: Charge Density Waves, Magnetism, and Superconductivity

Moderators: An-Ping Li, Oak Ridge National Laboratory, **Xiaomeng Liu**, Princeton University

2:20pm **2D+EM+MI-WeA-1 Tunable Electronic Structure and Correlations in Quasi-Freestanding Monolayer Transition Metal Disulfides***, **Thomas Michely**,* Universität zu Köln, Germany **INVITED**

In situ reactive molecular beam epitaxy using single crystal graphene as a substrate enables to grow transition metal disulfides as quasi-free standing monolayers under well controlled conditions. Thereby access to their undisturbed electronic properties of as well as to those of their intrinsic defects is provided.

A non-invasive technique to shift the chemical potential in semiconducting transition metal disulfide layers like MoS_2 or WS_2 through p- and n-type doping of graphene is presented, while graphene remains a well-decoupled 2D substrate. These shifts induce giant band gap renormalizations, insulator-to-metal to insulator transitions and affects the metallic states in mirror twin boundaries.

Electronic correlations are known to be strong for dimensional reasons in transition metal dichalcogenide monolayers and often give rise to charge density waves and other competing electronic phases. The dependence of charge density waves on the environment and its layer dependence are investigated for several transition metal disulfides. We show that monolayers of VS_2 realize a CDW which stands out of our expectations. It displays a full CDW gap residing in the unoccupied states of monolayer VS_2 and the CDW induces a topological metal-metal (Lifshitz) transition. Non-linear coupling of transverse and longitudinal phonons is essential for the formation of the CDW and the full gap above the Fermi level.

Lastly we will focus to mirror twin boundaries in MoS_2 and investigate how to determine quantized polarization charges on these domain boundaries, whether they are subject to Fermi level pinning and how shifts in the Fermi level change screening of their line charge.

Contributions to this work by Clifford Murray, Camiel van Efferen, Wouter Jolie, Jeison Fischer, Timo Knispel, Joshua Hall, Stefan Kraus, Felix Huttmann, Carsten Busse, Niels Ehlen, Boris Senkovskiy, Martin Hell, Alexander Grüneis, Hannu-Pekka Komsa, Arkady Krasheninnikov, Jan Berges, Erik van Loon, Arne Schobert, Malte Rösner, Tim Wehling, Nico Rothenbach, Katharina Ollefs, Lucas Machado Arruda, Nick Brookes, Gunnar Schönhoff, Kurt Kummer, Heiko Wende, Philipp Weiß, Fabian Portner, and Achim Rosch are gratefully acknowledged.

3:00pm **2D+EM+MI-WeA-3 Dopants Modulated Interplay of Charge Density Wave and Superconductivity in 2D VdW Layered ZrTe3***, **Xiao Tong**,* . Center of Functional Nanomaterials, Brookhaven National Laboratory*; Y. Liu, Z. Hu,* Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory*; D. Leshchev,* National Synchrotron Light Source II, Brookhaven National Laboratory*; X. Zhu, H. Lei,* Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory*; E. Stavitski, K. Attenkofer,* National Synchrotron Light Source II, Brookhaven National Laboratory*; C. Petrovic,* Condensed Matter Physics and Materials Science, Department, Brookhaven National Laboratory

Two-dimensional transition metal trichalcogenides ZrTe3 holds atomic chains in the crystal structure give rise to quasi one-dimensional (quasi 1D) conduction, and features the charge density wav (CDW) below TCDW ¼ 63 K and filamentary superconductivity below 2 K, Here, we report that superconductivity(SC) is enhanced as the consequence of suppressed CDW for Hf dopped ZrTe3, in contrast, SC is suppressed as the consequence of enhanced CDW for the Se dopped ZrTe. Our XPS and Raman studies suggested the suppressed CDW is due to Hf caused disorder in Te2-Te3 atomic chains, while the enhanced CDW is due to Se induced enhanced electron-phonon coupling in unperturbed periodicity of the Te2-Te3 chains, respectively.

3:20pm **2D+EM+MI-WeA-4 Magnetic Order in a Coherent Kondo Lattice in 1T/1H $TaSe_2$ Heterostructures***, W. Wan, **Rishav Harsh**, P. Dreher, S. Sajan,* Donostia International Physics Center , Spain*; A. Menino, I. Errea,* Centro de Física de Materiales (CSIC-UPV-EHU), Spain*; F. de Juan, M. Ugeda,* Donostia International Physics Center , Spain

Kondo lattice systems are of fundamental importance for our understanding of quantum criticality and unconventional superconductivity. At the heart of their complexity lies the competition between the opposing forces of Kondo screening and magnetic interactions, which is revealed at very low temperatures as the moments start behaving coherently and eventually determines the fate of the ground state. While our understanding of Kondo lattices has traditionally relied on technically challenging strongly correlated bulk f-electron systems, new light is being shed on the problem thanks to heterostructures of 2D transition metal dichalcogenides, which realize a tunable Kondo lattice platform in a simple material. Here, we study the 1T/1H-$TaSe_2$ heterostructure by high-resolution Scanning Tunneling Spectroscopy at 300 mK, and show a well resolved splitting of the Kondo peak, which increases monotonically in a nonlinear fashion in the presence of an out-of-plane magnetic field. This behavior is unexpected for a fully screened Kondo lattice, and it originates instead from a ground state with residual magnetic order, consistent with a Kondo coupling much below the critical point in the Doniach phase diagram.

4:20pm **2D+EM+MI-WeA-7 Structural and Magnetic Properties of Ultrathin $Cr_{(1+\delta)}Te_2$ Films Grown by Van Der Waals Epitaxy***, **Kinga Lasek**, P. Coelho,* University of South Florida*; P. Gargiani , M. Valvidares,* ALBA Synchrotron Light Source, Spain*; K. Mohseni , H. Meyerheim , I. Kostanovskiy,* Max Planck Institute of Microstructure Physics, Germany*; K. Zberecki,* Warsaw University of Technology, Poland*; M. Batzill,* University of South Florida

Over the past years, researchers have proved that the layered structure of transition metal dichalcogenides (TMDs) enables the synthesis of novel materials. Specifically, introducing extra transition metal atoms into the vdW gap of the TMDs host lattice leads to various structural, electrical, and magnetic properties modulations. Exploring the latter, in particular, aligns with a recent search for ferromagnetic 2D materials.

In this talk, we will explore the epitaxial growth, structural, surface, and magnetic properties of a bi- to few-layer thick $Cr_{(1+\delta)}Te_2$ ($0 < \delta < 1$)films that represent a group of self-intercalated TMDs materials. These materials demonstratewell-known ferromagnetic ordering and exist in different compositional phases that vary by the amount of Cr intercalated (δ) between $CrTe_2$ layers.By detailed compositional and structural characterization, using scanning tunneling microscopy (STM), and high-resolution Rutherford backscattering (HR-RBS) we will show that the amount of self-intercalated Cr atoms can be controlled by post-growth annealing. Such modified films are characterized by an increased T_c up to 190K, a coercive field being reduced from 0.5 T to 0.3 T, and an isotropization of the magnetic anisotropy confirmed by XMCD measurements.

Finally, we will demonstrate that ultrathin vdW films can be prepared with the ultimate limit of a single self-intercalated layer by vdW epitaxy. These vdW materials maintain their ferromagnetic properties with desirable out-of-plane anisotropy and thus are potential ferromagnetic 2D materials that can be combined in vdW heterostructures by a bottom-up growth process.

4:40pm **2D+EM+MI-WeA-8 Transition Metal Silicates as a Platform for Robust Single Layer, Two-Dimensional Ferromagnetism***, **Nassar Doudin**, K. Saritas,* Yale University*; P. Shafer, A. T. N'Diaye,* Lawrence Berkeley National Laboratory (LBNL)*; S. Ismail-Beigi, E. Altman,* Yale University

Two-dimensional (2D) materials have received extensive attention and rapid development since the discovery of graphene in 2004.[1] Magnetism in two dimensions has long been at the heart of theoretical, experimental, and technological advances, where great efforts have been made to realize magnetism in 2D materials.[2] To date, 2D magnetic materials have been obtained via exfoliation from bulk samples; however, this makes it difficult to precisely control the thickness and domain size of the samples. Moreover, the most intensely studied 2D magnetic materials (e.g. CrI_3, $Cr_2Ge_2Te_6$) are unstable in air and are only ferromagnetic below ~50 K. Hence, exploring new 2D magnetic materials is of grand significance. Recently, vdW epitaxy techniques have fulfilled the growth of 2D vdW materials on metal substrates, such as 2D silica bilayers and related transition metal silicates which break inversion symmetry guaranteeing at least a piezoelectric response. The arrival of these 2D vdW materials opens up exciting opportunities for preparing 2D multiferroic materials. In this talk, we demonstrate air stable, single layer 2D $M_xSi_2O_5(OH)_y$ (M= Fe, Cr) structures consisting of a silica-capped metal oxide grown on Pd and Au substrates that exhibit ferromagnetic order at room temperature as measured by x-ray magnetic circular dichroism (XMCD) spectroscopy. Application of small magnetic fields proves that the observed magnetic structures follow a hysteretic behavior. SQUID magnetometry confirms these results and reveals high spin-polarization at room temperature with in-plane magnetic anisotropy. The measurements are further supported by first-principles theoretical calculations which highlight approaches to stabilize the magnetic order. Thus $M_xSi_2O_5(OH)_y$ based 2D materials represent a new platform for single layer 2D ferromagnetism with potential multiferroic behavior.

1. Meyer, J. C. *et al.* The structure of suspended graphene sheets. *Nature***446**, 60–63 (2007).
2. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. G. and A. A. F. Electric Field Effect in Atomically Thin Carbon Films. *Science.***306**, 666–669 (2004).

5:00pm **2D+EM+MI-WeA-9 Novel Materials for Quantum Computing Devices: Monolayer Topological Superconductors***, **Yi-Ting Hsu,*** University of Notre Dame **INVITED**

Atomically thin superconductors that possess 'topological properties' have attracted extensive attention since many of them are predicted to host exotic zero-energy quasi-particles called Majorana zero modes (MZMs). MZMs are proposed to be the building blocks in a type of fault-tolerant quantum computation scheme known as topological quantum computation (TQC). One of the pressing challenges in the field of TQC is to experimentally realize such a superconducting film and detect the existence of MZMs. In this talk, I will first discuss what a topological superconductor is and why it is a promising platform for a TQC device. I will then talk about candidate materials in the family of transition metal dichalcogenides. Finally, I will discuss our theory-experiment combined effort to systematically identify more candidates in two-dimensional material databases.

5:40pm **2D+EM+MI-WeA-11 Tuning Magnetism and Superconductivity in Single Layer FeSeTe by Chemical Pressure***, **Basu Oli,** Q. Zou, H. Zhang,* West Virginia University*; T. Shishidou, M. Weinert,* University of Wisconsin, Millwaukie*; L. Li,* West Virginia University

The interplay of topology, magnetism, and superconductivity in a single-layer FeX (X = S, Se, Te) epitaxially grown on $SrTiO_3$ (STO) substrate provides a model system for investigating a wide range of quantum phenomena. This work explores the impact of chemical pressure on magnetism and superconductivity in single-layer $FeSe_{1-x}Te_x$/STO grown by molecular beam epitaxy using *in-situ* angle-resolved photoemission spectroscopy and scanning tunneling microscopy/spectroscopy. We find that the Fermi surface consists of only an electron pocket at the M point, which decreases in size with increasing Te concentration and disappears completely for $x > 0.75$. At the Γ point, a hole pocket appears with $x > 0.65$, while the bands changes from parabolic to linear up to $x = 0.9$, where it reverts back to parabolic. Accompanying the changes in the band structure, the top of bands at the Γ also shift towards and then away from the Fermi level, indicative of a topological phase transition in $FeSe_{1-x}Te_x$/STO. At 4.3 K, while the FeTe films are non-superconducting, dI/dV tunneling spectra indicate the emergence of superconductivity when Se concentration is greater than 25%. Our spin spiral calculations indicate that the FeTe system exhibits long-range bi-collinear antiferromagnetic (AFM) order, which is tuned toward the checkerboard (CB) AFM fluctuations with the incorporation of Se. Our findings indicate that CB AFM fluctuations are critical for superconductivity in epitaxial single layer iron chalcogenide superconductors on STO.

This research is supported by DOE (DE-SC0017632).

6:00pm **2D+EM+MI-WeA-12 Peculiar Near-Contact Regime of Andreev Reflection at the Breakdown of a Tunnel Junction***, **Petro Maksymovych**, S. Song,* Oak Ridge National Laboratory*; J. Lado,* Aalto University, Finland*; W. Ko,* Oak Ridge National Laboratory

Recently we introduced non-contact Andreev reflection (NCAR) - a new experimental approach to quantify Andreev reflection in a tunable tunnel junction [1]. The technique utilizes the fundamental connection between the physics of the scattering process and the strength of exponential non-linearity of the tunneling current, and therefore adopts the tunneling current decay rate as the observable. NCAR simultaneously achieves spectroscopy of quasiparticle density of states, atomic-scale resolution and quantitative Andreev reflection, while avoiding the necessity to form invasive and mesoscale mechanical contacts. One surprising observation of NCAR is that Andreev reflection does not have a monotonous dependence on tip-sample separation. In particular, the decay rate signature of Andreev reflection proceeds through a maximum just before the mechanical contact. In this talk, we will explore in detail the origin of this near-contact regime and its significance for the characterization of superconductivity. In particular, we will rationalize the observations within the accepted BKT model as well as accurate tight-binding simulations, revealing the fundamental connection between the tunneling barrier dependence of Andreev reflection and the order in perturbation theory responsible for the tunneling current. Furthermore, we will highlight the importance of higher order Andreev reflection for the measurement of unconventional superconductors. In general, tunneling and near-contact regimes will qualitatively differ from each other in the case of unconventional superconducting order parameters, enabling direct inference of their symmetry.

