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_2Se_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_2Se_3 is a two-dimensional semiconductor that has long been believed to have a centrosymmetric crystal structure. α-In_2Se_{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_2Se_3 in electronic devices due its unique combination of properties; however large-area thin-film synthesis of α-In_2Se_3 has not been established. Since 2018 there have been reports of polarization in a β'-In_2Se_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_2Se_{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_2Se_3 [9]. If β-In_2Se_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_2Se_3 thin-films and electrical characterization of β-In_2Se_3 transistors. We link processing parameters such as synthesis substrate temperature, and Se/ In flux ratio to resulting β-In_2Se_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)

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[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.

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

2D Materials Technical Group

Room 303 - Session 2D+AS+SS-MoA

2D Materials: Defects, Dopants, Edges, Functionalization, and Intercalation

Moderators: Chih-Kang (Ken) Shih, University of Texas at Austin, **Young-Woo Son**, Korea Institute for Advanced Study, Republic of Korea

2:20pm **2D+AS+SS-MoA-3 Effect of Defects in 2D Materials on the Dielectric Breakdown***, **Abdulrahman H. Basher**, M. Lanza, U. Schwingenschlogl,* King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Two-dimensional (2D) materials are one of today's hot topics in the semiconductor industry due to the fact that they can be used to fabricate nanodevices with attractive properties [1, 2]. However, they may lose their features in the presence of defects. For instance, 2D hexagonal boron nitride (hBN) is an excellent insulator but defects lower its breakdown voltage in the experiment [3]. Therefore, the aim of this study is to understand the mechanism of the dielectric breakdown in hBN as compared to amorphous boron nitride (aBN), using first-principles calculations based on density functional theory. The CP2K quantum chemistry and solid-state physics software package is used (quickstep algorithm based on the Gaussian and plane waves method) [4, 5]. The generalized gradient approximation of Perdew-Burke-Ernzerhof [6] is employed, and Grimme's dispersion correction [7, 8] with Becke-Johnson damping [9] is used as the van der Waals forces play a significant role in 2D materials. The obtained densities of states show that the size of the band gap decreases for increasing defect density, confirming that 2D materials are sensitive to defects. We explain the experimental observation that the breakdown voltage decreases from hBN (crystalline) to aBN (amorphous).

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[1] Y. Shi, X. Liang, B. Yuan, V. Chen, H. Li, F. Hui, Z. Yu, F. Yuan, E. Pop, H. S. P. Wong, and M. Lanza, Nat. Electron. **1**, 458 (2018).

[2] C. Wen, X. Li, T. Zanotti, F. M. Puglisi, Y. Shi, F. Saiz, A. Antidormi, S. Roche, W. Zheng, X. Liang, J. Hu, S. Duhm, J. B. Roldan, T. Wu, V. Chen, E. Pop, B. Garrido, K. Zhu, F. Hui, and M. Lanza, Adv. Mater. **33**, 2100185 (2021).

[3] Y. Shen, K. Zhu, Y. Xiao, T. Knobloch, D. Waldhör, A. H. Basher, F. Saiz, S. Pazos, X. Liang, W. Zheng, Y. Yuan, J. B. Roldan, U. Schwingenschlögl, H. Tian, H. Wu, T. Grasser, and M. Lanza, submitted to Nat. Electron. (2022).

[4] J. Van de Vondele and J. Hutter, J. Chem. Phys. **127**, 114105 (2007).

[5] J. Hutter, M. Iannuzzi, F. Schiffmann, and J. Vandevondele, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **4**, 15–25 (2014).

[6] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[7] S. Grimme, S. Ehrlich, and L. Goerigk, Theory. J. Comput. Chem. **32**, 1456−1465 (2011).

[8] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

[9] E. R. Johnson and A. D. Becke, J. Chem. Phys., **123**, 024101 (2005).

2:40pm **2D+AS+SS-MoA-4 Palladium Nucleation and Alloying at the WTe$_2$(001) Surface***, **Prescott E. Evans**, P. Sushko, Z. Dohnálek,* Physical and Computational Sciences Directorate and Institute for Interfacial Catalysis, Pacific Northwest National Laboratory

A deeper understanding of atomic-scale functionalization of transition metal dichalcogenides, especially topologically interesting variants such as WTe$_2$, is critical in developing deployable structures in quantum information science. Discerning the role of intrinsic surface defects as adsorption and functionalization sites is a key step towards device realization. In this study, scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS), and density functional theory (DFT) were utilized to examine the initial nucleation and growth of palladium on the WTe$_2$(001) surface as both a function of coverage and temperature. XPS measurements of the WTe$_2$(001) surface after palladium deposition at room temperature show significant interaction between Pd and surface tellurium reminiscent of PdTe$_2$ in electronic structure with an absence of interaction between Pd and tungsten. Using STM, we found palladium deposited at room temperature, where Pd clusters outnumber surface defects more than 10:1, produced no change in surface defect density. This indicates a lack of interactions between deposited Pd clusters with intrinsic surface defects. The annealing temperature-dependent STM studies further show that palladium clusters are stable to about 475 K. Palladium deposition at an elevated temperature of 425 K was performed to determine that the lack of nucleation on defects is, in fact, not a result of diffusion limitations during the growth. Complementary theoretical studies predict that palladium atoms interact strongly with Te adatoms and Te vacancies, while only binding weakly on pristine WTe$_2$(001). Based on these results, we conclude that the nucleation of Pd clusters is initiated by mobile Te adatoms that likely significantly outnumber other surface defects. Our high-temperature Pd deposition studies further support this assertion. Atomically resolved images of large Pd nanoparticles annealed above 475 K exhibit a superstructure on the top terrace indicating alloying with tellurium. Atomically precise, tailored heterostructures with tunable electronic, and topological properties are necessary for the growing need for quantum devices. A full account of the surfaces of these quantum materials, as in with WTe$_2$(001) where excess chalcogenide complicate interactions at the surface, is vital in directing both accurate predictive theory and material synthesis efforts.

3:00pm **2D+AS+SS-MoA-5 Advanced Doping Schemes for 2D Nb:WS$_2$ for Catalysis and Electronics***, **Jeff Schulpen**, C. Lam, W. Kessels, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; A. Bol,* University of Michigan, Ann Arbor

Two-dimensional semiconductors such as WS$_2$ are promising materials for use in next-generation nanoelectronics due to their high mobility and scalability allowing for ultra-short gates. Doping is required to make the p-type FETs needed for CMOS logic and doping can also reduce the contact resistance, which is another important challenge to overcome for transistors based on 2D materials.[1] Separately, doped 2D materials are receiving interest as affordable catalysts, as the dopants enhance the catalytic activity of the basal plane in addition to the already high activity of the edge sites.[2]

Essential for both electronic and catalytic applications is the precise control over the amount and distribution of dopants in the film. The synthesis method of atomic layer deposition (ALD) allows excellent control over these parameters such that e.g. graded doping profiles and edge decorations can be achieved.[3]

In this work we synthesize Nb-doped WS$_2$ by plasma-ALD and characterize the electronic and catalytic performance of the films.Conventional supercycles of type (AC)$_m$(BC)$_n$ were used to achieve excellent composition control from W-rich to Nb-rich films. Optimal hydrogen evolution reaction (HER) activity was found for Nb-rich films (~85% Nb). Beyond composition tuning, we investigate the effect of different edge terminations on the HER activity by modifying the cycle order in the ALD process. For electronic applications where low dopant concentrations are relevant, we use a modified (AC)$_m$(ABC)$_n$ scheme, where adsorbed W precursor largely inhibits adsorption of the Nb precursor. This allows for better dopant distribution than conventional supercycles, thereby improving the resistivity and Hall mobility of the films by a factor of two. Further characterization of devices based on the grown films is presented.

These results confirm that ALD-grown Nb-doped WS$_2$ is a promising material for both electronics and catalysis, and that the use of advanced doping schemes can further improve the performance of these films. This also serves as a demonstration of inhibition-assisted doping using ALD, which could be of interest for other material systems.

1. Feng, L., *et al. Nanoscale* **8**, 6507–6513 (2016).
2. Tang, L. *et al. Adv. Funct. Mater.***31**, 2006941 (2021).
3. Schulpen, J. J. P. M. *et al. 2D Mater.***9**, 025016 (2022).

4:00pm **2D+AS+SS-MoA-8 Atomic Imaging of Dynamic Behaviour at 2D Material Solid-Solid and Solid-Liquid Interfaces***, **Sarah Haigh**,* University of Manchester, UK **INVITED**

Transmission electron microscopy (TEM) is used for understanding the local structure of nanomaterials. Although, we are frequently concerned about understanding behaviour during chemical reactions or while undergoing physical processes, most TEM is performed with the sample exposed to high vacuum, which can change the atomic structure of surfaces and interfaces. Unfortunately, commercial in-situ liquid, gas or electrochemical cell TEM imaging holders often severely limit atomic resolution imaging and chemical analysis.