At the same time, we will demonstrate how quantitative comparison of statistical distributions of decay rate enables a complementary, probabilistic analysis of the Andreev reflection [2]. This purely informational approach is particularly important given the narrow parameter space that separates the now rich variety of techniques to directly probe superconductivity, enabling robust control over crossovers between non-contact, near-contact, multiple Andreev reflection as well as quasiparticle tunneling in atomic-scale junctions.

Research sponsored by Division of Materials Science and Engineering, Basic Energy Sciences, Office of Science, US Department of Energy. SPM experiments were carried out as part of a user project at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, a US Department of Energy Office of Science User Facility.

1. W. Ko, J. Lado, P. Maksymovych, Nano Lett. 22, 4042 (2022).

2. W. Ko, E. Dumitrescu, P. Maksymovych, Phys. Rev. Res. 3, 033248 (2021).

Electronic Materials and Photonics Division
Room 330 - Session EM-WeA

Compound Semiconductors

Moderator: Erica Douglas, Sandia National Laboratories

5:20pm **EM-WeA-10 Strain-Induced Semiconducting to Metallic Phase Transition in Suspended $MoTe_2$ using a Single-Ion Conductor***, **Shubham Awate,*** University of Pittsburgh*; K. Xu,* Rochester Institute of Technology*; J. Liang, B. Mostek,* University of Pittsburgh*; B. Katz,* Pennsylvania State University*; R. Muzzio,* Carnegie Mellon University*; V. Crespi,* Pennsylvania State University*; J. Katoch,* Carnegie Mellon University*; E. Backman, S. Fullerton-Shirey,* University of Pittsburgh

Commonly studied transition metal dichalcogenide (TMD) crystals exhibit polymorphism, where the electronic structure of the material changes significantly with a change in the crystal structure. $MoTe_2$ has gained particular interest because the potential energy difference between the semiconducting 2H and semi-metallic 1T' phase is the lowest (40 meV) among TMD polymorphs, making it promising for low voltage phase change memory and transistors. Although the 2H phase is the most stable form, it can be transformed to 1T' by 0.3 - 3% by tensile strain thereby causing a large change in the electronic conductivity. Recent studies have experimentally shown this phase transition by mechanically stretching the entire substrate or applying local mechanical strain using atomic force microscopy (AFM) tip, but both strain methods would be difficult to implement in CMOS. What is needed is a straining mechanism driven by field-effect, where a single device can be controlled electrically by a nearby gate.

Here, we employ an 'ionomer' or single-ion conductor to impart strain. An ionomer contains mobile cations but has anions that are covalently bonded to a polymer backbone. Under an applied electric field, the cations accumulate at the $MoTe_2$ surface, effectively controlling electron transport in the material, while anions maintain their position in the polymer backbone creating a charge imbalance. The imbalance causes the ionomer to bend, which then induces strain in the $MoTe_2$.

In this work, the electrical and structural properties of a suspended $MoTe_2$ FET are measured simultaneously using a home-built set-up combining electrical measurements with Raman spectroscopy. With no gate voltage (V_G) applied, the insulating 2H phase is confirmed. For $V_G > 2.5$ V, the 1T' phase is detected by a significant decrease in the electrical resistance accompanied by a characteristic 1T' peak in the Raman spectra. Mapping the 2H and 1T' peaks across the entire flake reveals that the phase transition is reversible (i.e., the flake reverts to the semiconducting 2H phase when the voltage is removed), which is an essential feature of memory. The output characteristic of the FET shows a large change in the I_D-V_G slope for $V_G > 1.5$ V. Further, metallic conduction is confirmed by the positive temperature coefficient of resistance for $V_G = +2$ and $+3$ V. Lastly, time-dependent Raman spectroscopy is performed to study the phase change dynamics. The demonstrated gate-controlled reversible straining method can be easily extended to strain other types of two-dimensional materials to explore fundamental properties as well as discover new device mechanisms.

5:40pm **EM-WeA-11 Investigation of Thermal Stability of Pure-Metal Schottky Contacts to β-Ga_2O_3,** ***Elizabeth Favela**, K. Zhang, A. Ho, S. Kim,* Carnegie Mellon University*; K. Das,* North Carolina State University*; L. Porter ,* Carnegie Mellon University

Due to its ultra-wide band gap ($E_G \sim 4.8$ eV) and the availability of melt-grown single-crystal substrates, gallium oxide (Ga_2O_3) has attracted intense interest for (opto)electronic devices that can operate under extreme conditions. However, for these devices to operate reliably, electrical contacts to Ga_2O_3 that are chemically and electrically stable at elevated temperatures must be demonstrated. In this study we investigated the electrical properties, interfacial chemistry and surface morphology of Co/Au and Ni/Au Schottky contacts on Sn-doped ($N_D = 10^{18}$ cm^{-3}) (-201) β-Ga_2O_3 substrates through two different annealing series. Current-voltage and capacitance-voltage measurements were conducted at room temperature after sequential annealing treatments totaling >400 h at 300 °C and >150 h at 500 °C in air. Schottky barrier heights were relatively stable through the annealing series at 300 °C. However, gradual degradation in the electrical behavior was observed through the annealing series at 500 °C. Whereas the contacts were relatively stable after 300 °C anneals, characterizations using scanning transmission electron microscopy, energy dispersive x-ray spectroscopy, and scanning electron microscopy of samples annealed at 500 °C showed substantial changes in morphology, multi-element diffusion, and phase segregation within the contacts. The results suggest that these pure-metal contacts could be useful in Ga_2O_3 Schottky diodes at temperatures below, or possibly up to, 300°C. However, alternative contact compositions, possibly incorporating metal-oxides [1], will be required for Ga_2O_3-based device operation at or above the 300 °C temperature range. The results of this work in context of other Ga_2O_3 contact studies and the implications for future research directions will also be presented.

[1]C. Hou, R. M. Gazoni, R. J. Reeves, and M. W. Allen, Direct Comparison of Plain and Oxidized Metal Schottky Contacts on β-Ga_2O_3, Appl. Phys. Lett. 114, 033502 (2019).

6:00pm **EM-WeA-12 Electrical and Chemical Effects of Metal Contacts to β-Ga_2O_3 Surfaces*, Luke Lyle,*** Pennsylvania State University

Over the last decade significant progress has been demonstrated for ⍰-Ga2O3, with its ultrawide bandgap of 4.6-4.8 eV, controllable range of n-type, shallow dopants (Sn, Si, Ge), and a scalable melt-growth process allowing the production of large-area, native substrates this material has garnered strong interest for applications as UV photodetectors and high-power electronics. A critical piece of development for ultrawide bandgap materials is the optimization of the metal-semiconductor interface for high-power applications. This talk focuses on the electrical properties of various metallizations to differently oriented β-Ga2O3 crystals and focuses on the resulting chemistry of certain metal-semiconductor interfaces. The Schottky barriers of Ti/Au, Mo, Co, Ni, Pd, and Au on (100) β-Ga2O3 substrates were analyzed using a combination of current-voltage (J-V), capacitance-voltage (C-V), and current-voltage-temperature (J-VT) measurements. The ideality factors and Schottky barrier heights from J-V and C-V methods are documented and discussed. J-V-T measurements of Ti/Au, Co, and Pd diodes reveal inhomogeneity of the Schottky energy barrier. These combined results reveal a strong positive correlation between the calculated Schottky barrier heights and the metal work functions: the index of interface behavior, S, for J-V and C-V data. Additionally, Ti and Au metallizations reveal peculiar electrical properties (higher ideality factors, different J-V and C-V Schottky barrier heights, etc) and further characterizations are pursued. Au contacts to (100) β-Ga2O3 were subsequently examined with transmission electron microscopy (TEM) due to the electrical properties exhibited via J-V and C-V measurements. The contacts exhibited a chemical reaction with void formation 5-20 nm below the Au/β-Ga2O3 interface, a reacted region at the interface that is structurally dissimilar to the bulk β-Ga2O3 structure, the presence of Ga interstitials diffusing to the metalsemiconductor interface, and EDS mapping reveals Ga diffusion into the Au overlayer. Chemical measurements of Ti/(010) and Ti/(001) β-Ga2O3 contacts were examined with x-ray photoelectron spectroscopy (XPS). XPS revealed partial Ti oxidation at both interfaces in the as-deposited condition, with more Ti oxidation on the (001) β-Ga2O3 epilayer surface than the (010) β-Ga2O3 substrate surface. The amount of oxidized Ti increased with annealing temperature. J-V and C-V measurements of contacts made from these devices reveal a strong orientation dependence of the electrical properties of Ti/β- Ga2O3 diodes.

Nanoscale Science and Technology Division
Room 304 - Session NS2+AS+EM-WeA

Scanning Probe Metrology of 1D and 2D Materials

Moderators: Maryam Ebrahimi, lakehead University, Canada, **Aubrey Hanbicki**, Laboratory for Physical Sciences

4:20pm **NS2+AS+EM-WeA-7 New on-Surface Synthesis Techniques for Creating Precise 1D Graphene Nanoribbon Heterojunctions and Device-Tunable 2D Molecular Arrays*, Michael Crommie,*** UC Berkeley Department of Physics*; G. Dong,* University of Chicago Department of Chemistry*; J. Lischner,* Imperial College London Department of Materials, UK*; A. Zettl, P. Jacobse, Z. Wang,* UC Berkeley Department of Physics*; J. Yin,* University of Chicago Department of Chemistry*; H. Tsai, F. Liou, A. Aikawa,* UC Berkeley Department of Physics **INVITED**

Bottom-up fabrication techniques for assembling molecular nanostructures at surfaces typically exploit various surface interactions that (along with random thermal processes) can be biased toward achieving desired structural results via the clever design of molecular precursors. Great progress has been made using this approach, but surface-grown molecular structures remain plagued by random, uncontrolled processes that make complex structural control difficult. Overcoming this problem is one of the grand challenges of this subfield. Here I will discuss two new approaches to molecular surface assembly that have allowed us to improve order in surface-based nanostructures. The first involves 1D materials and utilizes a solution-based polymerization scheme combined with a new surface deposition procedure. The second involves combining molecular surface assembly with 2D field-effect transistors (FETs). The first method is focused on graphene nanoribbons (GNRs), nanometer-wide strips of graphene. Fabricating complex heterostructure sequences in GNRs remains a difficult challenge because we can't sequence GNRs the way we sequence DNA. This makes it hard to fulfill the promise of GNR-based molecular electronics because of the difficulty of fabricating GNRs composed of well-ordered segments that each have controlled properties (e.g., bandgap, doping, magnetism, optical response). We have made progress toward overcoming this challenge by using a new protecting-group-aided-iterative-synthesis strategy. This allows us to create GNR oligomers with perfectly defined monomer sequences in solution that can be deposited onto surfaces for cyclodehydrogenation using a matrix-assisted deposition (MAD) procedure. This has enabled the synthesis of GNR heterojunctions that would not be possible via other techniques. The second technique I will discuss involves the use of an "active substrate" (a graphene FET) to induce *reversible* 2D molecular assembly through a combination of Coulomb and van der Waals interactions. The trick here is to use a molecule (in our case F_4TCNQ) whose LUMO level (E_L) lies in an energy range accessible to the Fermi level (E_F) of the 2D FET. Manipulating E_F relative to E_L via the device backgate allows charge in the device to reversibly flow between substrate states and the LUMO level of adsorbed molecules. This results in unexpected mechanical responsivity of the molecules, including tunable 2D array formation and a reversible quasi-1D phase transition that we have imaged using scanning tunneling microscopy.

5:00pm **NS2+AS+EM-WeA-9 Temperature-Mediated Adsorption and Assembly of Internally Fluorinated Chevron Graphene Nanoribbon Precursors on Au(111)**, ***Jacob Teeter,*** Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *M. Sarker,* University of Nebraska - Lincoln; *C. Tao, J. Huang,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *W. Lu, J. Bernholc,* North Carolina State University; *A. Sinitskii,* University of Nebraska - Lincoln; *A. Li,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

The archetypical chevron-shape graphene nanoribbon (GNR) broke new ground in the on-surface synthesis of carbon-based nanomaterials with its development in 2010 by Cai *et al*[1]. Subsequent innovation predicated on this discovery introduced a wide variety of GNRs with differing shapes, edge types, heteroatomic substitutions, topological phases, and more. One drawback to studying GNRs arising from surface-assisted synthesis is the intrinsic electronic hybridization between the GNR and the surface upon which it was grown. This convolutes electronic characterization such as scanning tunneling spectroscopy (STS), but can be mitigated somewhat through tip-based manipulation of the GNRs onto an insulating layer on the surface, or by introducing a powder of solution-synthesized GNRs to a semiconducting substrate. Only recently has a method been developed - utilizing rutile TiO_2(011), rationally designed fluorinated precursors, and a surface-assisted cyclodehydrofluorination reaction - to achieve bottom-up-synthesized atomically precise GNRs on such a surface[2].

In this work, we have developed more fluorinated precursors to expand the set of atomically precise GNRs grown on semiconducting surfaces and studied their assembly on Au(111) using scanning tunneling microscopy. In particular, we have produced and prototyped on Au(111) a fluorinated chevron precursor intended to yield chevron-type GNRs on TiO_2(011). With all other factors equivalent, the adsorption of the precursor is heavily dependent on the temperature of the surface of the Au(111) crystal on which it is deposited. The lack of adsorption at room temperature is in sharp contrast with the non-fluorinated precursor, which can be deposited at room temperature and post-annealed to produce GNRs in good yield. We attribute this discrepancy to interactions between the internal F atoms and the Au(111) surface, which is supported by theoretical calculations.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

1.Cai, J.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Müllen, K.; Fasel, R., Atomically precise bottom-up fabrication of graphene nanoribbons. Nature 2010, 466.

2.Kolmer, M.; Steiner, A.-K.; Izydorczyk, I.; Ko, W.; Engelund, M.; Szymonski, M.; Li, A.-P.; Amsharov, K., Rational synthesis of atomically precise graphene nanoribbons directly on metal oxide surfaces. Science 2020, 369 (6503), 571-575

5:20pm **NS2+AS+EM-WeA-10 STM Study of Superconducting Film FeTe(1-x)Se(x) on Topological Insulator Bi_2Te_3**, ***Hoyeon Jeon****, W. Ko, M. Brahlek, R. G. Moore II, A. Li,* Oak Ridge National Laboratory, USA

Topological superconductors (TSCs) have attracted great attention because they can host Majorana fermions for quantum computation. Because natural TSCs are rarely found, alternative ways to make TSCs are badly needed. One of them is using proximity effect by combining two-dimensional Dirac surface states of topological insulator (TI) with s-wave superconductivity (SC) to generate localized topological Majorana zero modes in vortex cores. Here we report the epitaxial growth of SC films of FeTe(1-x)Se(x) on TI of Bi_2Te_3, their electronic structures and surface inhomogeneities of superconductivity using scanning tunneling microscope/spectroscopy (STM/STS). A variety of samples are examined with different thicknesses of superconducting layer and selenium concentrations. We expect our results to be relevant for searching for materials platforms to host topological superconductivity.

The research is supported by the U.S. Department of Energy (DOE), Office of Science, National Quantum Information Science Research Centers., the Quantum Science Center (QSC), a National Quantum Information Science Research Center of the U.S. Department of Energy (DOE).

5:40pm **NS2+AS+EM-WeA-11 Atomic-Scale Mapping of Thermoelectric Properties of Noble Transition Metal Dichalcogenides**, ***Saban Hus****, A. Li,* Oak Ridge National Laboratory; *L. Liu, Y. Chen,* Purdue University

Monolayer noble transition metal dichalcogenides with hexagonal lattice structure are predicted to be high performance thermoelectric materials at room temperature [1]. Their pentagonal counterparts promise even better performance due to the in-plane anisotropy of the lattice [2]. However, like many other features of 2D materials, their thermoelectric properties can significantly be altered by the heterogeneities in the atomically thin layers [3]. Using a scanning tunneling microscope (STM), we investigate the thermoelectric properties of both pentagonal and hexagonal noble transition metal dichalcogenide monolayers in atomic resolution. We observe that atomic-scale defects and variations in 2D layer-substrate interface create a rich thermoelectric landscape invisible to mesoscopic scale measurements. Precise control and utilization of these heterogeneities can lead to next-generation thermoelectric devices and materials for energy applications.

[1] B. Marfoua and J. Hong, ACS Appl. Mater. Interfaces 11, 38819 (2019)

[2] D. Qin, et al., Sci. Reports. 8, 2764 (2018).

[3] S.M. Hus, A-P. Li, Progress in Surface Science 92, 176 (2017)

* This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

Quantum Information Science Focus Topic
Room 302 - Session QS+EM+MN+NS-WeA

Systems and Devices for Quantum Information

Moderators: Megan Ivory, Sandia National Laboratories, **Dave Pappas**, Rigetti Computing

2:20pm **QS+EM+MN+NS-WeA-1 Photonics-Integrated Microfabricated Surface Traps for Trapped Ion Applications**, ***Megan Ivory****, W. Setzer, N. Karl, J. Schultz, J. Kwon, M. Revelle, R. Kay, M. Gehl, H. McGuinness,* Sandia National Laboratories **INVITED**

Some of the more advanced quantum systems for applications spanning clocks, sensors, and computers are based on the control and manipulation of atoms.While these atomic systems have led to promising results in laboratory systems, the transition of these devices from the laboratory to the field remains a challenge.Recently, advances in compact vacuum technology, microfabricated surface traps, and integrated photonics are paving the way toward deployable solutions.Here, I discuss ongoing efforts at Sandia National Laboratories to leverage microfabricated surface traps for low size, weight, and power (SWaP) deployable trapped-ion systems, and the unique systematics presented by these integration efforts.In particular, I present initial demonstrations of trapped ions utilizing multilayered waveguides for UV and visible/IR light and single photon avalanche detectors integrated with microfabricated surface traps.I also present characterization of heating rates and frequency shifts in these integrated devices, and an outlook for further reducing SWaP via compact vacuum systems.

Sandia National Laboratories is 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. *SAND2022-5950 A*

3:00pm **QS+EM+MN+NS-WeA-3 Toward Heterogeneous Quantum Networks: Interfacing Trapped Ion, Superconducting, and Integrated Photonic Qubits***, **Kathy-Anne Soderberg**, A. Paul,* Air Force Research Laboratory*; N. Barton, A. Brownell,* Murray Associates*; D. Campbell,* Air Force Research Laboratory*; C. Craft,* Technergetics*; M. Fanto, D. Hucul,* Air Force Research Laboratory*; A. Klug,* Griffiss Institute*; M. LaHaye,* Air Force Research Laboratory*; M. Macalik,* Booz Allen Hamilton*; K. Scalzi,* Technergetics*; J. Schneeloch,* Air Force Research Laboratory*; M. Senatore,* Griffiss Institute*; E. Sheridan,* National Academies of Sciences, Engineering, and Medicine*; D. Sica,* Griffiss Institute*; A. Smith, Z. Smith, C. Tison,* Air Force Research Laboratory*; C. Woodford,* Griffiss Institute **INVITED**

Effective and efficient ways to connect disparate qubit technologies is an outstanding challenge in quantum information science. However, the ability to interface different qubit modalities will have far-reaching implications for quantum computing and quantum networking. Here we present plans and progress toward interfacing trapped ion, superconducting, and integrated photonic qubits for the purpose of entanglement distribution in a quantum network. We will also discuss how this work connects to the AFRL distributed quantum networking testbed.

Approved for Public Release [Case number AFRL-2022-1621] Distribution Unlimited

4:20pm **QS+EM+MN+NS-WeA-7 Superconductor/Semiconductor Heterostructures for Quantum Computing Applications***, **Chris Palmstrøm**,* University of California, Santa Barbara **INVITED**

Superconductor/semiconductor heterostructures have potential for quantum computing applications. Coupling superconductivity to near surface quantum wells (QW) and nanowires of high spin-orbit semiconductors have allowed the observation of zero bias peaks, which can be a signature of, but not proof of, Majorana Zero Modes, a key ingredient for topological computing. These results of induced superconductivity pave the way for lithographically defined complex superconductor/semiconductor nanostructured networks necessary for quantum computation.

Our efforts have focused on developing high mobility of near surface quantum wells of the high spin-orbit semiconductors InAs, InSb and $InAs_ySb_{1-y}$. Rather than relying on post growth lithography and top down etching to form semiconductor nanostructures, we have investigated the development of shadow superconductor growth on atomic hydrogen cleaned MOVPE-grown vapor-liquid-solid InSb nanostructures and in-vacuum chemical and molecular beam epitaxy selective area grown InAs nanostructures. We have identified Sn as an alternative for Al for use as superconductor contacts to InSb vapor-liquid-solid nanowires, demonstrating a hard superconducting gap, with superconductivity persisting in magnetic field up to 4 Tesla. Further, a small island of Sn-InSb exhibits the two-electron charging effect, a clear indication of a supercurrent.

In more conventional superconductor qubits, a dramatic size reduction of the superconducting transmon devices is predicted by the development of merged element transmon devices based on superconductor/semiconductor/superconductor heterostructures. These superconductor/semiconductor/superconductor heterostructures also allow for selective control of conductance modes in planar lateral multi-terminal Josephson Junctions

In this presentation, progress in developing superconductor/semiconductor heterostructures for quantum computing applications will be presented. This will include progress in in-situ patterning and selective area growth, multi-terminal Josephson Junctions and the recent progress towards developing a Si fin based merged element transmon – the FinMET.

5:00pm **QS+EM+MN+NS-WeA-9 High Throughput Measurements of III-V Semiconductor Materials Stack of 2DEG-Based Tunable Couplers***, **Nicholas Materise**,* Colorado School of Mines*; J. Pitten,* University of Colorado at Boulder*; W. Strictland,* New York University*; A. McFadden,* National Institute for Science and Technology (NIST)*; J. Shabani,* New York University*; E. Kapit,* Colorado School of Mines*; C. McRae,* University of Colorado at Boulder

Recent success in integrating cryogenic semiconductor classical systems with superconducting quantum systems promises to reduce the room temperature classical signal processing bottleneck. Incorporating semiconductor quantum devices with superconducting ones as tunable couplers and hybrid quantum systems requires quantitative estimates of the loss introduced by those devices. We report loss measurements of the III-V semiconductor stack used in 2DEG-based gatemon qubits and couplers using a superconducting microwave cavity. Extending the high throughput, low-cost substrate measurement method to thin films grown by molecular beam epitaxy, we can investigate surface roughness losses, bulk losses, and interface losses in a single microwave package. As with our previous measurements of substrates, we perform comparison studies with CPW resonators to validate our approach.

5:20pm **QS+EM+MN+NS-WeA-10 Strong Coupling between a Superconducting Microwave Resonator and Low-Damping Magnons Using Vanadium Tetracyanoethylene Thin Films***, Q. Xu, H. Cheung,* Cornell University*; D. Cormode, H. Yusuf,* The Ohio State University*; Y. Shi,* University of Iowa*; M. Chilcote,* Cornell University*; M. Flatté,* University of Iowa*; E. Johnston-Halperin,* The Ohio State University*; **G. D. Fuchs**,* Cornell University **INVITED**

Hybrid quantum systems – in which excitations with distinct origin are hybridized through a resonant interaction – are attractive for quantum technologies because they enable tunability and the ability to combine desirable properties of each excitation. Here we study the hybrid excitation of a superconducting microwave resonator mode and a ferromagnetic resonance mode of vanadium tetracyanoethylene ($V[TCNE]_x$) thin films. Our work addresses a key challenge for hybrid superconducting resonator-magnon devices: the integration of a low damping thin-film material with microfabricated superconducting circuits. $V[TCNE]_x$ is a molecular-based ferrimagnet with exceptionally low magnetic damping – as low as 5×10^{-5} at room temperature. The ability to grow thin films of this material at low temperature via chemical vapor deposition and pattern it via lift-off processing enables the fabrication of integrated quantum magnon devices using this material. We couple a $V[TCNE]_x$ magnon mode to the mode of a thin-film Nb lumped-element LC resonator and demonstrate strong coupling, characterized by cooperativities in above 10^2. Characterization of this hybrid resonator-magnon system in both the frequency domain and the time domain reveals hybridization between resonator photons and magnons. This work demonstrates a pathway for scalable and integrated quantum magnonic technologies.

6:00pm **QS+EM+MN+NS-WeA-12 Role of Point Defect Disorder on the Extraordinary Magnetotransport Properties of Epitaxial Cd_3As_2***, **Jocienne Nelson**, A. Rice, C. Brooks, I. Leahy, G. Teeter, M. van Schilfgaarde, S. Lany, B. Fluegel, M. Lee, K. Alberi,* NREL

Three-dimensional topological semimetals host extremely large electron mobilities and magnetoresistances making them promising for a wide range of applications including in optoelectronic devices, renewable energy, and quantum information. However, the extent to which disorder influences the properties of topological semimetals remains an open question and is relevant to both the understanding of topological states and the use of topological materials in practical applications. As a particular example, epilayers of the prototypical Dirac semimetal Cd3As2 exhibit high electron mobilities despite a having very high dislocation densities.[1,2]

Native point defects are inevitable in crystalline materials and introduce long and short-range disorder potentials that will impact carrier transport behavior. To understand their role in topological semimetals, we use molecular beam epitaxy to achieve unmatched and systematic control of point defect concentrations in Cd_3As_2. By reducing the concentration of scattering point defects, we increased the mobility from 5000 to 18,000 cm2/Vs and the magnetoresistance from 200% to 1000%. We find good agreement with the guiding center diffusion model, which indicates point defects are essential to the large linear magnetoresistance in topological semimetals.[3] However, the degree of linear magnetoresistance, is found to correlate inversely with measures of disorder. Our results demonstrate the importance of engineering high quality material with dilute concentrations of point defects to optimize the magnetoresistance properties in topological semimetals.[4]

[1] A.D. Rice, K. Park, E.T. Hughes, K. Mukherjee and K. Alberi, *Phys. Rev. Mater.*, **3**, 121201(R) (2019)

[1] M. Goyal, S. Salmani-Rezaie, T.N. Pardue, B. Guo, D.A. Kealhofer and S. Stemmer, *APL Mater.*, **8**, 051106 (2020)

[1] I.A. Leahy, Y.-P. Lin, P.E. Siegfried, A.C. Treglia, J.C.W. Song, R.M. Nandkishore and M. Lee, *PNAS*, **115**, 10570 (2018)

[1] J. N. Nelson, A. D. Rice, C. Brooks, I. A. Leahy, G. Teeter, M. Van Schilfgaarde, S. Lany, B. Fluegel, M. Lee, K. Alberi *arXiv:2206.10023* (2022).