For investigating the chemical reactivity and degradation of 2D materials without exposing them to the TEM vacuum, an effective approach is to encapsulate the sample between two inert and impermeable few-layer 2D sheets (such as graphene or hexagonal boron nitride). This also enables transfer of air sensitive specimens from an inert vacuum or glove environment to the TEM without exposing the material to atmospheric conditions. We have applied this approach to study air sensitive 2D materials, including local point defects, doping and edge structures in a wide range of structures (e.g. CrBr3, GaSe, black phosphorus) (Fig. 1c)[1,2]. We also find that encapsulation with inert 2D materials is an effective route to preserve the delicate surface structure of hydrated 2D materials, enabling the visualization of exchangeable surface cations on few layer clays and micas [3] and a route to understand the changes in atom/ion motion at interfaces where the 2D materials are twisted with respect to each other (Fig. 1d).[3,4]

This 2D heterostructure approach can also be used to investigate solid-liquid interfaces. Building on nanochannel technology developed by the group of Andre Geim (Fig. 1b)[5] we have developed in-situ liquid phase TEM imaging using 2D heterostructure nanochannels. The in-situ 2D heterostructure liquid cell approach provides atomic resolution imaging and analysis and makes it possible to study the earliest stage of chemical synthesis [6]. It also reveals the large differences in adatom adsorption sites on 2D surfaces in vacuum compared to hydrated environments and allows study of dynamic adatom motion at solid liquid interfaces [7]; something that was not previously possible by any technique (Fig. 1a).

[1] Hopkinson, et al. ACS Nano, (2019), 13, 5, 5112; [2] Hamer et al. Nano Lett. (2020), 20, 9, 6582 [3]Zou et al, Nature Materials (2021), 20, (12) 1677; [4] Weston et al, Nature Nanotechnology (2020), 15 (7), 592; [5] A Keerthi et al, Nature, (2018), 558 (7710), 420; [6] Kelly et al, Advanced Materials, (2021) 33, 29, 2100668; [7]Clark et al. https://arxiv.org/abs/2203.04906 (2022);

4:40pm **2D+AS+SS-MoA-10 Electrodeposition of Nanofiberous H-Type MnO₂ Birnessite on Epitaxial Graphene Silicon Carbide Heterostructures, and transformation to Alkali Birnessites (Na, Li, K) via Simple Intercalation***, **Michael Pedowitz**, D. Lewis, K. Daniels,* University of Maryland, College Park

Mixed valence manganese oxides (MnO_x) have attracted significant research interest in recent years due to the reversible low energy redox reactions between manganese oxidation states (Mn^{+2}, Mn^{+3}, and Mn^{+4})[1], which has enabled its use in catalysis[2], energy storage[3], and gas sensing[4]. Of these manganese oxide compounds, manganese dioxide (MnO_2) has been of particular interest due to its wide variety of synthesized structural polymorphs (α (1x2 tunnel), β (1x1 tunnel), γ (spinel), and δ (layered))[5] which allow for significant control over the active surface area and reactive properties MnO_2. In particular, the Mn^{+3} defect density, which has been found to increase the reactivity of the MnO_2 film[6], is highly variable between polymorphs, with the δ phase exhibiting the highest defect density. Water stabilized δ-MnO_2 (H-δ-MnO_2) in particular contains the highest number of Mn^{+3} defects due to the presence of $Mn^{+2/+3}$ in the interlayer, which neutralize the layer charge from lattice defects[7]. However, the production of H-δ-MnO_2 has proven challenging in the literature. In this work, we present the synthesis of H-δ-MnO_2 on epitaxial graphene silicon carbide via electrodeposition. The electrodeposition was carried out in a 3 electrode electrochemical cell in a 3-step process with a duration of 1.25 seconds. The resulting films were then characterized using a combination of Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) to confirm the formation of H-δ-MnO_2 and probe its surface morphology. The Raman spectra indicated the successful formation of H-δ-MnO_2, while the AFM and SEM indicated the surface has a nanofibrous character, increases the active surface area of the thin film. We then demonstrated that the material can be converted to Alkali type (Li, Na, K) δ-MnO_2 via intercalation without damaging the EG substrate. After the process, the material was characterized again with Raman, AFM, and SEM, which confirmed the transformation from H-type to Alkali-Type. As the interlayer spacing of δ-MnO_2 and its applications are related to the intercalated ions, this demonstrates the tunability of this heterostructure and its potential to be a platform for a variety of applications, including energy storage and gas sensing.

References: [1]L. Spinelli et al. Sensors 17(7) (2017)[2] F. Cheng et al. Chem. Mater 22(3) (2010)[3] Y.J. Huang et al. Electrochim Acta 99 (2013)[4]N. Joshi et al. Microchim. Acta 185 (2018)[5]Z. Chang et al. Proc Natl Acad Sci USA 115(23) (2018) [6] Julien et al. Spectrochim Acta A 60 (2004) [7] Drits et al. Am Mineralogist 82 (1997)

5:00pm **2D+AS+SS-MoA-11 Signature of Coexistence of Ferroelectricity and Ferromagnetism in a Quantum Material***, **I-Hsuan Kao**, S. Yuan, J. Katoch, S. Singh,* Carnegie Mellon University

Electric field-controlled magnetism by combining van der Waals (vdW) based semiconducting ferromagnets and Weyl semimetal is appealing because of the gate tunability and efficient charge-spin transduction[1], which can be exploited for modular memory and logic devices. Ferroelectric switching has been previously demonstrated in bilayer and trilayer WTe_2[2-4], where the polarity can be controlled by electric gating. VdW based semiconducting FMs, such as $Cr_2Ge_2Te_6$ (CGT), provide the opportunity to study tunable magnetic phenomena and to build superlattices with other quantum materials[5]. By coupling a semiconducting ferromagnet to a Weyl semimetal, magnetization can be induced at the interface by magnetic proximity effect. We have fabricated WTe_2/CGT devices and observed anomalous Hall effect, which is a signature of magnetic proximity effect. In the same device, we are able to perform ferroelectric switching of WTe_2 by applying an electric field. Furthermore, the presence of the anomalous Hall effect can be enhanced (suppressed) by negative (positive) electric gating. We will present detailed measurements, which are required to understand this novel platform where ferroelectricity and ferromagnetism coexist.

1.Kao *et al*., Nature Materials (2022).

2.Fei, Z. *et al*. Nature **560**, 336–339 , (2018).

3.de la Barrera, S. C. *et al*.Nature Communications **12**, 5289, (2021).

4.Xiao, J. *et al*. Nature Physics **16**, 1028, (2020).

5.Verzhbitskiy, I. A. *et al*. Nature Electron **3**, 460, (2020).

MEMS and NEMS Technical Group
Room 302 - Session MN+2D-MoA
Emerging Materials and Structures for MEMS/NEMS Devices

Moderators: Azadeh Ansari, Georgia Institute of Technology, **Yanan Wang**, University of Nebraska - Lincoln

1:40pm **MN+2D-MoA-1 Phononic Crystals based on Two-Dimensional Materials***, **Yanan Wang**,* University of Nebraska - Lincoln **INVITED**

Thanks to the ultimate thinness, excellent elastic properties, and unparalleled advantages in device integration, two-dimensional (2D) materials have emerged as compelling candidates for enabling high frequency nano-/microelectromechanical systems (NEMS/MEMS). This talk will discuss the further exploration of 2D materials in phononic devices, such as quasi-1D phononic waveguides and tunable phononic crystal lattices, emphasizing their potential applications in quantum information processing and quantum sensing systems.

2:20pm **MN+2D-MoA-3 Scaling Acoustics into mm-Wave: Higher-Order Lamb Mode Devices in Piezoelectric Thin Films***, **Ruochen Lu**, J. Kramer, S. Cho, O. Barrera,* The University of Texas at Austin **INVITED**

The evolving wireless communication moves to higher frequency bands with broader bandwidth for faster data rate. New types of front-end elements are required to perform the signal processing at the new bands. Acoustic devices are among the processing candidates, thanks to their compact footprints and low loss. However, It has been a long-standing challenge to scale piezoelectric resonators beyond 6 GHz without significantly losing quality factor (*Q*) and electromechanical coupling (k^2).

Until now, three approaches have been investigated, including reduced wavelength, higher-order modes, and multi-layer periodically poled piezoelectric films (P3F) structures. The first method requires small feature sizes, e.g., the electrode pitch width of laterally vibrating devices or the thickness of film bulk acoustic wave resonators (FBARs). The direct scaling inevitably leads to fabrication challenges and more importantly, severely reduced *Q* from the electrical resistance and acoustic damping. The second approach utilizes the additional thickness component in higher-order Lamb modes to relax the lateral feature size requirement. However, sub-400 nm piezoelectric thin films are needed if operated at the first-order thickness mode, e.g., first-order antisymmetric (A1) mode, inducing limited *Q* below 500 from the surface damages during the implementation. Alternatively, one can operate at higher frequencies using increased thickness mode order acoustic modes, e.g., second-order antisymmetric (A2) mode. Nevertheless, further increasing the mode order in the thickness direction without modifying the transducer configuration leads to reduced k^2, as the generated charge tends to cancel out, limiting the applications.

Recently, we proposed the P3F platforms using thin-film lithium niobate ($LiNbO_3$) to address the challenge. By stacking transferred thin-film $LiNbO_3$ with alternating orientations in the thickness direction, we can achieve remarkable frequency scaling without losing k^2 or relying on thinner films. Complementarily oriented bi-layer acoustic resonator (COBAR) following thickness-shear modes have been demonstrated. We will report COBARs leveraging the thickness-extensional (TE) modes at 15.8 GHz using sixth-order antisymmetric (A6) mode COBAR with a high loaded Q of 720. The measured loaded Q and $f{\cdot}Q$ product (1.14×10^{13}) are among the highest for piezoelectric acoustic resonators beyond 6 GHz.

3:00pm **MN+2D-MoA-5 AlScN Piezoelectric Metamaterials for Next Generation RF Systems***, C. Cassella, **Dan Zhao**,* Northeastern University **INVITED**

In the last two decades, microacoustic resonators (μARs) have played a key role in integrated 1G-to-4G radios, providing the technological means to achieve compact radio frequency (RF) filters with low loss and moderate fractional bandwidths (BW<4%). More specifically, Aluminum Nitride (AlN) based filters have populated the front-end of most commercial mobile transceivers due to the good dielectric, piezoelectric and thermal properties exhibited by AlN thin-films and because their fabrication process is compatible with the one used for any Complementary Metal Oxide Semiconductor (CMOS) integrated circuits (ICs). Nevertheless, the rapid growth of 5G and the abrupt technologicalleap expected with the development of sixth-generation (6G) communication systems are expected to severely complicate the design of future radio front-ends by demanding Super-High-Frequency (SHF) filtering components with much larger fractional bandwidths than achievable today. Even more, the recent invention of on-chip nonreciprocal components, like the circulators and isolators recently built in slightly different CMOS technologies, has provided concrete means to double the spectral efficiency of current radios by enabling the adoption of full-duplex communication schemes. Nevertheless, for such schemes to be really usable in both military and commercial wireless systems, self-interference cancellation networks including wideband, low-loss and large group delay lines are needed. Yet, the current on-chip delay lines that are also manufacturable through CMOS processes, which rely on the piezoelectric excitation of Surface Acoustic Waves (SAWs) or Lamb Waves in piezoelectric thin films, have their bandwidth and insertion-loss severely limited by the relatively low electromechanical coupling coefficient exhibited by their input and output transducers. As a results, these components are hardly usable to form the delay lines forming any desired self-interference cancelation networks. In order to overcome these challenges, only recently, new classes of microacoustic resonators and delay lines exploiting the high piezoelectric coefficient of Aluminum Scandium Nitride (AlScN) thin films and the exotic dispersive features of acoustic metamaterials have been emerging. These devices rely on forests of locally resonant piezoelectric rods to generate unique modal distributions, as well as unconventional wave propagation features that cannot be found in conventional SAW and Lamb wave counterparts. In this talk, the design, fabrication and performance of the first microacoustic metamaterials based resonators and delay lines will be showcased.

4:00pm **MN+2D-MoA-8 Fabrication, Actuation and Control of 3D-Printed Microscale Robots***, **Azadeh Ansari**,* The Georgia Institute of Technology **INVITED**

This talk covers the fabrication methods of micro scale robots using two photon lithography nanoscale 3D printing of various micro robot designs for biomedical applications. The polymer-based 3D printed robots are integrated with piezoelectric actuators, or magnetic thin films/cubes. Tiny polymer legs/bristles and contacts are designed for precise robot motion control. Furthermore, the microbots are equipped with various mechanical add-ons such as micro-tips/needles for penetration into soft tissues, micromanipulators, micro-drillers, and PH sensitive drug delivery units.

4:40pm **MN+2D-MoA-10 Fabrication of Resistor-based Zinc Devices using Selective Chemical Deoxidation of Screen Printed Zinc Inks by Inkjet Printing***, A. Radwan*[1]*,* Case Western Reserve University*; Y. Sui,* University of Colorado at Boulder*; **Christian Zorman**,* Case Western Reserve University

Zinc (Zn) is a common metal that harmlessly decomposes in the environment and thus is considered a leading metal for use in environmentally-friendly electronics. Zn readily oxidizes under ambient conditions forming a thin, electrically-insulating zinc-oxide (ZnO) layer on the surface of Zn particles. Fortunately, conductive Zn structures can be formed by etching the ZnO layer using aqueous solutions of acetic acid dispensed by drop casting. Although drop-casting is simple to implement, dispensing extremely small volumes is difficult . As such, drop casting is limited to producing structures with high conductivity (i.e., electrodes) but is not suitable to produce structures with tunable resistivity.Although designed to dispense inks, inkjet printers are precision liquid dispensing systems capable of depositing picoliter droplets at designated locations. Therefore, it is feasible to use an inkjet printer as an acetic acidic dispenser to form Zn structures by selective etching of Zn-based inks. Unlike drop casting, this reactive inkjet printing (RIJ) process enables the resistivity of Zn structures to be tuned by controlling the amount of acetic acid dispensed. Moreover, inkjet printing offers precision lateral control of the dispensing process which could enable the fabrication of both conductive and resistive structures in the same Zn layer.

In this paper, a selective RIJ method to dispense an etching agent on screen printed Zn structures with a high degree of volumetric and spatial control is described. This RIJ process is used in conjunction with screen printing to precisely control the amount of acetic acid deposited on the surface of printed Zn structures. The number of print passes and drop spacing are utilized to precisely regulate the exposure of the Zn structures to acetic acid thus enabling unparalleled control of the etching process. The screen printing and RIJ processes are performed at room temperature, making them compatible with temperature sensitive substrates including many that are attractive for flexible, implantable and biodegradable electronics. The substrate only needs to be inert to acetic acid. This study specifically focuses on the formation of Zn structures with tunable resistivity and explores the relationships between key printing parameters and electrical resistivity of the resulting Zn structures. As process demonstrators, microheaters and RC filters are fabricated and characterized.

5:00pm **MN+2D-MoA-11 Mechanically Tunable One-Dimensional Photonic Crystals Fabricated by Two-Photon Polymerization***, **Victoria P. Stinson**[2], N. Shuchi, M. McLamb, G. Boreman, T. Hofmann,* University of North Carolina at Charlotte

Photonic crystals have attracted interest in optical applications, due to their highly reflective photonic bandgaps [1-3]. These photonic bandgaps are formed by creating a dielectric periodicity. Depending on the complexity of this periodicity the photonic crystal can be described as being one-, two-, or three-dimensional. In the one-dimensional case, this periodicity is created in a single direction. One-dimensional photonic crystals fabricated by two photon polymerization have demonstrated high-contrast photonic bandgaps in the infrared spectral range [2]. This is achieved by alternating layers of high- and low-density. In order to allow additional spectral filtering of the photonic bandgap, defects have also been implemented into these designs, allowing narrow band transmissions to exist within the otherwise reflective photonic bandgap [3]. While the spectral position of these features can be easily designed for a desired range, there are currently few methods for manipulating these features post-fabrication. Introducing mechanically sensitive flexures as low-density layers into these one-dimensional photonic crystals could fill this gap. Opto-mechanical devices fabricated by two-photon polymerization is an emerging field which has applications in areas such as MEMS and microrobotics [4]. The ability to control the spectral response via an external mechanical stimuli opens the door for more complex and adaptable sensing and filtering bandgap devices. The use of two-photon polymerization in the development of these devices allows for three-dimensional design freedom with efficient fabrication times. In this study we report on the use of sub-wavelength mechanical flexures in the low-density layers of one-dimensional photonic crystals fabricated by two-photon polymerization. Upon compression the change in thickness of these low-density layers will result in an overall spectral shift of the photonic bandgap. The degree of spectral shifting, as well as an analysis of the mechanical properties of one-dimensional photonic crystals with flexures are presented and discussed.

[1] H. Shen, Z. Wang, Y. Wu, B. Yang, RSC Adv. **6**, 4505-4520 (2016).

[2] Y. Li, D. Fullager, S. Park, D. Childers, R. Fesperman, G. Boreman, T. Hofmann, Opt. Lett. **43**, 4711-4714 (2018).

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

[4] Z. Lao, N. Xia, S. Wang, T. Xu, L. Zhang, Micromachines **12**, 465 (2021).