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

Photovoltaic Materials, Characterization, and Applications

Moderator: Seth King, University of Wisconsin - La Crosse

11:00am **EM+AS-ThM-10 Translating Materials-Level Characterization of Carbon-Nanotube-Reinforced Composite Gridlines To Module-Level Degradation***, **Sang Han**,* The Univeristy of New Mexico and Osazda Energy*; A. Chavez,* The University of New Mexico and Osazda Energy*; B. Rummel,* The University of New Mexico and Osazda Energy*; A. Jeffries,* Osazda Energy*; N. Bosco,* National Renewable Energy Laboratory*; B. Rounsaville , A. Rohatgi,* Georgia Institute of Technology

Cell cracks in PV modules caused by environmental stressors and extreme weather events can lead to gradual or immediate power degradation. To directly address cell-crack-induced degradation, we have formulated a carbon nanotube additive for commercial silver pastes used in screen printing. We have shown in earlier work that these metal matrix composites do not impact the cell efficiency, while enhancing the metallization's fracture toughness and electrical gap-bridging capability. In this work, we focus on translating materials-level characterization techniques to module-level degradation. We found that we get conflicting results from two different materials characterization methods of measuring the metallization's ability to electrically bridge gaps in cracked solar cells. To determine which materials characterization method correlates better with the mini-module degradation characteristics, we have conducted stress testing for a small dataset of mini-modules.

The first characterization method for measuring the metallization's ability to electrically bridge cell cracks is dubbed as Resistance Across Cleaves and cracKs (RACK), in which a piezoelectric stage pulls apart fractured cells in submicron increments while the resistance of the gridlines on top of the fractured cells is measured until the gridlines electrically fail. The tensile stress applied to the metallization during the RACK test is intended to mimic the stress encountered by the metal gridlines during thermal cycling after cell fracture, in which cell fragments translocate within the module. Another common method for characterizing the metallization's ability to electrically bridge cell cracks is three-point bending test, where a rectangular substrate with two parallel gridlines, laser-diced from a cell, is mounted on an acrylic beam and placed in a three-point bend fixture while the resistance of gridlines is monitored as a crack in the cell is slowly opened. The failure mechanism with this testing method could be an alternative representation of how a cell would fracture when the module is being flexed under heavy mechanical loads or being stepped on.

The two materials-level characterization methods described above are designed to measure the metallization's ability to electrically bridge a cracked cell; however, they give conflicting results as to which composition and geometry of carbon nanotubes performs best. To better understand which materials-level test correlates to module-level degradation, 2x2 minimodules were constructed with pre-fractured cells and subjected to thermal cycling.

11:20am **EM+AS-ThM-11 Effects of Carbon-Nanotube-Reinforced Composite Gridlines on Photovoltaic PERC Cell and Module Efficiency***, **Andre Chavez**,* The University of New Mexico and Osazda Energy*; S. Han,* The Univeristy of New Mexico and Osada Energy*; A. Jeffries,* Osazda Energy*; S. Huneycutt,* The Univeristy of North Carolina at Charlotte*; A. Ebong,* The University of North Caronlina at Charlotte*; D. Harwood, N. Azpiroz,* D2 Solar

Abstract — The addition of carbon nanotubes (CNTs) in commercial silver pastes used for the front metallization of Passivated Emitter and Rear Contact (PERC) solar cells not only helps improve the materials toughness and resilience to cell cracks, but also offers some improvement to cell efficiency. A large data set of 87 cells containing the CNT-enhanced metal matrix composite (MMC) gridlines, when compared to a set of 66 baseline PERC cells, shows an increased efficiency by 0.03%, which is the threshold that cell and module manufactures care about. Six mini-modules, each of which consists of two PERC cells connected in series, were fabricated with the baseline metallization, and six mini-modules were fabricated with MMC-enhanced PERC cells. Three modules were subjected to 200 cycles of thermal shock (TS) from -40 to +85 °C, and the remaining three were subjected to highly accelerated stress testing (HAST), where damp heat is applied at 120 °C for 100 hours and 100% relative humidity. After these two tests, the MMC metallization shows comparable corrosion to the baseline metallization and power loss of less than 0.6% after TS-200 and less than 4% after HAST-100. The inclusion of CNTs to conventional screen printable silver pastes has the ability to improve cell efficiency, while showing statistically identical beginning-of-life cell and module performance as well as corrosion characteristics and infant failure rate (e.g., solder bond failure) comparable to the baseline. These results show strong promise for commercial implementation of the MMC-enhanced metallization to improve PV module reliability.

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office Award Number DE-EE0009013.

11:40am **EM+AS-ThM-12 Atomic Layer Deposition of NiO for Single Junction Perovskite and Tandem Perovskite/Silicon Photovoltaics***, N. Phung, C. van Helvoirt,* Eindhoven University of Technology, The Netherlands*; D. Zhang, V. Zardetto, B. Geerligs,* TNO Science and Industry, the Netherlands*; M. Verheijen, E. Kessels, B. Macco, **Mariadriana Creatore**,* Eindhoven University of Technology, The Netherlands

Metal halide perovskite absorbers have attracted major attention due to their excellent opto-electronic properties. Recent advancements in performance and stability of perovskite solar cells (PSCs) have been achieved with the application of self-assembled monolayers (SAMs), serving as hole transport layers in the p-i-n PSC architecture [1]. However, a reproducible implementation of SAM in the PSC device requires knowledge of its surface coverage on ITO since non-covered areas in direct contact with perovskite may lead to shunts and low open-circuit voltage.

In this contribution, we investigate the influence of an atomic layer deposited (ALD) NiO film (7 nm) on the surface coverage of SAM for single junction PSC as well as tandem PSC/silicon devices. NiO is processed either by plasma-assisted ALD [2] or thermal ALD [3]. The latter has also been developed since thermal ALD is often adopted in upscalable technologies such as batch and spatial ALD.

We observe that the SAM of MeO-2PACz ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid) inhomogeneously covers ITO. Instead, when adopting NiO as intermediate layer between ITO and SAM, the SAM homogeneity and surface coverage improve, as witnessed by transmission electron microscopy (TEM) and conductive atomic force microscopy. This result is explained in terms of chemisorption reactions between SAM phosphonic acid groups and NiO hydroxyl groups. The SAM homogeneity on NiO leads to higher shunt resistance in the device with respect to the one with SAM directly processed on ITO. Moreover, the combination of NiO and SAM results in a narrower distribution of device performance reaching more than 20% efficient champion device.

The above-mentioned merits of ALD NiO are further exploited in a monolithic tandem device, consisting of a c-Si passivated emitter rear cell (PERC) bottom cell and a perovskite top cell. In the case of ITO/SAM tunnel junction, several devices present electrical shunts in the top cell, leading to a standard deviation of efficiency of 4.6% across device batches. In the case of ITO/NiO/SAM tunnel junction, the tandem device exhibits a narrow distribution of efficiency (standard deviation of 2% across device batches) because of the uniformity and conformality of NiO on ITO, as witnessed by TEM analysis. A champion efficiency of 23.7% is recorded, among the best tandem cell efficiency implementing an industrial standard bottom cell.

[1] Al-Ashouri, *et al.* (2019) Energy & Environ. Sci., *12*(11), 3356.

[2] Koushik *et al*. (2019) J. Mat. Chem. C 7, 12532.

[3] Phung *et al*. (2022) IEEE Journal of Photovoltaics, under review.

[4] Phung, *et al.* (2021) ACS Appl. Mat. Interfaces, 14(1), 2166.

12:00pm **EM+AS-ThM-13 XPS Depth Profiling of Single Film and Two-Layer Heterojunction Metal-Halide Perovskites***, **Jennifer Mann**,* Physical Electronics*; C. Clark, W. Hsu, E. Pettit,* University of Minnesota*; K. Artyushkova,* Physical Electronics*; R. Holmes,* University of Minnesota

The goal of an XPS depth profile is to obtain accurate identification of layer thicknesses and composition as a function of depth within film structures. Monatomic Ar^+ has been available for many years and is often the gun of choice for inorganic thin film profiling despite its issues with preferential sputtering, material migration, and chemical reduction that may occur, thus altering the apparent profile of the analyzed material.

The introduction of C_{60} cluster ion beam and argon gas cluster ion beam (GCIB) sputtering in recent years has expanded the types of materials that may be studied by depth profiling beyond that of inorganic thin films.Cluster type ion guns have shown successful depth profiling of polymer and organic materials as well as inorganic thin film structures while preserving the stoichiometry and chemical structures.

Organo-metal-halide perovskites are of interest due to their promising application in solar cells, where they have achieved efficiencies above 25%.In this work, we present XPS depth profiles of single films of metal-halide perovskites, with an ABX$_3$ structure(A = MA - methylammonium or Cs, B = Sn or Pb, X = Br or I).Maintaining stoichiometry while sputtering can be very challenging, so in addition, MAPbI$_3$ was analyzed with hard X-ray photoelectron spectroscopy (HAXPES). A Cr Kα (5414.8 eV) X-ray source provides information depths three times greater than the standard Al Kα (1486.6 eV) X-ray source.Using a higher energy photon provides a non-destructive method to probe deeper into the sample, minimizing the contribution from surface oxides and carbon contamination.

XPS depth profiles were obtained on a single layer perovskite film using the two cluster ion guns, available on the PHI *VersaProbe* III - C$_{60}$ and argon gas cluster (GCIB) The viability of each gun in maintaining both the stoichiometry and chemistry of the film as it was sputtered was determined before measuring a more complex perovskite system.

A more complex two-layer heterojunction of organo-metal-halide perovskites was also investigated using optimized ion sputtering conditions.This is a particularly well-suited system for XPS depth profiling due to the accessible thicknesses of the layers and the significant difference in the chemistry of carbon and nitrogen in different organic A-site cation environments. Indeed, this difference is exploited to probe ion migration and mixing across perovskite interfaces.

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$_2$O$_3$?***, **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$_2$O$_3$) 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$_2$O$_3$ devices as relevant contenders for practical applications. In this talk, the achievements on various types of Ga$_2$O$_3$ 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$_2$O$_3$ power transistors as an illustration. We are also developing a novel Ga$_2$O$_3$ 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$_2$O$_3$. This as well as other types of Ga$_2$O$_3$ 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$_2$O$_3$ Polymorphs for Ultra-Wide Bandgap Semiconductor Devices***, **Lisa Porter**, K. Jiang, J. Tang, M. Cabral, R. Davis,* Carnegie Mellon University, USA

Gallium oxide (Ga$_2$O$_3$) 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ – 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$_2$O$_3$ and β-Ga$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$. 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).

Quantum Information Science Focus Topic
Room 302 - Session QS+AP+EM+MN+NS+SS-ThM

Systems and Devices for Quantum Computing

Moderators: Vivekananda Adiga, IBM, T.J. Watson Research Center, **Kathy-Anne Soderberg**, Air Force Research Laboratory

8:00am **QS+AP+EM+MN+NS+SS-ThM-1 Effects of Environmental Radioactivity on Superconducting Qubits***, L. Cardani, **Ambra Mariani**,* Istituto Nazionale di Fisica Nucleare, Italy **INVITED**

Environmental radioactivity was recently discovered as a potential limit for superconducting quantum bits.

We review recent works proving that ionizing radiation lowers the coherence of singe qubits and induces correlated errors in qubits arrays. We also present preliminary studies showing that operating qubits in a low-radioactivity environment improves their performance. These results fuelled the interest of several European and US groups in further investigating and mitigating radioactivity for next-generation quantum processors.

Using radioactivity measurements and simulations, we estimated the separate contribution of "far" radioactive sources (cosmic rays and laboratory radioactivity) and close materials contamination (chip holder, magnetic shield, …) on a typical chip, focussing on a qubit prototype developed within the SQMS center. We present such contributions and discuss the possibility of mitigating them in "standard" qubit laboratories or, eventually, in deep underground facilities.

8:40am **QS+AP+EM+MN+NS+SS-ThM-3 Dynamics of a Dispersively Coupled Transmon in the Presence of Noise from the Control Line***, **Antti Vaaranta**,* Bluefors Oy, Finland*; M. Cattaneo,* University of Helsinki, Italy*; R. Lake,* Bluefors Oy

In this talk we present theoretical results from a complete description of transmon qubit dynamics in the presence of noise introduced by an impedance-matched resistor (50 Ohm) that is embedded in the qubit control line, acting as a noise source [1]. We derive a model to calculate the qubit decoherence rate due to the noise emanating from this noise source [2]. The resistor is treated, using the Caldeira-Leggett model, as an infinite collection of harmonic LC-oscillators making it a bosonic bath [3]. To obtain the qubit time evolution affected by this remote bath, we start with the microscopic derivation of the Lindblad master equation using the dispersive Jaynes-Cummings Hamiltonian with added inductive coupling to the bath. To solve the resulting master equation, we transform it into a block diagonal form by exploiting its underlying symmetries following Ref. 4. The block diagonalization method reveals that the long time decoherence rate is given by the slowest decaying eigenmode of the Liouvillian superoperator. Moreover, when the readout resonator is in the equilibrium thermal state, the rate of exponential decoherence of the qubit is almost exactly exponential for all times with the predicted rate given by the slowest decaying eigenmode. We also study how the decoherence rate depends on the temperature of the noise source and explore the strong and weak dispersive coupling regimes. The model captures the often used dispersive strong limit approximation of the qubit decoherence rate being linearly proportional to the number of thermal photons in the readout resonator. However, in the dispersive weak limit we predict remarkably better decoherence rates. The model parameters are completely determined by the values of the circuit components, allowing for the exact study of the dynamics on the level of each individual circuit element.