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[1] **MEMS/NEMS Best Research Work Award**

[2] **MEMS/NEMS Best Research Work Award**

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

2D Materials Technical Group
Room 303 - Session 2D+MI-TuA

2D Materials: Heterostructures, Twistronics, and Proximity Effects

Moderators: Francesca Tavazza, National Institute of Standard and Technology, **Suyang Xu**, Harvard University

2:20pm **2D+MI-TuA-1 Strategies for Controlling Structure and Magnetic Texture in 2D Magnets***, **Frances Ross,*** MIT*; J. Klein,* MIT, USA **INVITED**

Electronic devices that incorporate two dimensional (2D) materials often require contacting or patterning the 2D layer for their fabrication. This is particularly important when we aim to build exciting new nanoscale magneto-electric devices based on 2D magnetic materials. CrSBr is such a 2D magnet that shows stability in air, giving this material a key advantage in practical device fabrication compared to other, less stable 2D magnets. Here we discuss strategies for controlling the structure and properties of CrSBr and related 2D magnets at the local, nanoscale level. We approach this via transmission electron microscopy, based on promising results for other 2D materials. We first discuss local control of structure. We find that electron beam irradiation in a scanning transmission electron microscope (STEM) induces a surprising structural change, where Cr atoms migrate into the van der Waals gap to create a new phase with layer direction (and, in theory, magnetization) perpendicular to the initial layers. The ability to modulate the magnetization direction deterministically is of great interest for quantum devices. Furthermore, since we find that defects in this material can be optically active and correlated with magnetic order and phases, the ability to use STEM to control individual defects will ultimately help to achieve precise control of the material's properties. We next discuss strategies for contacts. For other 2D materials, the 2D/3D contact resistance is known to improve when the contact layers have fewer grain boundaries. We therefore focus on epitaxial growth of metals and other 3D crystals onto the 2D surface. We show how *in situ* TEM imaging helps to clarify the growth mechanisms and interface structures formed during single crystal or heterostructured metal growth on graphene, hBN and transition metal dichalcogenides. We then explore how nucleation and epitaxy phenomena play out for pristine and patterned CrSBr and other 2D magnets. Overall, we conclude that atomic level structural and chemical modification are crucial for understanding properties and designing devices that use the exciting properties of the new 2D magnets. We suggest that rapidly advancing *in situ* TEM instrumentation promises exciting future opportunities where nanoscale growth and patterning create complex devices based on 2D materials.

3:00pm **2D+MI-TuA-3 Bidirectional Phonon Emission in van der Waals Heterojunctions During Ultrafast Charge Transfer***, **Aditya Sood,*** Stanford University

Photoinduced charge transfer in van der Waals heterostructures occurs on ultrafast timescales of order 100 fs, despite the weak interlayer coupling and momentum mismatch. Little is understood about the microscopic mechanism behind this fast process and the role of the lattice in mediating it. Here, using femtosecond electron diffraction, we directly visualize lattice dynamics in photoexcited heterostructures of WSe_2/WS_2 monolayers. Following selective excitation of WSe_2, we measure unexpectedly concurrent heating of both WSe_2 and WS_2 on a 1 picosecond timescale, corresponding to an "apparent" interlayer thermal conductance that is >100x larger than that due to phonons alone. Using first-principles calculations, we identify a fast channel, involving an electronic state hybridized across the heterostructure, enabling phonon-assisted interlayer transfer of photoexcited electrons. Phonons are emitted in both layers on femtosecond timescales via this channel, consistent with the simultaneous lattice heating observed experimentally. Taken together, our work indicates strong electron-phonon coupling via layer-hybridized electronic states – a novel route to control energy transport across atomic junctions.

4:20pm **2D+MI-TuA-7 Understanding Structural, Chemical, and Number of Layer-Dependent Properties in 2D Lateral and Vertical Structures for Subsequent Optical Measurements***, U. Kaiser, **Michael Mohn,*** University of Ulm, Germany **INVITED**

Properties of 2D materials can manifest at very different length scales. Charge density waves, magnetic ordering, inter- and intralayer excitons are studied also to understand their atomistic origin. Moreover, starting from exciting properties of low-twist angle graphene, twisted transition metal dichalcogenides are now explored, whereby the future of moiré superlattices is also dependent on reliable twist angle control. In addition, interfaces of transition metal dichalcogenide heterostructures such as Janus monolayers or lateral heterostructures have potential applications in optoelectronics, however very critical for carrier and exciton transport is that they are atomically sharp.

Here we use the low-voltage- spherical and chromatic aberration-corrected transmission electron microscope to measure and introduce structural and chemical variations in free-standing 2D materials on the atomic scale. In-situ and ex-situ optical measurements are performed and together with quantum-mechanical calculations their atomic-structure-based properties are understood.

We first report on advances in TEM sample preparation both for oxygen-sensitive TMDs as well as describe our sample platform to relate atomic defects in 2D materials produced by TEM with subsequent measurements in stacked devices. Then we describe studies on electron-beam-induced defects and observe the migration paths and associated property changes in a variety of single and few-layered free-standing structures of transition metal di-chalcogenides (TMDs) and transition metal phosphorus tri-chalcogenides (TMPTs). We also investigate the twist-angle-dependent moiré pattern formation in bilayers of TMDs by theoretical prediction-followed TEM experiments. From the comparison of monolayer, bi-layer and 2° twisted bilayer experimental images, we determine twist-angle-induced inhomogeneous stacking-related localized strain in the layers as well as the twist-angle-induced changes of the interlayer excitons located in the low-loss range of the EELS spectrum. We further report on the number of layer-dependent electronic properties of Pt-dichalcogenide family. We also show proof-of-principle experiments in which we transfer electron-exposed TMD flakes from a TEM grid to arbitrary substrates and measure the produced defects in photoluminescence and transport measurements. Moreover, the investigated lateral heterostructures show near-atomically sharp junctions with a typical extent of 3 nm for the covalently bonded $MoSe_2$-WSe_2 interface, determined by high-resolution transmission electron microscopy. This explains the considerably narrowed optical transition linewidth in the photoluminescence, reflectance contrast and Raman spectroscopy.

5:00pm **2D+MI-TuA-9 Determination of Band Offsets in Semiconductor Heterostructures (2D/3D) by Using XPS***, **Mohamed Nejib Hedhili**, ⍰. NG, B. Ooi,* King Abdullah University of Science and Technology, Saudi Arabia

Electrical and optical properties of heterojunction semiconductors are heavily influenced by the relative alignment of their energy band edges at the interface [1]. That is why the knowledge of this alignment is crucial for the design of heterostructure devices. In this regard, high-resolution X-ray photoemission spectroscopy (HR-XPS) has been shown to measure the valence band offset of heterojunction semiconductors quite accurately [2]. In this report, we present a study devoted to the characterization of 2D/ 3D heterojunction semiconductor materials using a myriad of techniques including HR-XPS, scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), micro-Raman, absorbance, and microphotoluminescence spectroscopy.

The samples for this study were prepared by depositing an epitaxial GaN ($In_{0.15}Al_{0.85}N$) thin layer with molecular beam epitaxy (MBE) on chemically vapor deposition (CVD) grown single-layer (SL) MoS_2/c-sapphire (WSe_2/c-sapphire) substrates. The formation of SL of MoS_2 (WSe_2)was crucial to device properties and hence was confirmed by using both STEM and AFM techniques. HR-XPS analysis of samples was performed in two-steps to measure the valence band discontinuity for GaN ($In_{0.15}Al_{0.85}N$) / SL of MoS_2 (WSe_2) heterojunction interface. In first step, the core level binding energies with respect to the valence band maximum in both GaN ($In_{0.15}Al_{0.85}N$) and MoS_2 (WSe_2) bulk films were measured. Second, the subsequent measurements on the separation between Ga (In) and Mo (W) core levels for GaN ($In_{0.15}Al_{0.85}N$) thin layer grown SL-MoS_2 (SL-WSe_2)was measured. The valence band and conduction band offset values are determined.

The band alignment parameters determined here provide a route toward the integration of group III nitride semiconducting materials with transition metal dichalcogenides (TMDs) for designing and modeling their heterojunction-based electronic and optoelectronic devices.

References:

[1] U. Gnutzmann and K. Clausecker, Appl. Phys. 3, 9 (1974).

[2] J. C. Bernède, L. Cattin, P. Predeep, XPS Study of the Band Alignment at the Interface

ITO/CuI, Technology Letters 1 (1), 2 (2014).