[1] S. Simbierowicz et al., Rev. Sci. Instrum. 92, 034708 (2021).

[2] A. Vaaranta, Study of environmental effects on a dispersive transmon qubit, MSc thesis, Univ. of Helsinki, (2022).

[3] M. Cattaneo and G. Paraoanu, Adv. Quantum Technol. 2100054 (2021).

[4] M. Cattaneo et al., Phys. Rev. A 101, 042108 (2020).

9:00am **QS+AP+EM+MN+NS+SS-ThM-4 Accurate Microwave Characterization for Superconducting Quantum Technology***, Slawomir Simbierowicz,* Bluefors Oy, Finland

Recent breakthroughs in quantum technology have highlighted a need for methods for accurate characterization of cryogenic microwave devices at millikelvin temperatures. In this two-part talk, I will highlight recent progress on microwave measurements at the quantum device reference plane including: (1) system noise characterization of amplifier chains, and (2) calibrated S-parameters of qubit drive line components.In the first part, I will discuss an impedance-matched variable temperature noise source which can be installed in a coaxial line of a cryostat. Using the method of hot/cold source with many input noise temperature points, the system noise temperatures of qubit readout amplifier cascades can be determined. I present measurement results in terms of added noise in Kelvins or photons from a four-wave (4WM) mixing traveling wave parametric amplifier (TWPA) [1], a Josephson parametric amplifier [2], 3WM TWPA, and high electron mobility transistor amplifiers [1].In the second part of the talk, I will present measurements of the 1-port S-parameters of qubit drive line components using a data-based short-open-load calibration at a temperature of 30 mK [3]. The measurement enables us to model systematic errors in qubit state preparation due to non-idealities in qubit control lines such as impedance mismatch. We model the results using a master equation simulation of all XY gates performed on a single qubit. Our work directly addresses the gap between electrical engineering parameters of individual measurement components and performance of the quantum device itself.

REFERENCES

[1] Slawomir Simbierowicz, Visa Vesterinen, Joshua Milem, Aleksi Lintunen, Mika Oksanen, Leif Roschier, Leif Grönberg, Juha Hassel, David Gunnarsson, and Russell E. Lake, "Characterizing cryogenic amplifiers with a matched temperature-variable noise source", Rev. Sci. Instr. **92**, 034708 (2021)

[2] Mustafa Bal et al., “Overlap junctions for superconducting quantum electronics and amplifiers”, Appl. Phys. Lett. **118**, 112601 (2021)

[3] Slawomir Simbierowicz, Volodymyr Y. Monarkha, Suren Singh, Nizar Messaoudi, Philip Krantz, and Russell E. Lake, "Microwave calibration of qubit drive line components at millikelvin temperatures", Appl. Phys. Lett. **120**, 054004 (2022)

9:20am **QS+AP+EM+MN+NS+SS-ThM-5 Improving Qubit Performance Through Engineering of the Substrate-Josephson Junction Interface***, **Cameron Kopas**, H. Cansizoglu, R. Cochrane, B. Ercan,* Rigetti Computing*; D. Goronzy, C. Torres-Castanedo,* Northwestern University*; J. Oh,* Ames Laboratory*; A. Murthy,* Fermi Lab*; E. Lachman,* Rigetti Computing*; A. Romanenko, A. Grassellino,* Fermi Lab*; M. Kramer, L. Zhou,* Ames Laboratory*; M. Bedzyk,* Northwestern University*; J. Mutus,* Rigetti Computing*; M. Hersam,* Northwestern University*; K. Yadavalli,* Rigetti Computing **INVITED**

The performance of a superconducting qubit is often limited by dissipation and two-level systems (TLS) losses. The dominant sources of these losses are believed to come from interfaces and surfaces, likely as a result of fabrication processes, materials, or atmospheric exposure. We show that certain chemical surface treatments can be used to modify the silicon surface before Josephson junction deposition, reducing the number of strongly-coupled TLS, and improving T1. While identifying specific microscopic sources for loss and TLS is still an open question, targeted characterization of test structures will show which physical changes correlate with performance improvements. We report chemical, structural, and low-temperature microwave characterization of superconducting qubits and films fabricated with different Si surface treatments.

11:00am **QS+AP+EM+MN+NS+SS-ThM-10 Design and Optimal Control of Superconducting Qubits to Achieve Quantum Speed Limits***, **Meenakshi Singh**,* Colorado School of Mines, USA **INVITED**

Fast two-qubit entangling gates are essential for quantum computers with finite coherence times. The finite interaction strength between qubits introduces a theoretical speed limit on the speed of these two-qubit entangling gates. This speed limit has been analytically found only for a two-qubit system under the assumption of negligible single qubit gate times. Here, we demonstrate such a speed limit experimentally using optimal control on two superconducting transmon qubits with a fixed capacitive coupling and finite single qubit gate times. Furthermore, we investigate the effect of additional couplings on the speed limit, both through introduction of an ancillary qubit as well as through utilization of higher transmon energy states. Finally, we discuss the generalization to many qubit systems where properly leveraging all available couplings can provide dramatic speedups.

11:40am **QS+AP+EM+MN+NS+SS-ThM-12 Atomic Scale Processing for Quantum Computing***, **Harm Knoops**,* Oxford Instruments Plasma Technology, Netherlands **INVITED**

With the increasing technological readiness of quantum technology (QT) the field has to start focussing on scalable fabrication methods for quantum bits (qubits) and quantum circuits. This contribution will focus on the enabling role atomic scale processing (ASP) methods such as atomic layer deposition (ALD) and atomic layer etching could play in scaling of QT. The main focus will relate to superconducting qubits and processing of superconducting nanolayers.

Superconducting nanolayers (metals, metal-nitrides) are required for various roles in QT including use in resonators, single-photon detectors, and interconnects.[1] The electrical contacts needed to control the qubits will require non-planar connectivity using superconducting interconnects.[2]Adequate routes for fabrication of planar superconducting layers exist, but for 3D interconnects or through-silicon vias (TSVs), the excellent conformality of ALD nanolayers could be essential. Although for resonators conformality is not a challenge, ALD’s thickness control and uniformity should allow high-quality resonators with low spread in properties. For these superconducting nanolayers, metal-nitride compounds have been identified as particularly promising since they exhibit limited surface oxidation (compared to pure metals such as Nb), combined with relatively high critical temperature (T_c) for superconductivity (e.g., as compared to Al). Despite the challenges that the synthesis of high-quality nitrides pose, plasma ALD has demonstrated the capability to deposit high-quality nitrides (e.g., low O content, high electrical conductivity).[3] Furthermore, substrate-biased plasma-ALD offers unique opportunities to obtain and tune high-quality nitrides.[4] For removal of surface oxides or smoothing of resonator surfaces and interfaces, approaches combining ALD and ALE could be of interest.[5] Both ALD and ALE are envisaged to be key tools to allow scaling of these devices and advance the QT field.

References

1. Giustino et al., *J. Phys. Mater.***3**, 042006 (2021)
2. Kjaergaard et al., *Annu. Rev. Condens. Matter Phys.***11**, 369 (2020)
3. Knoops et al., *J. Vac. Sci. Technol. A***37**, 030902 (2019)
4. Faraz et al., *ACS Appl. Mater. Interfaces***10**, 13158 (2018)
5. Chittock et al, *Appl. Phys. Lett.* **117**, 162107 (2020)

2D Materials Technical Group
Room 303 - Session 2D+AS+EM-ThA

2D Materials: Electron Microscopy and Photoemission Spectroscopy

Moderators: Keun Su Kim, Yonsei University, Republic of Korea, **Dmitry Kireev**, University of Texas at Austin

2:20pm **2D+AS+EM-ThA-1 Periodic Lattice Displacements in Low Dimensional Materials***, **Robert Hovden,*** University of Michigan **INVITED**

Dramatic electronic changes are associated with periodic lattice displacements [1] where structure, even in 2D materials, requires higher dimensional measurement using scanning / transmission electron microscopy. In particular charge density waves are an emergent periodic modulation of the electron density that permeates a crystal with strong electron-lattice coupling. Strong evidence suggests that transformative correlated electron behavior may exist only in unrealized clean 2D materials such as 1T-TaS_2. Unfortunately, experiment and theory suggest that extrinsic disorder in free standing 2D layers impedes correlation-driven quantum behavior. Here we demonstrate a new route to realizing fragile 2D quantum states through epitaxial polytype engineering of van der Waals materials. The isolation of truly 2D charge density waves (CDWs) between metallic layers stabilizes commensurate long-range order and lifts the coupling between neighboring CDW layers to restore mirror symmetries via interlayer CDW twinning. The twinned-commensurate (tC-) CDW reported herein has a single metal–insulator phase transition at ~350 K as measured structurally and electronically [2]. Fast in-situ transmission electron microscopy and scanned nanobeam diffraction map the formation of tC-CDWs. This work introduces epitaxial polytype engineering of van der Waals materials to access latent 2D ground states distinct from conventional 2D fabrication.

Here we show the critical temperature for spatially-coherent, commensurate (C-) CDW in 1T-TaS_2 can be raised to well above room temperature (~150 K above the expected transition) by synthesizing clean interleaved 2D polytypic heterostructures. This stabilizes a collective insulating ground state (i.e. C-CDW) not expected to exist at room temperature. We show the formation of these spatially coherent states occurs when 2D CDWs are confined between metallic prismatic polytypes. At the same time, interleaving disables interlayer coupling between CDWs. This raises the critical temperature of the C-CDW and forms out-of-plane twinned commensurate (tC) CDWs as revealed by scanned nanobeam electron diffraction. These results demonstrate polytype engineering as a route to isolating 2D collective quantum states in a well-defined extrinsic environment with identical chemistry but distinct band structure.

[1] *Nature and evolution of incommensurate charge order in manganites visualized with cryogenic STEM,* I. El Baggari et al. **Proc. Natl. Acad. Sci. U.S.A. 115**, 1445 (2018)

[2] *Two-dimensional charge order stabilized in clean polytype heterostructures*, S. H. Sung et al. **Nature Communications**, **13** 413 (2022)

3:00pm **2D+AS+EM-ThA-3 Engineering of Nanoscale Heterogenous Transition Metal Dichalcogenide-Au Interfaces***, **Alex Boehm,*** Sandia National Laboratories*; J. Fonseca,* Naval Research Laboratory*; K. Thuermer, J. Sugar,* Sandia National Laboratories*; J. Robinson,* Naval Research Laboratory*; T. Ohta,* Sandia National Laboratories

2-D transition metal dichalcogenides (TMDs) have recently garnered much attention owing to their extraordinary physical, chemical, electrical, and optical properties. However, early material and device studies have revealed that these properties can be greatly impacted by extrinsic factors such as substrate interactions, mechanical strain, and charge transfer. Thus, a careful understanding of the nuanced interactions between TMDs and other materials is critical for high performance devices. Of particular importance are the interfaces with metallic contacts. Here, one barrier are the spatial nonuniformities recently reported at these types of interfaces. Uncovering the impact of these heterogeneities on TMD properties and establishing strategies to control TMD-metal interfaces could enable an array of engineering pathways for future applications. In this work, we find that the electronic structures of mechanically exfoliated TMD-Au interfaces exhibit pronounced heterogeneity arising from microstructure of the supporting metal. Pertinent for device applications these electronic structure variations indicate fluctuating doping levels and Schottky barrier height across the junction. We examined the electronic structures of WS2 and WSe2 at high spatial resolution via photoemission electron microscopy (PEEM) revealing key differences in work function and binding energies of the occupied states. Furthermore, the inherent role of the underlying Au microstructure on the TMD electronic structure is revealed by electron backscatter diffraction (EBSD) and scanning tunneling microscopy (STM). Finally, simple processing methods are employed to fabricate homogenous TMD-Au interfaces while also tuning the electronic properties of the TMDs. Our findings illustrate that the electronic properties of TMDs are greatly impacted by metal interface interaction and provide a means to engineer these important junctions.

The work at Sandia National Laboratories was supported by Sandia's LDRD program. The work at the US Naval Research Laboratory was funded by the Office of Naval Research. Sandia National Laboratories is a multi-mission 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. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

3:20pm **2D+AS+EM-ThA-4 Advanced Laboratory-Based Momentum Microscopy and PEEM Analysis***, **Stefan Böttcher Böttcher,*** SPECS Surface Nano Analysis GmbH, Germany*; D. Singh, T. Conard,* IMEC, Belgium*; M. Wietstruck,* SPECS Surface Nano Analysis GmbH, Germany*; P. van der Heide,* IMEC, Belgium*; A. Thissen,* SPECS Surface Nano Analysis GmbH, Belgium

Momentum Microscopy is a new technology for comprehensive surface analysis, providing high energy and angular resolved band structure mapping combined with advanced surface imaging capability. Extending this technology with laboratory-based instrumentation opens the possibility for detailed studies of new materials under well controlled environments. The combination of a PEEM lens for surface microscopy and momentum microscopy, allows for small spot analysis in ARPES and chemical sensitive surface mapping. In a joint project between IMEC and SPECS the possibilities for laboratory-based momentum microscopy, laser ARPES and x-ray spectroscopy and microscopy are evaluated in the framework of semi-industrial environment. We present a status report at the intersection between fundamental and applied research in surface science. We focus on the use of ARPES characterization in novel materials close to applied research and the functionality of x-ray analysis in PEEM and spectroscopy for chemical analysis.