5:20pm **2D+MI-TuA-10 Investigation of a Novel Layer-by-Layer Growth Methodology for Surface Metal-Organic Frameworks*, Nicholas Stucchi,*** Clarkson University

The fabrication of highly ordered and crystalline surface-confined metal-organic frameworks (SURMOFs) has garnered interest in applications such as catalysis, gas storage, and gas separation. At present, the state of the art of SURMOF fabrication is a layer-by-layer (LBL) growth, wherein a functionalized substrate undergoes sequential immersions in solutions of the desired metal or ligand. This LBL strategy is commonly performed using gold substrates modified with carboxylate-terminated self-assembled monolayers (SAMs) which act as an initial nucleation site for the metal cluster. Careful control over deposition conditions and reaction times results in the formation of crystalline SURMOFs with tunable thicknesses. However, this technique is limited to substrates that can undergo the necessary SAM functionalization as well as being highly sensitive to the deposition conditions. I will discuss the development of a new LBL methodology that utilizes a pre-formed covalent-organic framework (COF) on the surface of highly oriented pyrolytic graphite (HOPG) as the template for SURMOF growth. The COF template should have the same geometry and a lattice parameter close to that of the desired SURMOF to minimize the strain of the first few layers. As such, COF-366-Zn was chosen as the template for UiO-67, which has a 3% lattice mismatch between the COF template and MOF. The COF was reacted with isonicotinic acid (INA) in which the pyridine axially coordinates to the zinc centers of the COF and the exposed carboxylate moieties of the INA serve as nucleation sites for the zirconium acetate clusters of UiO-67. The SURMOF was formed following several sequential reactions in the cluster and benezene-1,4-dicarboxylic acid (BDA) ligand solutions. The COF and initial INA binding will be characterized by scanning tunneling microscopy (STM) and Fourier-Transform Infrared (FTIR) spectroscopy. Atomic force microscopy (AFM) will be used to characterize the LBL growth of UiO-67. The crystallinity of the SURMOF will be determined using diffraction techniques.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy*, T. Mitch Wallis,*** *S. Berweger, P. Kabos,* National Institute of Standards and Technology **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy*, Sidney Cohen,*** *S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein,* Weizmann Institute of Science, Israel*; I. Rosenhek-Goldian,* weizmann Institute of Science, Israel*; R. Weatherup,* Oxford University, UK*; B. Eren,* Weizmann Institute of Science, Israel

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO_2 reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod*, Jiyoung Son,*** Pacific Northwest National Lab*; J. Gao,* PNNL*; G. Sevigny, S. Tripathi, B. Matthews,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (^{3}H) and lithium isotope (^{6}Li, ^{7}Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography*, Si Chen,*** Argonne National Lab*; Y. Luo,* Argonne National Laboratory*; T. Paunesku,* Northwestern University*; O. Antipova, Y. Liu, N. Zaluzec, Z. Di,* Argonne National Laboratory*; G. Woloschak,* Northwestern University **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobes are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 in Situ Molecular Imaging of Green Solvents for CO_2 Capture***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory, USA

Switchable ionic liquids are emerging green solvents in for carbon dioxide (CO_2) capture, cleaner separation, and efficient biomass production.However, the liquid structure and composition of SWILs are not fully understood.Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited.We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work.This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI).Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS.Two model systems are illustrated in this talk.The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings.The second has koechanol with various CO_2 loadings.Koechanol acts as both acid and base in the latter.Our results show two coexisting liquid phases in these green solvents.This phenomenon was only hypothesized in previous theory prediction.We provide the first physical evidence of the complex liquid – liquid (l – l) interface using three-dimensional chemical mapping with submicrometer resolution.In addition, more complex stoichiometry is discovered due to CO_2 uptake.More importantly, we have provided the first chemical spatial visualization elucidating the evolving l – l interface.The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis, CO_2 capture, and other versatile applications.

5:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy***, A. Siebert, K. Goodman, **Monika Blum**,* LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2] However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. $CaCl_2$,at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

[1] Havala O. T. Pye et al., Atmos. Chem. Phys., 20, 4809–4888, 2020.
[2] Barbara J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 2009, 11, 7760–7779.

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:

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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.

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

Role of Defects in Materials

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

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

Two-dimensional (2D) materials offer the freedom to create novel condensed matter systems, with unique properties, by mechanically assembling different (or same) 2D materials layer-by-layer to form atomically sharp vertical or lateral heterostructures. The van der Waals (vdW) heterostructures with small lattice mismatch and a relatively small twist angle between the constituent layers, have shown to exhibit coexisting complex phases of matter including Mott insulating state, superconductivity, bound quasiparticles, and topological states. The advent of the state-of-the-art angle-resolved photoemission spectroscopy with high spatial resolution (micro- and nano-ARPES) and the ability to perform these measurements on fully functional devices, has made it possible to directly probe many exotic physical phenomena in 2D based material systems. In this talk, I will discuss the utilization of the nanoARPES to investigate the highly tunable many-body effects in 2D based heterostructures and their devices.

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

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

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

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

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

References:

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

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

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

Surface Science Division
Room 319 - Session SS+2D+AS-TuA
Structure, Adsorption and Reaction at 2D Material Surfaces

Moderators: Florencia C. Calaza, Instituto de Desarrollo Tecnológico para la Industria Química, Argentina, **Arthur Utz**, Tufts University

2:20pm **SS+2D+AS-TuA-1 Chemically Identifying Single Adatoms with Single-Bond Sensitivity During Oxidation Reactions of Borophene**, *L. Li, N. Jiang, **Sayantan Mahapatra**,* University of Illinois - Chicago

The chemical interrogation of individual atomic adsorbates on a surface significantly contributes to understanding the atomic-scale processes behind on-surface reactions. However, it remains highly challenging for current imaging or spectroscopic methods to achieve such a high chemical spatial resolution. Here we show that single oxygen adatoms on a boron monolayer (i.e., borophene) can be identified and mapped via ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS) with ~4.8 Å spatial resolution and single bond (B–O) sensitivity. With this capability, we realize the atomically defined, chemically homogeneous, and thermally reversible oxidation of borophene via atomic oxygen in UHV. Furthermore, we reveal the propensity of borophene towards molecular oxygen activation at room temperature and phase-dependent chemical properties. In addition to offering atomic-level insights into the oxidation of borophene, this work demonstrates UHV-TERS as a powerful tool to probe the local chemistry of surface adsorbates in the atomic regime with widespread utilities in heterogeneous catalysis, on-surface molecular engineering, and low-dimensional materials.

2:40pm **SS+2D+AS-TuA-2 Tailoring the Interfacial Properties of 2D Transition Metal Silicates on Metal Supports**, *N. Doudin, K. Saritas,* Yale University; *J. Boscoboinik, G. Li,* Brookhaven National Laboratory; *S. Ismail-Beigi, **Eric Altman**,* Yale University

Two-dimensional (2D) transition metal (TM) silicates have the potential to add magnetic, piezoelectric, and multiferroic functionalities to the toolkit of 2D layers used to develop new technologies. To date, these 2D TM silicates have been chemically bound to the growth substrate through oxygen atoms; the ability to weaken the interaction with the substrate to isolate the materials as single vdW layers is crucial for realizing their potential. Hydration or hydrogenation of the 2D TM silicate presents an ideal modification methodology to pacify the bonds to the substrate and create tailored interface properties and functionalities. Towards this end, here we report the interaction of Au- and Pd-supported 2D TM silicates with H_2O, H_2, and O_2. We employed a range of characterization tools to assess the materials before and after treatment with the probe molecules. Ambient pressure x-ray photoelectron spectroscopy (AP-XPS), ambient pressure infrared reflection absorption spectroscopy (AP-IRRAS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM) in conjunction with first principles theory were utilized to assess surface morphology, interface characteristics, surface chemistry, and chemistry in in the confined spaces between the 2D TM silicate and metal support. The interaction of probe molecules with TM silicates on Pd(111) and Au(111) was studied over wide pressure (10^{-6}–1 mbar) and temperature (300–600 K) ranges. The data show that the dissociative adsorption of H_2 takes place to form OH bonds on the oxide surfaces under UHV conditions. When the pressure is increased to several mbar, the metal silicate surfaces are saturated with H atoms at 300 K. Exposure to H_2 at higher surface temperatures (≥ 600 K) reduces the TM silicate. Also, water dissociates readily on the metal silicate surfaces at 300 K. With an increase in H_2O pressure, a greater degree of surface hydroxylation was observed for all samples. At 1 mbar H_2O, molecular and dissociated water coexist (hydrogen bond OH/H_2O). In temperature-dependent studies, desorption of weakly bound water and surface dehydroxylation were observed with increasing temperature. Via AP-XPS combined with IRAS we study in detail the interaction of oxygen with the oxide surfaces, which shows that H_2-induced reduction can be reversed and the original structure restored. Our studies provide an effective avenue to achieve hydrated metal silicate layers and shed light on how to tune the chemical reactions of these overlayers by choosing suitable substrates.

3:00pm **SS+2D+AS-TuA-3 Metal Oxide and Metal Dichalcogenide 2D Nanocrystals: Structure, Adsorption and Catalytic Properties**, ***Jeppe V. Lauritsen**,* Aarhus University, Denmark **INVITED**

Nanocrystals of two-dimensional materials may exhibit fascinating optical, electronic or chemical properties. In heterogeneous catalysis, the edge sites of some planar metal oxide and metal sulfide nanocrystals have been demonstrated be far more active than the majority sites exposed on basal planes. These observations have motivated us to obtain a better understanding of the edge site structure of 2D nanocrystals and try to establish the fundamental connection to their behavior in heterogeneous catalysis and electrocatalysis. I will discuss two examples showing how we investigated the structure and adsorption properties at the atomic scale by using scanning tunneling microscopy (STM) and photoemission spectroscopy techniques (XPS) on well-defined planar 2D nanocrystals supported on model substrates:

i. We used to atom-resolved STM images investigate edge reactivity of monolayer $CoOOH_x$ particles, widely considered as the active phase of cobalt-based catalysts in alkaline electrochemical water splitting. Water exposure experiments combined with atom-resolved STM imaging directly show an increased capacity to dissociate water on the edge sites, which is further substantiated by theoretical modelling [1]. Moreover, addition of Fe has strong promotional effect on the oxygen evolution. We have compared how the $CoOOH_x$ nanocrystals and chemical composition develops after the sample has been used as the working model electrode directly in a homebuilt *in situ* electrochemical cell attached to the STM chamber [2]. Our activity measurements confirm the expected increased oxygen evolution (OER) activity for Co-oxides mixed with Fe, which however depends in a highly non-linear way on the actual Fe content. Based on this information we found a model where the main effect of Fe doping in Co oxide is that of a structural edge stabilizer [3].

ii. MoS_2 nanocrystals are active catalysts in heteroatom extrusion from hydrocarbons (O, N, S) in oil and bio-oil processing (hydrotreating). Atom-resolved STM studies of MoS_2 nanocrystals as a supported model catalysts was used in combination with DFT analysis of molecule adsorption on MoS_2 edge to evidence an interesting new mechanism where adsorption of heteroatom-bearing hydrocarbons on a vacancy pushes neighboring S atoms aside. Thereby the adsorption event itself creates better catalytic active sites capable of adsorbing large hydrocarbons, explained the unusually wide selectivity of MoS_2 towards these reactions [4].

[1] J. Fester, et al., Nat. Comm **8**, 14169 (2017).

[2] Z. Sun, et al., Rev. Sci. Inst. **92**, 094101 (2021).

[3] Z. Sun, et al., ACS Nano **15**, 18226 (2021).

[4] N. Salazar, et al., Nat. Comm **11**, 4369 (2020).

4:20pm **SS+2D+AS-TuA-7 Intercalated $Cu_{2-x}O$ Thin Film Confined Underneath Hexagonal Boron Nitride***, J. Trey Diulus,* *Z. Novotny, N. Dongfang, N. Comini, J. Beckord, Y. Al-Hamdani,* University of Zurich, Switzerland*; M. Muntwiler,* Paul Scherrer Institute, Switzerland*; M. Hengsberger, M. Iannuzzi, J. Osterwalder,* University of Zurich, Switzerland

Confined catalysis has been achieved in zero and one dimensions using zeolites, metal-organic frameworks, and carbon nanotubes for optimized catalytic performance. Confinement can also be achieved in two dimensions by intercalation of reactants between solid layers. 2D materials grown on metal surfaces have become widely used model systems to study 2D-confined catalysis. Yet, numerous transition metals have been found to be more active in their oxidized form. Unfortunately, the growth of h-BN *via* chemical vapor deposition (CVD) has proven to be more difficult on metal oxides than on metals. Instead, a metal substrate underneath an h-BN monolayer can be oxidized *via* O_2 intercalation. Due to weak interactions between h-BN and Cu(111), the Cu(111) substrate is a prime candidate for intercalated oxidation, forming a thin oxide film (~3 Å) while the h-BN remains intact. Growth of h–BN on Cu(111) was achieved through CVD by borazine exposure in ultra-high vacuum at the In Situ Spectroscopy beamline at the Swiss Light Source (SLS). The surface structure, chemical composition, and uniformity of the as-grown h-BN/Cu(111) heterostructure were determined with low-energy electron diffraction, Auger electron spectroscopy, and X–ray photoelectron spectroscopy (XPS). Oxidation of the Cu(111) under h-BN *via* O_2 intercalation was executed by exposure to near-ambient partial pressures of O_2 (0.001 to 1 mbar) at temperatures ranging from 25 to 200 °C. Ambient pressure XPS and X-ray absorption spectroscopy were utilized at each temperature and pressure to determine the oxidation state of Cu and develop a recipe for preparing an ordered h–BN/$Cu_{2-x}O$/Cu(111) heterostructure. Further characterization of an ordered h–BN/$Cu_{2-x}O$/Cu(111) was obtained at the PEARL beamline at the SLS. Scanning tunneling microscopy (STM) provided atomic-resolution imaging of the sample held at 78 K, displaying a Cu_2O-like structure. STM further shows the oxidation of the Cu(111) substrate occurs *via* O intercalation at the h-BN grain boundaries. Density functional theory calculations, X-ray photoelectron diffraction experiments, and multiple-scattering simulations using the Electron Diffraction in Atomic Clusters code, provided further structural information, suggesting O atoms first adsorb to HCP-Cu sites on Cu(111), followed by the formation of a Cu_2O-like trilayer in between the substrate and h–BN. Ultimately, we fully characterize the structure and oxidation mechanism of a well-defined nano–reactor system that is ideally suited to study reactions in confined space. Furthermore, we propose this preparation method can be applied to more systems comprising of a 2D monolayer on a metal substrate.

4:40pm **SS+2D+AS-TuA-8 Imaging Surface Defects on MoS_2***, Blake Birmingham,* Baylor University

MoS_2 is an exciting hydrogen evolution reaction (HER) catalyst that exhibits promising activity in acidic media. However, the role of density and reactivity of defect sites to the HER performance of MoS_2 is currently unclear. Up to now, correlation of localized HER activity to atomic scale defects have been inferred via ex-situ measurements, where the macroscopic electrode activity is determined via bulk electrochemical techniques and correlated with the number of active sites that are measured separately via nanoscale surface imaging such as Scanning Tunneling Microscopy (STM) or Transmission Electron Microscopy.

In the presented experiment, the structural and chemical properties of bulk mineral MoS_2 catalyst during HER were monitored in-situ by electrochemical scanning tunneling microscopy (EC-STM). The nanoscale structure of the MoS_2 is correlated with its electrochemical activity in 0.5 M H_2SO_4(aq) electrolyte. Defects on the MoS_2 basal plane were atomically resolved before and after several rounds of cyclic voltammetry (CV) measuring the HER current vs applied potential against a carbon reference. Atomically resolved imaging of the same nanoscale area before and after HER does not show an increase in atomic defect site density after prolonged HER probed by many rounds of CVs. This indicates that new sulfur vacancies are either not produced during HER on MoS_2 basal plane or are produced and immediately occupied by hydrogen atoms. The surface was imaged near the HER onset potential, the evolution reaction was directly imaged as strong local tunneling instability. The tunneling destabilization effect is strongest near the nanoscale defect sites potentially due to local hydrogen gas bubbling.

5:00pm **SS+2D+AS-TuA-9 Modifying 2D Transition Metal Dichalcogenides (TMDs) by Incorporating Excess Transition Metals***, Matthias Batzill,* University of South Florida **INVITED**

Crystal modifications in 2D materials can introduce new functionalities in these materials. Here we discuss compositional and structural crystal modifications in some transition metal dichalcogenides (TMDs). Specifically, we show that excess metals can be incorporated into the crystal structures of Mo-, and W- dichalcogenides and in PtTe2. In the former the excess metals result in the formation of metal rich mirror twin grain boundary networks, while in the latter a phase transition from PtTe2 to Pt-monotelluride can be induced. In this presentation we discuss the transformation mechanisms and the properties that arise from these compositional modifications.

5:40pm **SS+2D+AS-TuA-11 SSD Flash Poster Session: Oral Presentations***,*

5:40: SS-TuP-7 - Dr. Pierluigi Bilotto

5:43: SS-TuP-12 - Dr. Benjamen Reed

5:46: SS-TuP-13 - Mr. Xiao Zhao

5:49: SS-TuP-6 - Dr. J. Trey Diulus

5:52: SS-TuP-9 - Mr. Dustin Johnson

5:55: SS-TuP-18 - Aman Patel

Thin Films Division

Room 316 - Session TF2+2D-TuA

Low Dimension Material Application

Moderator: Mark Losego, Georgia Institute of Technology

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

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

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

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

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

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

Manipulation of bulk material properties by controlling layer-by-layer chemistry and structure of nanomaterials has remained an overarching goal of nanoscience and nanoengineering. In the case of 2D materials, heterostructures consisting of different compositions, stacking and orientation have been demonstrated leading to possibilities of artificially

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

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

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

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

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

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$_2$Te$_4$***, **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$_2$Te$_4$ 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~10^{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$_2$Ge$_2$Te$_6$) 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$_x$Si$_2$O$_5$(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).