3:40pm **2D+AS+EM-ThA-5 Epitaxial Growth and Electronic States of Ultrathin Bi (111) Films on Insb (111)B: Evidence of Inversion Symmetry Breaking via Film-Substrate Interactions***, **Hadass S. Inbar**, J. Dong, A. Engel, C. Dempsey, Y. Chang,* University of California Santa Barbara*; A. Fedorov,* Advanced Light Source, Lawrence Berkeley National Laboratory*; C. Palmstrom,* University of California Santa Barbara

Quantum size effects in bismuth films have been the focus of the scientific community for decades. The spin–split Rashba surface states and large mass anisotropy in surface state valleys have made Bi films a promising system for future applications in spintronics and valleytronics. Moreover, in the field of topological materials, the Bi (111) bilayer (BL) is predicted to behave as a quantum Hall spin insulator[1]. Along the Bi (111) step edges, 1D helical modes were observed[2], an ingredient in one proposed platform to construct Majorana zero modes[3]. However, the synthesis of continuous ultrathin (<6 BL) Bi (111) epitaxial films on semiconducting substrates has remained a materials challenge. We report a study of ultrathin large-area Bi (111) layers grown on InSb (111)B substrates by molecular beam epitaxy and in-vacuo transferred for scanning tunneling microscopy and synchrotron-based angle-resolved photoemission spectroscopy. We show that large-area single-domain ultrathin Bi films can be stabilized through strong film-substrate interactions. Our study follows the evolution of tensile strain in the films, which is predicted to lead to a semimetallic to semiconducting transition. With decreasing film thickness from 13 to 1 BL, we quantify the confinement-induced shifts in the bulk band structure and trace the quantum well energy levels with a phase shift accumulation model. Significant substrate-film interactions breaking inversion symmetry affect the surface state dispersion leading to a surface state degeneracy which allows us to assign the topological order in Bi(111) thin films. The findings of this study offer a new route for epitaxial growth and integration of band-engineered Bi films with III-V substrates.

[1] Murakami, S. (2006). Quantum spin Hall effect and enhanced magnetic response by spin-orbit coupling. Physical Review Letters, 97(23), 236805.

[2] Drozdov, I. K., Alexandradinata, A., Jeon, S., Nadj-Perge, S., Ji, H., Cava, R. J., ... & Yazdani, A. (2014). One-dimensional topological edge states of bismuth bilayers. Nature Physics, 10(9), 664-669.

[3] Jäck, B., Xie, Y., Li, J., Jeon, S., Bernevig, B. A., & Yazdani, A. (2019). Observation of a Majorana zero mode in a topologically protected edge channel. Science, 364(6447), 1255-1259.

4:00pm **2D+AS+EM-ThA-6 Band Modulations: Revealing Moiré Effects in Twisted Bilayer 2D Materials*, Ryan Muzzio,*** Carnegie Mellon University*; A. Jones, P. Majchrzak,* Aarhus University, Denmark*; H. Martins, S. Singh,* Carnegie Mellon University*; C. Jozwiak, A. Bostwick, E. Rotenberg,* Lawrence Berkeley National Laboratory*; P. Hofmann,* Aarhus University, Denmark*; S. Ulstrup,* aarhus University, Denmark*; J. Katoch,* Carnegie Mellon University

Two dimensional (2D) materials are a wonderful template to explore novel quantum phenomena in the ultra thin limit.They can be exfoliated to the desired thickness, stacked with other 2D flakes, and be integrated in device fabrication for electrical measurement.The addition of a twist angle between stacked 2D flakes produces a moiré lattice which can lead to drastic changes in their physical properties.For the case of bilayer graphene, introducing a ~1.1 degree rotation (the magic angle) leads to a low temperature superconducting state[1].This remarkable transport result has been explained via band structure theory and experiment[2,3,4] of the hybridization of the out-of-plane Pi orbitals of the graphene layers which forma weakly dispersing state at the fermi level.Beyond graphene, twist-angle dependent bilayer transition metal dichalcogenides (TMDCs) also display extraordinary novel moiré physics[5,6].In this presentation, we will discuss our ongoing analysis of nano- and micro-focused angle resolved photoemission spectroscopy (ARPES) performed on twisted bilayer graphene and TMDCs systems placed on hBN.We demonstrate, over a wide range of twist angles, the effect of the moiré lattice and proximity effects on the band structure by investigating the effective masses, band positionings, and location of the moiré bands across four TMDC heterobilayers.Our work demonstrates the tunability of the electronic properties in twisted 2D bilayers and the power of ARPES to provide a momentum-resolved view of their electronic structure.

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.

Electronic Materials and Photonics Division
Room 304 - Session EM+AS+EL+NS+SS-ThA

Interfaces and Defect Engineering in Electronic & Photonic Materials & Devices

Moderator: Erin Cleveland, U.S. Naval Research Laboratory

2:20pm **EM+AS+EL+NS+SS-ThA-1 Design and Control of Defect-Mediated Properties in Electronic Ceramics**, ***Elizabeth Dickey**,* Carnegie Mellon University **INVITED**

Crystalline lattice defects, e.g. vacancies, interstitials or substitutional ions, play an important role in the conductivity and dielectric properties of electronic ceramics. The material “defect chemistry” can be tuned to optimize the electronic and ionic conductivities for particular applications via doping, oxygen-activity and temperature control during processing. Beyond controlling the majority defect (carrier) concentrations, it is also important to control the minority defect concentrations as these can be especially relevant to the time-dependent electrical behavior. For example, applied electric fields in device applications provide a strong driving force for the electromigration of charged lattice defects. Furthermore, external conditions such as humidity, which can lead to proton incorporation, can also strongly influence time-dependent material properties. This talk will review our current understanding and implications of point defect equilibria, partial equilibria and dynamics in several prototypical electronic ceramics. Recent efforts to effectively co-dope dielectric materials to improve simultaneously limit both the electronic and ionic conductivity will be discussed.

3:00pm **EM+AS+EL+NS+SS-ThA-3 In-Situ Investigation of the Interface Formation between Si-Terminated Diamond and a NbxOy Electron Acceptor Layer for Electronic Applications**, ***Gabrielle Abad**, P. Hopkins, S. McDonnell,* University of Virginia

Ultra-wide band gap semiconductors present one avenue for the next generation of semiconductor devices. Diamond, specifically, has shown promise in high power, frequency, and temperature electronics; however, issues with impurity doping has limited the development of diamond-based devices. Instead, surface charge transfer doping (SCTD), which avoids introduction of foreign atoms into the diamond lattice, has been used for inducing a two-dimensional hole gas at the diamond surface thus increasing its conductivity. The established method to achieve SCTD is to hydrogen-terminate the diamond surface prior to the addition of an electron acceptor layer; however, the degree of SCTD induced by H-termination is largely dependent on atmospheric exposure. Alternatively, silicon-termination of the diamond surface has been shown to produce the ordered surface with the negative electron affinity necessary for the SCTD mechanism. In this work, we investigate the combination of Si-terminated diamond with a Nb_xO_y electron acceptor layer, wherein we focus on understanding interface formation and chemistries, as well as elucidating if the band alignment mechanism is responsible for SCTD for this material system. Ultra-high vacuum (UHV) electron beam (e-beam) deposition of Si onto diamond substrates was carried out, followed by UHV annealing to produce the Si-terminated (100) diamond surface. X-ray photoemission spectroscopy (XPS) of core-level and valence band spectra was used to analyze chemical composition. To form the electron acceptor layer, Nb films were e-beam deposited onto the Si-terminated diamond surface by depositing Nb under varying oxygen partial pressures. XPS was used to observe how interfacial chemistry, electronic structure, and band alignment evolve with different Nb_xO_y compositions. The air stability of the electron acceptor layers was also investigated after atmospheric exposure via XPS. Analysis of the valence band spectra shows that band alignment would not result in SCTD for the Nb_xO_y/Si/diamond material system.

3:20pm **EM+AS+EL+NS+SS-ThA-4 Effects of Atmospheric UV-O_3 Exposure of WSe_2 on the Properties of the HfO_2/WSe_2 Interface**, ***Maria Gabriela Sales**,* University of Virginia*; A. Mazzoni,* University of Maryland College Park*; W. Sarney,* Army Research Laboratory*; J. Pearson,* University of Maryland College Park*; S. Najmaei,* Army Research Laboratory*; S. McDonnell,* University of Virginia

Transition metal dichalcogenides (TMDCs) are a class of two-dimensional (2D) layered materials, in which each layer is held in-plane by strong chemical bonds, but held in the out-of-plane direction by weak van der Waals forces. For integration in an electronic device, TMDCs are typically capped in the gate region with a high-quality dielectric layer, where ultrathin (sub-5 nm) dielectric thicknesses are desired in order to achieve sufficient gate to channel electrostatic coupling. The unreactive basal plane of TMDCs makes atomic layer deposition (ALD) of dielectric films directly on top of these 2D materials challenging. In this work, we investigate the effects of atmospheric ultraviolet-ozone (UV-O_3) exposures of WSe_2 and use the UV-O_3 functionalized WSe_2 surfaces as substrates for ALD of HfO_2. We report two UV-O_3 functionalization regimes observed on WSe_2: lower exposure times, which do not result in oxidation of the WSe_2 surface, and higher exposure times, which result in a tungsten oxyselenide top layer. The properties of this oxidized layer, such as its thickness, structure, air stability, and thermal stability, are also investigated. Additionally, we note that both functionalization regimes result in variably doped WSe_2. We report on the interface chemistry observed after subsequent ALD of HfO_2, as measured with X-ray photoelectron spectroscopy (XPS). We note that variable, depth-sensitive doping states are found in the WSe_2 functionalized with higher exposure times. We also study the resultant morphologies of our deposited HfO_2 films with atomic force microscopy (AFM), and we find that both of our UV-O_3 functionalization regimes result in uniform and smooth HfO_2 films directly deposited by ALD. With the different functionalization regimes (with different interface chemistries) all providing uniform dielectric film deposition, our atmospheric UV-O_3 exposure technique on WSe_2 presents unique tunability and flexibility in the design of interfaces in devices.

3:40pm **EM+AS+EL+NS+SS-ThA-5 Near Zero Field Magnetoresistance and Electrically Detected Magnetic Resonance Studies of Instabilities in Semiconductor/ Insulator Systems**, ***Patrick Lenahan**,* Pennsylvania State University **INVITED**

We have utilized both electrically detected magnetic resonance(EDMR) and near zero field magnetoresistance (NZFMR) spectroscopy to investigate the physics involved in instabilities such as stress induced leakage currents and time dependent dielectric breakdown in Si/SiO_2 and SiC/ SiO_2 systems. Both techniques are extremely sensitive and extend the sensitivity of conventional electron spin based techniques down to near nanoscale device structures. We find that the very simple spin-based NZFMR technique has significant analytical power in these investigations. The NZFMR studies can complement the more established EDMR measurements with simple and relatively inexpensive apparatus.

Quantum Information Science Focus Topic
Room 302 - Session QS+EM+MN+NS-ThA

The Quantum Metrology Revolution
Moderator: Dave Pappas, Rigetti Computing

2:20pm **QS+EM+MN+NS-ThA-1 Magnetic Textures in Quantum Materials Revealed by SQUID-on-tip Microscopy*, Ella Lachman,*** Rigetti Computing **INVITED**

Quantum materials are rapidly emerging as the basis for possible novel computation devices. However, fully understanding the interplay between magnetic and electronic excitations prevents us from realizing their full potential. In my talk, I will present the nano-SQUID-on-tip device and the scanning microscope built around it. Originally built to study superconducting vortex dynamics, this microscope has unprecedented magnetic sensitivity and spatial resolution.

I will show how expanding the microscope's range and realizing the microscopic magnetic textures in quantum materials is crucial to the understanding of transport phenomena on the macro scale. This will be demonstrated with two examples from two different types of materials. First, I will show how scanning nanoSQUID-on-tip magnetic imaging of magnetically doped topological insulators reveals the underlying fragility of the Quantum Anomalous Hall effect at elevated temperatures. Then, I will show how with a combination of transport, magnetization, and magnetic imaging of the Weyl semimetal $Co_3Sn_2S_2$, we find that the dynamics of domain walls are responsible for the anomalous transport behavior in the material.

These examples show that better understanding of the microscopic magnetism in these systems reveal new phenomena and deepen our understanding of the interplay between magnetic textures and electronic properties.