2D Materials Technical Group

Room 303 - Session 2D+AS+NS+SS-ThM

2D Materials: Scanning Probe Microscopy and Spectroscopy

Moderators: Matthias Batzill, University of South Florida, **Yi-Ting Hsu**, University of Notre Dame

8:00am **2D+AS+NS+SS-ThM-1 Atomically Precise Graphene Nanoribbons for Quantum Electronics***, An-Ping Li,* Oak Ridge National Laboratory **INVITED**

An-Ping Li, Chuanxu Ma, Marek Kolmer, Wonhee Ko, Kunlun Hong, Peter Bonnesen, Alex Puretzky, Jingsong Huang, Liangbo Liang, Bobby Sumpter

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Graphene nanoribbons (GNRs) possess high mobility and current-carrying capability, sizeable bandgap, long mean free path, localized spin and topological edges states [1]. These properties make them attractive candidates for quantum electronic applications. Atomically precise GNRs can be synthesized bottom-up using controlled on-surface chemical reactions from rationally designed molecular precursors [2]. The on-surface reactions of molecular precursors performed under ultra-high vacuum conditions can further be combined with scanning tunneling microscopy (STM) for in situ characterization of atomic, electronic, and magnetic properties. In this talk, I will discuss our recent progress in realizing novel quantum states in GNR heterostructures at atomic precision. First, a bottom-up approach is developed to couple graphene nanodot (GND) covalently at the edges of GNR to create quantum-well-like states for well-defined narrow-band light emission [3], which highlights a route to programmable and deterministic creation of quantum light emitters. Second, atomically precise GNRs are obtained by the on-surface synthesis approach on a model metal oxide, showing entangled magnetic states decoupled from the substrate [4]. These works illustrate that by using bottom-up synthesis—complemented by advanced microscopy and spectroscopy, as well as theory/simulation to enable atomistic level control—a rational approach to graphitic quantum electronic materials can be established with atomic precise.

The research was conducted at the Center for Nanophase Materials Sciences (CNMS), a US Department of Energy User Facility. The electronic characterization was funded by ONR grants N00014-20-1-2302 and N00014-16-1-3153.

[1] H. Wang et al., Graphene nanoribbons for quantum electronics, *Nat. Rev. Phys.* 3, 791 (2021). https://doi.org/10.1038/s42254-021-00370-x

[2] C. Ma et al., On-surface cyclodehydrogenation Reaction Pathway Determined by Selective Molecular Deuterations, Chemical Science 12, 15637 (2021). https://doi.org/10.1039/D1SC04908A

[3]C. Ma et al., Engineering Edge States of Graphene Nanoribbons for Narrow-Band Photoluminescence, *ACS Nano* 14, 5090 (2020). https://doi.org/10.1021/acsnano.0c01737

[4] M. Kolmer et al., Rational synthesis of atomically precise graphene nanoribbons directly on metal oxide surfaces, *Science* 369, 571 (2021). https://www.science.org/doi/10.1126/science.abb8880

8:40am **2D+AS+NS+SS-ThM-3 Band Gaps of Single-Layer Transition-Metal-Dichalcogenides Determined by Scanning Tunneling Spectroscopy***, **Randall Feenstra**, G. Frazier, J. Lou,* Carnegie Mellon University*; Y. Pan, S. Foelsch,* Paul Drude Institute, Germany*; Y. Lin, B. Jariwala, K. Zhang, J. Robinson,* Penn State University

Using scanning tunneling spectroscopy at a temperature of 5 K, the electronic states of single-layer MoS_2 and WSe_2, grown on epitaxial graphene, have been investigated. Data is acquired utilizing a high-dynamic-range method in which the sample-tip separation is varied as a function of the sample-tip voltage (separation is decreased linearly as the magnitude of the voltage is reduced). Resulting spectra, when normalized to constant sample-tip separation, display conductance values that range over 5 – 6 orders of magnitude above the noise level [1]. The resulting edges of the conduction and valence bands, as well as onsets of higher/lower lying bands, are clearly defined. A theory for fitting the spectra is developed in which the varying wave-vector of the electronic states is explicitly included, yielding significant improvement in the quality of the fits compared to prior work [2]. Band onset energies can be determined with an accuracy of ~20 meV [1]. However, certain features in the data remain poorly explained by the model, in particular, an apparent broadening or smearing of the band edges which is 5x larger than that given by any instrumental effect (kT broadening together with modulation voltage of the measurement). Tentatively, this additional broadening is attributed to tip-induced band bending. Results of fitting which includes this effect will be described.

[1] R. M. Feenstra, G. R. Frazier, Yi Pan, St. Fölsch, Y.-C. Lin, B. Jariwala, K. Zhang, and J. A. Robinson, J. Vac. Sci. Technol. A **39**, 011001 (2021).P. Mårtensson and R. M. Feenstra, Phys. Rev. B **39**, 7744 (1989).

[2] H. M. Hill, A. F. Rigosi, K. T. Rim, G. W. Flynn, and T. F. Heinz, Nano Lett. **16**, 4831 (2016).

9:00am **2D+AS+NS+SS-ThM-4 Open-Source Controller for Scanning Probe Microscopy Applications***, M. Kangül, N. Asmari Saadabad, M. Penedo, **Georg Fantner**,* École Polytechnique Fédéral de Lausanne, Switzerland

Transferring the outcomes of academic research into patented industrial products converts the conceptual proof into accessible and sustainable technology. However, it is not always beneficial for researchers; as scientific studies often push the limits of instruments, requiring custom functionalities. In order to resolve these needs, several options are available, among which, hacking off-the-shelf products or rebuilding a simple copy of the existing technology are the most common ones. Either of these solutions slows down the research in a multidisciplinary field like Scanning Probing Microscopy (SPM). To not be limited by the disadvantages of the aforementioned solutions, we have developed an open-source SPM controller as a technology that eases innovation in not only our research but also in the whole SPM community.

In this regard, we have chosen a modular design strategy. A commercial FPGA (NI-7856R) with embedded real-time controller code sits at the core of the controller hardware. An FPGA adapter board for the flexibility of choosing different FPGAs, interconnect boards to perform digitally controlled (SPI) analog signal conditioning, such as filters and gain-offset stages, and a microscope adapter board to easily customize the input/output terminals of the controller for various SPM instruments are the other components of the modular hardware design. To run the controller, a custom software suite was developed in the graphical programming language LabVIEW (National Instruments). Similar to hardware, the software is also implemented in a highly modular fashion. The functions have been formulated into separate modules with minimum cross-dependency to reduce the complexity of coding for new developers.

The interest of our scientific and industrial collaborators in adapting and using our SPM controller in their instruments has motivated us to put an extra effort into building supporting documentation and creating an open-source platform. For the hardware, the documentation comprises design files, manufacturing guides, and assembly notes. For the software, documentation explaining the functionality of the real-time controller is provided, while the user interface side of the software is documented with user guides.

Here we report an open-source modular SPM controller provided with detailed documentation on both hardware and software levels. Modularity and documentation make it an easy-to-adapt instrument for various SPM applications. This platform has already been successfully adapted to control different SPMs such as contact mode AFM, AM-AFM, high-speed off-resonance tapping mode AFM, scanning ion conductance microscope, correlative AFM/SEM, and STM.

9:20am **2D+AS+NS+SS-ThM-5 Activation of Resistive Switching in TaOx on the Nanoscale***, **Olha Popova**,* ORNL

In present work we have shown two an alternative pathways to induce resistive switching of prototypical TaOx –(1) via direct biasing with a nanoscale AFM probe in oxygen free environment and (2) via He-ion patterning. Both approaches were carried out with fine control over the net amount of dissipated energy during activation. With direct AFM probe activation in oxygen free environment, we were able to switch conducting properties of the material in poorly controlled conditions. This is a similar pathway to electroforming, albeit combined with microscopy, which revealed directly the changes induced in the film during field-induced insulator-metal transition. Filamentary regions down to 20 nm in dimension could be routinely achieved by reducing the peak current during the activation cycle. Nevertheless, the process remains extremely stochastic. In contrast, by use of He ion irradiation pristine insulating state can be easily converted to conducting and resistively switching state without any breakdown, but the transition itself is a smooth function of ion-irradiation dose. These findings revealed numerous intermediate states of TaOx can be created by controlled ion-irradiation. Remarkably, this effect is directly compatible with device architectures, potentially allowing for a high-degree of on-demand tunning of neuromorphic circuitry and materials. By combining AFM and SEM-CL we were able to determine dependence of the ion dose/materials damage correlated with the chemical, structural and compositional tunability of thin TaOx films which offers significant opportunities to neuromorphic nanoelectronic materials in comparison with more mature technologies based on traditional bulk electronic materials.