3:00pm **QS+EM+MN+NS-ThA-3 Quantum-Based Measurements for Pressure and Vacuum and the NIST on a Chip Program*, Jay Hendricks,*** *B. Goldstein,* NIST

The world of pressure and vacuum measurements and standards is currently undergoing a revolution in both measurement traceability, “the fundamental philosophy behind a measurement chain back to primary units”, and measurement technology, the “how a measurement is made”.This keynote presentation covers a bit of metrology history of how we got to where we are today and gives a forward-looking vision for the future.The role of NIST as a National Metrology institute is described along with an explanation of how and why our world-wide standards changed on May 20th, 2019.The NIST on a Chip program (NOAC) is introduced which seeks to utilize fundamental physics and laws of nature to develop quantum-based sensors and standards that one day may be miniatured to the chip scale.The technical core of the lecture will be a deeper dive into new research on measurement methods for pressure, the Fixed Length Optical Cavity (FLOC) and for vacuum, the Cold Atom Vacuum Standard (CAVS).What is exciting about these new measurement approaches is that they are both primary (relying on fundamental physics), are quantum-based and use photons for the measurement readout which is key for taking advantage of the fast-growing field of photonics. The FLOC will enable the elimination of mercury barometers pressure standards worldwide and the CAVS will be first primary standard for making vacuum measurements below 1.3x10-5 Pa.

3:20pm **QS+EM+MN+NS-ThA-4 Materials and Devices for Efficient Quantum Memories and Sensors*, Lee Bassett,*** University of Pennsylvania **INVITED**

Certain point defects in semiconductors exhibit quantum-mechanical features comparable to isolated atoms or molecules, in a solid-state materials platform amenable to nanofabrication, heterointegration with other materials and classical devices, and large-scale system engineering. Well-known quantum point defects such as the diamond nitrogen-vacancy center are leading candidates as robust quantum memories, versatile quantum sensors, and efficient light-matter interfaces. Meanwhile it is increasingly clear that alternative materials and defect systems offer potential advantages and new capabilities for quantum science [1]. However, millions of potential defects exist, and their identification is often tedious and challenging. This talk will introduce the opportunities and challenges of identifying point defects, including several new approaches to efficiently predict, characterize, and engineer their properties for quantum science and technology.

[1] L. C. Bassett, A. Alkauskas, A. L. Exarhos, and K.-M. C. Fu, "Quantum defects by design" Nanophotonics 8, 1867 (2019).

Funding: We acknowledge support from the NSF (DMR-1922278 and DMR-2019444).

Electronic Materials and Photonics Division
Room Ballroom A - Session EM-ThP

Electronic Materials and Photonics Poster Session

EM-ThP-2 Synthesis and Characterization of $Pb(In_{1/2}Nb_{1/2}O_3)$-$Pb(Mg_{1/3}Nb_{2/3}O_3)$-$PbTiO_3$ Thin Films Grown by Pulsed Laser Deposition*, **Da-Ren Liu,*** Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Because of their extraordinary large electromechanical coupling coefficient and piezoelectric coefficient, relaxor-based ferroelectric crystals $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) and $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PIN–PMN–PT) with morphotropic phase boundary (MPB) have attracted extensive attention. They also become important materials in the fabrication of high-performance electromechanical devices including transducers, actuators and sensors. However, with its concentration of PT near the morphotropic phase boundary region, the PIN–PMN–PT not only has similar piezoelectric performance to that of the binary PMN–PT but also possesses higher phase transition temperature and coercive field. In this study, highly textured thin films of the PIN–PMN–PT were grown on $SrTiO_3$ substrates by Nd:YAG pulsed laser deposition(PLD). According to the results of glancing-angle x-ray powder diffraction (GAXRD), the PIN-PMN-PT films are polycrystalline with a preferential growth direction.The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR), and the piezoelectric constant d_{33} was measured by the piezoelectric force microscopy(PFM).The complex refractive indices were measured in the range from 1.5 to 4.2 eV by spectroscopic ellipsometry (SE). The average oscillator strength and its associated wavelength were estimated by using a Sellmeier-type dispersion equation.

EM-ThP-3 The Study of Magnetic and Electrical Properties of Co Spin Crossover Molecule Thin Films*, **Jared Phillips**, S. Yazdani,* Indiana University-Purdue University-Indianapolis*; T. Ekanayaka, E. Mishra,* University of Nebraska*; J. Soruco,* Indiana University-Purdue University-Indianapolis*; A. N'Diaye,* Advanced Light Source, Lawrence Berkeley National Laboratory*; P. Wang,* University of Florida*; M. Shatruk,* Florida State University*; P. Dowben,* University of Nebraska*; R. Cheng,* Indiana University-Purdue University-Indianapolis

Spin crossover complexes (SCO) exhibit a bistability, and can be switched between a low spin and a high spin state via a wide range of external stimuli, including temperature, irradiation and electric field. Accompanying the change in spin state there are often dramatic changes in other physical properties, such as color, magnetic moment, and conductance. A recently synthesized valence tautomeric SCO molecule, $[Co(SQ)_2(3\text{-tpp})_2]$, displays a bistable conductance with a noteworthy low resistance in the high state, making this SCO molecule particularly intriguing for organic device applications. In this work, we detail the temperature, light and voltage dependent conductance properties in the context of the spin state and magnetic field dependent properties of this molecule drawing from results acquired from X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD), and electronic transport studies. Conductance properties depend on the molecular thin film so we will also discuss the methods and the techniques used to fabricate high quality thin films and the challenges to better thin film growth.

EM-ThP-5 Multi-Frame Gated X-Ray Imager (MGXI) for Fast Hard X-Ray Imaging*, **Mary Ann Mort**, C. Hunt,* University of California at Davis*; A. Carpenter,* Lawrence Livermore National Laboratory

The proposed multi-frame gated x-ray imager (MGXI) is a fast, hard x-ray imaging diagnostic for use in inertial confinement fusion (ICF) and high energy density (HED) experiments at the National Ignition Facility (NIF), such as Compton radiography and hot spot imaging. Individual MGXI component testing is happening in phases at Lawrence Livermore National Lab (LLNL) and the UC Davis Vacuum Microelectronics Lab. The Icarus2 hCMOS sensor was tested with a class 1 laser in both the high speed timing (HST) and manual shutter testing (MST) modes. Microchannel plates (MCPs) will be tested under vacuum with an electron gun and a simple photodiode array. MGXI has goals to image 10-100keV x-rays with 100-1000 ps temporal resolution in 2-8 frames and >5% detector quantum efficiency (DQE).

Electronic Materials and Photonics Division
Room 304 - Session EM1+MN+NS-FrM

Piezoelectric, Ferroelectric, and Multiferroic Devices & Microelectronics

Moderators: M. David Henry, Sandia National Labs, **Stephen McDonnell**, University of Virginia

8:20am **EM1+MN+NS-FrM-1 Piezoelectric Adjustable X-ray Optics*, Susan Trolier-McKinstry,*** Penn State University **INVITED**

Next generation X-ray observatories require lightweight, high throughput optics that maintain a < 0.5 arcsecond resolution. Thin adjustable X-ray mirrors can correct deformations generated from fabrication errors, gravity release, mounting stresses, and thermal variations, maintaining the high angular resolution (< 0.5 arcsecond) and large effective area (> 2 m^2) required for future X-ray missions. This paper describes fabrication of adjustable mirrors for the Lynx X-ray observatory mission concept.Prototype X-ray mirrors were built on either a 400 µm thick curved *Corning EAGLE XG*®glass substrate or on polished Si.In both cases, a Cr/Ir X-ray mirror coating was deposited on the front (concave) side, and an array of 1.5 µm thick radio frequency (RF) sputtered $Pb_{0.995}(Zr_{0.52}Ti_{0.48})_{0.99}Nb_{0.01}O_3$(PZT) piezoelectric thin film actuators on the back (convex) side to enable correction of figure errors.A two-layer metal routing scheme with a polymeric insulator was used to independently address 288 actuators on the mirror. The two-layer metal allows narrow kerfs between actuators and increased actuator density. A chrome-iridium layer was deposited on the concave side to function as the X-ray reflective coating for the films deposited on the convex side.Anisotropic conductive film was used to bond thin flexible copper cables to flat edges of the mirror to interface with external control electronics. Improved stress balancing process was achieved using compressively stressed SiO_2 films deposited on the convex side of the mirror to balance the tensile integrated stress of the actuator array while also matching the film thickness distribution.Finite element methods were used to assess the impact of film thickness distributions on the convex and concave substrate surfaces.The resulting models show peak-to-valley figure errors of 105 nm, well within the 1 µm peak-to-valley dynamic range of the piezoelectric adjusters. In contrast, when stress compensation was done with an iridium mirror film deposited on the front side, the mismatched thickness distribution results in peak-to-valley figure errors over 3 µm.

9:00am **EM1+MN+NS-FrM-3 Oxide and Nitride Ferroelectric Wurtzite Crystals*, Jon-Paul Maria,*** Penn State University

In the past three years, the demonstration of ferroelectricity in wurtzite-based crystals introduced exciting opportunities to explore and discover new structure-property relationships in novel formulation spaces, and to investigate new integration and device implementations given new process compatibilities. The seminal discovery of ferroelectric $Al_{1-x}Sc_xN$ by Fichtner *et al.* initiated this excitement and was followed by comparable observations of polarization reversal in the structurally similar $Al_{1-x}B_xN^2$ and the $Zn_{1-x}Mg_xO^3$ systems.

In this presentation our group will present recent results that demonstrate the structure-process-property relationships in the B-substituted AlN and Mg-substituted ZnO nitride and oxide systems. The B-substituted materials exhibit square hysteresis loops with polarization values between 150 µC/cm^2 and 120 µC/cm^2 when boron concentrations range between 2% and 15% respectively. Coercive field values fall with additional boron, from 5.5MV/cm to about 5 MV/cm at B saturation. Bandgap values are approximately 5 eV or above in all cases. Material can be prepared between 100 °C and 350 °C with very little difference in electrical properties. W bottom and top electrodes are used in all cases. Capacitors can be prepared down to 50 nm thick before leakage current becomes problematic during low frequency hysteresis measurements. First principles calculations that rationalize the unit cell volume, bond angle distribution, and remanent polarization will be presented.

Comparable results are found in the $Zn_{1-x}Mg_xO$ system. Between 25% and 35% Mg substitution, square hysteresis loops with remanent polarization values above 100 µC/cm^2 are readily achieved. Transmission measurements show bandgap values between 4.0 eV and 4.2 eV in this range. In comparison to AlBN, coercive field values for ZMO are as low as 1.7 MV/cm. As is the case with AlBN and AlScN, sustaining high insulation resistance to arbitrarily low thickness is challenging, the current thinness limit for low-leakage switching is ~ 125 nm. SHG analysis will also be presented for the ZMO system – preliminary measurements suggest values comparable to ferroelectric niobates.

9:20am **EM1+MN+NS-FrM-4 Development and Processing of $Al_{1-x}Sc_xN$ (x<0.40) Films for Resonator and Filter Applications*, Giovanni Esteves,*** *S. Yen, T. Young,* Sandia National Laboratories*; Z. Tang,* The University of Pennsylvania*; E. Schmidt, L. Gastian, M. Henry, T. Bauer, C. Nordquist,* Sandia National Laboratories*; R. Olsson,* The University of Pennsylvania

As the development of aluminum scandium nitride ($Al_{1-x}Sc_xN$/AlScN) films continues to be pushed towards higher Sc content, fabricated devices yield insight into the challenges associated with processing while demonstrating increased electromechanical coupling coefficients (k_t^2) over AlN. The addition of Sc into AlN presents film development and fabrication challenges that increase with higher Sc content such as the reduction of abnormal grains (AG), higher compressive stress, and etching. The development of $Al_{0.6}Sc_{0.4}N$ films using a single-alloyed target poses a significant challenge in terms of managing stress and the density of AG. Compressive stress help in reducing the amount of AG density through tuning the Ar/N_2 flow and pressure, but the magnitude of stress needed to achieve a low density of AG exceed -600 MPa. The use of certain metal templates aid in reducing AG density but are not sufficient to achieve AG-free films. Etching AlScN leads to long etch times due to slow etch rates of 25 nm/min and result in sidewall angles of ~74°. Nevertheless, AlScN lamb wave resonators (LWR) have been fabricated to demonstrate k_t^2 over 10%. Additionally, LWR with varying k_t^2 were interconnected to fabricate ladder filter configurations to determine that amount of bandwidth increase that can be achieved over AlN. Though AlScN demonstrates higher k_t^2, that lead to higher bandwidth, pushing this current technology to achieve more desirable metrics requires more stringent process quality.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

9:40am **EM1+MN+NS-FrM-5 Formation of Aluminum Scandium Nitride Microelectromechanical Systems Via Etching in Aqueous Potassium Hydroxide (KOH)*, Zichen Tang,*** *M. D'Agati, R. Beaucejour, S. Sofronici, J. Zheng, K. Kaylan,* University of Pennsylvania*; G. Esteves,* Sandia National Laboratories*; R. Olsson,* University of Pennsylvania

We report on the etch rate of sputter deposited piezoelectric and ferroelectric Aluminum Scandium Nitride ($Al_{1-x}Sc_xN$) thin films in aqueous potassium hydroxide (KOH). Specifically, we report on the vertical etch rate, lateral etch rate, and sidewall angle as a function of the scandium alloying ratio (x), temperature, and KOH concentration. As the scandium alloying ratio is increased, the vertical etch rate in 30% KOH at 45 °C is reduced from > 100 nm/s for AlN to < 4 nm/s for $Al_{64}Sc_{36}N$. The lateral etch rate, however, follows a very different trend, arriving at a minimum values of 0.05 nm/sec for $Al_{88}Sc_{12}N$. This is in contrast to the much higher lateral etch rates observed for both AlN and $Al_{64}Sc_{36}N$ of 2 nm/s. These trends in vertical and lateral etch rate are shown to hold for KOH concentrations from 10 to 30% and etch temperatures from 45 to 65 °C. We show that the etched sidewall angle can be predicted from a combination of the crystal structure and the vertical and lateral etch rates. We report a technique that utilizes the crystal structure and the vertical and lateral etch rates to form vertical (i.e. 90°) sidewalls solely from aqueous KOH etching. The ability to control the sidewall angle is vitally important in the formation of microelectromechanical systems (MEMS). We report on several piezoelectric MEMS devices fabricated utilizing the KOH etching processes. Finally, we report on the etching of AlScN as a function of ferroelectric polarization.

10:00am **EM1+MN+NS-FrM-6 Interface Reactions During the Ferroelectric Switching of HfZrO Thin Films on InAs***, A. Irish, Y. Liu, R. Atle, A. Persson, R. Yadav, M. Borg, L. Wernersson,* ***Rainer Timm,*** Lund University, Sweden

Traditional MOSFET-based electronic components have reached severe bottlenecks regarding data handling speed and power dissipation. A very promising alternative approach builds on MOS material stacks with thin ferroelectric oxide films in novel device architectures for e.g. steep-slope transistors, neuromorphic networks, or in-memory computation [1]. $Hf_{1-x}Zr_xO_2$ (HZO) films grown by atomic layer deposition are widely used in this context, due to their excellent film quality and conformity with existing semiconductor technology. Ferroelectric MOS devices based on III-V semiconductors are especially promising for high-speed applications due to the high charge carrier mobility of e.g. InAs. Furthermore, InAs/HZO/TiN devices have shown an unexpectedly high remanent polarization of the ferroelectric film [2]. In spite of the excellent electrical performance, only little is known about the structure, chemical composition, and switching dynamics of the semiconductor-ferroelectric oxide interface. We have previously used X-ray photoemission spectroscopy (XPS) to investigate interfaces of ferroelectric HZO [3], but *in situ* structural characterization obtained during the ferroelectric switching has been lacking until now.

Here, we present operando hard X-ray photoelectron spectroscopy (HAXPES) results from ferroelectric InAs/HZO/TiN MOS devices obtained during electrical biasing and switching. We observe an interface layer consisting of In- and As-oxides at the InAs/HZO interface. As 2p and In 3d core level spectra were obtained after subsequent switching processes of a "positive-up-negative-down" (PUND) series, showing a reproducible increase of the amount of interface oxide upon upward polarization and a decrease upon downward polarization. Thereby, electrical PUND cycles confirm the ferroelectric nature of the MOS device. Such a redox reaction at the semiconductor-oxide interface upon ferroelectric switching has – to our knowledge – not been reported before. Furthermore, we observe that the major fraction of the applied bias does not drop over the 10 nm thin HZO layer, but instead over the thin InAs-oxide interface layer.

These observations are challenging the established understanding of ferroelectric behavior in thin oxide films and are a key to understanding the superior performance of III-V/HZO based devices.

[1] M. Park et al., MRS Commun. **8,** 795 (2018).
[2] A. Persson et al., Appl. Phys. Lett. **116**, 062902 (2020).
[3] R. Athle et al., ACS Appl. Mat. Int. **13**, 11089 (2021).

10:20am **EM1+MN+NS-FrM-7 The Effect of Hf Doping on Piezomagnetic Properties of FeCo for Magnetoelectric Heterostructure Devices***, **Thomas Mion**, K. Bussmann, M. Staruch, P. Finkel,* US Naval Research Laboratory

New developments in magnetoelectric devices have demonstrated increased energy efficiency and temperature stability with reduced size compared to current technologies. Artificial magnetoelectrics, built on the combination of ferromagnetic magnetostrictive materials structurally coupled to piezoelectric and ferroelectric materials, display the ability to control magnetic properties of the ferromagnet with electric voltage across the piezo/ferroelectric layer. The best performance requires the implementation of soft magnetic materials with large magnetostriction and large voltage-induced strain in the piezo/ferroelectric layer. Processing requirements for device fabrication often complicate the realization of these combined qualities as inherent stresses from the deposition technique are often detrimental to the magnetoelectric functionality. Solutions to these problems are rarely reported though alloying of FeCo and subsequent metalloid substitutions such as $(Fe_{0.5}Co_{0.5})_{1-x}C_x$, and $(Fe_{0.5}Co_{0.5})_{1-x}B_x$, have proven successful in reducing the coercive field while retaining high magnetostriction and piezomagnetic properties **[1,2]**.

In this work we present the systematic study of sputter-deposited Hf-doped $Fe_{50}Co_{50}$ alloy thin films with a focus on the correlation between film stress and magnetic softness and find an inflection point from tensile to compressive stress with increasing Hf composition. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) of the $(Fe_{0.5}Co_{0.5})_{1-x}Hf_x$ system reveal the magnetic softening is also correlated to emergence of an amorphous phase with reduced grain size for these sputter-deposited films. We will show the utilization of this new alloy in a multiferroic MEMS resonator device demonstrating a high magnetoelectric response required for magnetic sensors.

[1] Phys. Rev. Applied 12, 034011 (2019)

[2] Appl. Phys. Lett. 91, 182504 (2007)

Electronic Materials and Photonics Division
Room 304 - Session EM2-FrM

Advanced Devices & Fabrication Methods

Moderators: Parag Banerjee, University of Central Florida, **Bryan Wiggins**, Intel Corporation

10:40am **EM2-FrM-8 Two-Dimensional Steep-Slope Transistors Using Graphene Cold Sources***, M. Liu, H. Jaiswal, S. Shahi, S. Wei, Y. Fu, A. Chakravarty, A. Cabanillas, A. Ahmed, F. Yao, **Huamin Li,*** University at Buffalo

Two-dimensional (2D) steep-slope field-effect transistors (FETs) with low energy consumption have been considered to have great potential to continue the future exponential growth of semiconductor electronic devices. The performance of conventional 2D transistors is limited by "Boltzmann tyranny" which generates a relatively long thermal tail in energy distribution and limits the subthreshold swing (SS) at 60 mV/decade at room temperature. To break the limit of 60 mV/decade SS, tunneling FETs (TFETs) and negative capacitance FETs (NCFETs) have been proposed, yet they suffer a variety of challenges and issues. Here we investigate an emerging concept of the steep-slope transistors known as cold-source FETs (CSFETs) or Dirac-source FETs (DSFETs) where graphene (Gr) serves as the Dirac source to provide the cold electrons with a localized electron density distribution and a short thermal tail at room temperature, as shown in Fig. 1. For the CSFET with monolayer MoS2 as the 2D channel, the transport factor can be reduced due to the localized electron density distribution and a shorter thermal tail, giving rise to a minimum SS of 29 mV/decade at room temperature, an excellent on/off ratio (~107), and a record high sub-60-mV/decade current density (~4 µA/µm) which are comparable to current steep-slope technologies, as shown in Fig. 2. Similarly, the CSFET with a multilayer WSe2 channel also shows a sub-60-mV/decade SS, as shown in Fig. 3. The 2D MoS2 and WSe2 CSFETs in this work are benchmarked with the 14 nm Si-based FinFET CMOS technology, as shown in Fig. 4 (a). The sub-60-mV/decade SS as a function of drain current (JD) was compared with other steep-slope transistors, including TFETs, NCFETs, and one-dimensional (1D) CSFETs based on a variety of channel materials, as shown in Fig. 4(b). Our work demonstrated the 2D CSFETs as a steep-slope transistor concept for energy-efficient beyond-CMOS technology.

11:00am **EM2-FrM-9 High Performance, RF Interposer Fabrication on Glass with 3 Metal Layers and Embedded TGVs***, S. Herrera, A. Ruyack, S. Lepkowski, M. Hirabayashi, M. Powner, C. Nordquist, **Matthew Jordan**,* Sandia National Laboratories

We will show the fabrication of a 3-metal layer, low-k dielectric, interposer on glass capable of supporting RF and optoelectronic microsystems. Multi-chip modules (MCMs) allow for the combination of several disparate technologies, like wide bandgap MMICs (monolithic microwave integrated circuits) and CMOS mixed signal electronics, in one package. However, wirebond compatible MCMs suffer from long interconnect lengths as well as require many of the passive RF circuit components to be either incorporated on-chip (a loss of active space) or on the printed circuit board (increasing manufacturing complexity). In fact, much of the footprint of a typical RF chip is devoted to passive components such as decoupling capacitors and impedance matching networks. Disaggregating RF circuit components from transistor technologies through repeatable methods of interconnecting RF chips will reduce on-chip real estate leading to decreased cost. Removing components from the circuit board decreases the manufacturing complexity, as well as size, weight, and power. Therefore, an intermediate interposer that both improves upon MCM performance and reduces cost is an attractive solution.

The interposer approach discussed in this presentation utilizes a flip-chip method to electrically connect die, resulting in repeatable connections between the interposer and the die. This differentiates the approach from similar RF interposer methods like the HRL MECAMIC process in which die are embedded in the interposer[Herrault2020]. Integrated passive devices on the interposer include metal-insulator-metal capacitors, resistors, and inductors which further simplify RF integrated circuit chip design.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

11:20am **EM2-FrM-10 Single Step Fabrication Process of Alignment Markers for Direct-Write Electron Beam Lithography in Metal-Organic Negative Tone Resist***, **Guy DeRose**,* California Institute of Technology

Alignment markers, also referred to as fiducial marks, are commonly made by a process called liftoff. In the liftoff process, a bilayer electron beam resist, such as polymethyl methacrylate (PMMA), is spun and baked onto the substrate, then written by the electron beam pattern generator. Following the development of the resist, a metallization step, typically electron beam evaporation, takes place, followed by soaking the coated substrate in a solvent such as N-Methylpyrrolidone (NMP) during which the metal that is not stuck to the substrate "lifts off" and leaves behind the alignment markers of interest. While a standard process, there are many steps involved, and it is possible that the evaporation process might not be compatible with subsequent steps in the fabrication.

Previously we have demonstrated a negative tone resist that is comprised of a metal-organic material [1]. Using electron beam lithography, we have shown that it can produce high fidelity patterns of 15 nm half pitch. To build upon this work, we demonstrate the fabrication of the alignment markers by directly writing them into this resist in a single process step. Due to the fact that the resist contains chromium metal it was hypothesized that the metal content may be detected by the secondary electron detector (SED) has the metal would produce higher contrast. It can be seen from X-ray photoelectron spectra (XPS) of Figure 2 that the resist has reduced into a metallic oxide material to form CrO_x after it has been exposed by the electron beam; this means that the resist material is no longer soluble in the developing solvent, hence a pattern can be formed. The material can also be used as alignment markers because the density contrast between the silicon and the CrO_x material is dramatically increased by a factor of ~2.25 and this inherently increases the effective atomic number contrast which allows them to be detected by the SED, which can be seen by the Monte Carlo simulations of Figure 3. Figure 4 shows the results of writing an array of 20 um square alignment marks, which are commonly used for multi-layer electron beam lithography.

It can be seen by the SED that the pattern shows high pattern quality. We have demonstrated this at 20 KeV, however, we will present the results of using these patterns as alignment markers for direct-write electron beam lithography at 30 KeV and 100 KeV, along with detailed Monte Carlo simulations that describe the interaction between the incident electron beam and the resist/substrate combination.

11:40am **EM2-FrM-11 Non-Destructive Metrology Techniques for Characterizing a-C Hard Mask Films in 3D NAND Structures***, P. Mukundhan, **G. Andrew Antonelli,*** Onto Innovation

Growth in 3D NAND is driven by data-intensive applications that have changed the paradigm for manufacturing to achieve vertical scaling. One of the key steps in the process is the use of hardmask deposition to etch deep, high-aspect ratio features that conventional photoresist cannot withstand. Amorphous carbon (a-C)-based hard masks, grown using plasma-enhanced chemical vapor deposition (PECVD) have been adopted in high volume manufacturing.

Depending on the process condition, these films exhibit a wide range of hardness, electrical resistivity, optical transparency, and chemical inertness. The information needed during design of the material includes thickness uniformity, characterization of optical constants, density, elastic modulus, and bonding structure. The sp^3-to-sp^2 hybridization ratio and the H content determine the thermomechanical properties of the films. Given the complex nature of an a-C system, no single metrology technique provides all the relevant information needed for process tuning.

In this paper, we present results from two non-destructive techniques: picosecond ultrasonics (PULSE™) and FTIR for the qualification of next generation of advanced hard mask materials. A design-of-experiments (DOE) skew (~3µm a-C thickness target) covering different deposition temperature, pressure and time were generated. With the transition of a-C to thicker and more graphitic (opaque) films, the PULSE™ technique is uniquely qualified for measuring thickness and elastic modulus of these films. Results from the systematic study of different types of films demonstrated sensitivity to process variation and excellent correlation to cross-section microscopy. A second set of a-C films in the 0.2 µm -2µm thickness range was generated to test sensitivity to different processes and provide information regarding the bonding characteristics. Studies have shown the correlation between structural characteristics and the etching characteristics which is primarily determined by the sp3/sp2 ratio. Wafer maps have been collected using an Element™ 300mm automated FTIR. We observed that the absorbances for the sp^2 C=C and the sp^3 $C\text{-}H_x$ stretching bonds were significantly different and could be used to discriminate the processes. Furthermore, the sp^2/sp^3 ratio was successfully calculated for all samples. Current efforts are focused on finding correlation between the two metrology techniques and their application in etch process optimization for high volume manufacturing.

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) $2\theta/\omega$ 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]‖ w-AlN[11-20]‖ 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

Author Index

Author Index

Author Index

Author Index