9:40am **2D+AS+NS+SS-ThM-6 Probing Sub-Nanoscale Photophysical and Photochemical Processes via Localized Surface Plasmons: Vibrational Nano-Spectroscopy***, **Sayantan Mahapatra**, N. Jiang,* University of Illinois - Chicago

Conventional spectroscopic techniques are limited by the optical diffraction limit to about half wavelength and therefore offer about 200 nm x 200 nm microscopic zone for working in the visible light range. Tip-enhanced Raman spectroscopy (TERS) emerges as an advanced analytical technique, where the plasmonically active probe is not only used to detect the tunneling current but also to interrogate the local chemical environment of the surface adsorbed molecules with angstrom scale precision. In this work, we report a topological and chemical analysis of two regioisomers (positional isomers), trans- and cis-tetrakispentafluorophenylporphodilactone (trans- and cis-H_2F_{20}TPPDL) by scanning tunneling microscopy (STM), ultrahigh vacuum (UHV) TERS on Ag(100) with the spatial resolution down to 8 Å, which has a wide range of applications in various field of surface science & nanotechnology such as regioselective catalysis reaction, chemical reactions, molecular electronics, etc. We have shown that it is possible to distinguish these two structurally very similar forms with high accuracy & precision. The two-component molecular junction has been identified using high resolution two-dimensional (2D) Raman mapping. Furthermore, the nanoscale molecule-substrate interactions have been addressed at the single-molecule level by employing different single-crystals i.e., Ag(100), Cu(100), and Au(100). Strong surface interactions at Cu(100) surface converted the flexible porphodilactone structure inverted, which was further verified by STM. In another case, the chemical transformation of adsorbed ferrocene dicarboxylic acid molecule was also analyzed via TERS on Cu(100) due to significantly strong interaction. Apart from the Raman signal enhancement, the highly energetic localized surface plasmons generated at the tip apex were utilized for site-selective C—Si bond activation inside a single 5,10,15,20-(tetra-trimethylsilylethynyl)porphyrin molecule. The nano-confined plasmonic field dissociated only one chemical bond, in presence of multiple chemically equivalent bonds inside the single molecule. To this end, multiple sites were also activated one by one and different types of products were visualized which could prove extremely useful in plasmon-induced site-selective heterogeneous catalysis application.

11:00am **2D+AS+NS+SS-ThM-10 Visualize Emergent Electron Orders in Two-Dimensional Quantum Materials***, **Xiaomeng Liu**,* Princeton University **INVITED**

Recent developments have enabled scientists to isolate various 2D materials and assemble them into van der Waals heterostructures with elaborate stacking and alignments. These van der Waals materials, constructed layer-by-layer, host numerous novel quantum phases. However, most studies so far are done by electrical transport measurements, lacking spatial and energy resolution. Scanning tunneling microscopes (STM) can provide unique insights to these emergent quantum phases by visualizing the electron wave function in real space. Using our recent study of the graphene quantum Hall system as an example, I will demonstrate using STM techniques to identify broken symmetries, visualize electron wavefunctions, and imaging quasiparticles.

11:40am **2D+AS+NS+SS-ThM-12 Reconstruct the Intrinsic Force Landscape of Interfacial Interaction with Excitation-Enhanced Force Spectroscopy***, **Alan Liu**, T. Sulchek,* Georgia Institute of Technology

The advancement of sensitive force transducers has enabled scientists to measure the subtle forces of interactions between molecules and interfaces at nanometer scales. Force spectroscopy techniques, such as dynamic force spectroscopy (DFS), extract a single representative force from each measurement, and require thousands of measurements with model assumptions to extract useful physical parameters of the interaction. This process is not only time consuming, but also the preciseness of the results relies largely on model assumptions, which make the results highly variable and dependent on experimental conditions. Furthermore, because DFS models presume the interaction to be a reversible reaction under certain energy/force landscape, parameters extracted by DFS method can only represent the rough shape of interaction landscape but not able to probe the detail landscape of underlying intrinsic interactions. Using our recently developed force spectroscopy framework[1], we can obtain the definitive intrinsic force landscape using a high sampling rate (above 1 MHz) atomic force microscopy (AFM) measurement. While most studies deemed the "snap" of AFM force measurement as an instantaneous action, we successfully sampled the fluctuation and real-time movement of the AFM probe at snap under a high sampling rate. At the snap location of each AFM force-distance measurement, transition points can be identified that define the bound state (or probe-in-contact state) and unbound state (or free oscillation state). Sampling at these transition points are key to probe the normally inaccessible portion of force landscape where the intrinsic force landscape has higher force gradient than the stiffness of the force probe. Next, we demonstrated how to modulate the snap locations of the force-distance curves by tuning the bandwidth of the excitation applied to the AFM probe. Lastly, we integrated the definitive forces sampled at various locations to reconstruct the intrinsic force landscape of the interaction without any model assumption or curve fitting process.

[1] Alan Y. Liu and Todd A. Sulchek, Reconstructing the Intrinsic Potential Energy Landscape of Interfacial Interactions with Thermally Modulated Force Spectroscopy, Phys. Rev. Res. 3, (2021).

12:00pm **2D+AS+NS+SS-ThM-13 AVS Graduate Research Awardee Talk: True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy***, **Saima Sumaiya**[1], M. Baykara,* University of California, Merced

Atomic-scale characteristics of surfaces dictate not only the governing principles of numerous scientific phenomena ranging from catalysis to friction, but also the design and performance of billions of state-of-the art nanoscale devices ubiquitous in modern life. Despite such an enormous significance, our ability to visualize surfaces on the atomic scale is severely limited by the strict conditions under which the related methods are operated. In particular, the two prominent methods utilized to achieve atomic-resolution imaging – scanning tunneling microscopy (STM) and noncontact atomic force microscopy (NC-AFM) – are typically performed under ultrahigh vacuum (UHV) and often at low temperatures. Perhaps more importantly, results obtained under such well-controlled, clean environments bear little relevance for the great majority of processes and applications that often occur under ambient conditions. Therefore, a method which is able to reliably and robustly image surfaces with atomic-level spatial resolution under ambient conditions can be regarded as a "holy grail" of surface science. Here, we first show that the method of conductive atomic force microscopy (C-AFM) can be utilized to achieve true atomic-resolution imaging under ambient conditions by imaging single atomic vacancies on molybdenum disulfide (MoS_2), without any control over the operational environment or elaborate sample preparation. With our method, we are also able to image several other types of defects on MoS_2, demonstrating that C-AFM can be utilized to investigate surface defects in a reliable, straightforward fashion under ambient conditions, in contrast to the often extensive operational requirements of STM and NC-AFM. We further employ the method of C-AFM to record atomic-resolution images on different classes of materials such as gold (metal), WSe_2 (semiconductor), $PtSe_2$ (semimetal), and α-Mo_2C (metallic transition metal carbide), proving its versatility in terms of the material classes it can be applied to. Our approach overcomes many of the classical limitations associated with STM and NC-AFM, and the findings herald the emergence of C-AFM as a powerful tool for atomic-resolution imaging under ambient conditions.

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[1] **AVS Graduate Research Awardee**

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

Quantum Materials (2D)

Moderator: Zheng Gai, Oak Ridge National Laboratory

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

For bilayers of 2D magnets and TIs, we have focused on FGT and CGT films. A key step has been the optimization of FGT by studying its growth on Ge(111) substrates. Here, we learned that kinetics play an important role in the epitaxial growth. By varying the deposition rate, we control the formation or suppression of an initial tellurium-deficient non-van der Waals phase (Fe3Ge2) prior to realizing epitaxial growth of the vdW FGT phase. Using cross-sectional scanning transmission electron microscopy and scanning tunneling microscopy, we optimize the FGT films to have atomically smooth surfaces and abrupt interfaces with the Ge(111) substrate. The magnetic properties of our high quality material are confirmed through magneto-optic, magnetotransport, and spin-polarized

STM studies. Importantly, this demonstrates how the interplay of energetics and kinetics can help tune the re-evaporation rate of chalcogen atoms and interdiffusion from the underlayer. Utilizing these insights, we have developed the growth of FGT and CGT on Bi_2Te_3 for the integration of 2D magnets with TIs.

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

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

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

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

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

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.

2D Materials Technical Group
Room Ballroom A - Session 2D-ThP

2D Materials: Poster Session

2D-ThP-1 MoS_2 on Sapphire for Aligned Growth Using Liquid Precursor*, Anindita Chakravarty,* University at Buffalo

Aligned growth of MoS2 has been a hot topic for research due to the high quality of two dimensional (2D) films obtained by Chemical Vapor Deposition (CVD). This research paper demonstrates aligned growth of MoS2 on sapphire using liquid precursors. Importance of parameters like oxygen plasma etching, amount of precursor used and low temperature annealing has been experimented with in this research. It has been determined that the sapphire used should be c-type , and needs to have a relatively smooth surface for growth of aligned MoS2 on it. The bond between the substrate and the flakes plays a significant role on the properties of the material grown. To test the quality of the flakes, ionic liquid has been used as a side gate. Electronic properties were measured after directly performing electron beam lithography and metal deposition onto the sapphire substrate containing the flakes.

2D-ThP-2 Growing and Analyzing Ultra-Thin Polyaniline Films*, Anthony Annerino,* *P. Gouma,* The Ohio State University

Presented here are investigations on the growth and analysis of ultra-thin polyaniline films. Polyaniline is a highly studied intrinsically conducting polymer that has shown promise in a wide variety of applications but still proves relatively difficult to process on account of its negligible solubility in all but the most toxic organic solvents. This work aims at highlighting an uncommon avenue of polyaniline processing with great promise for many applications. Polyaniline films described here are grown via oxidative polymerization on the surface of an aqueous solution, and growth parameters including growth time, available growth area, and starting material concentrations are evaluated for their effects on various properties of the resultant films. Properties investigated include electrical properties, thermal properties, and film thickness.

2D-ThP-3 Modification of Bilayer VSe_2 by Intercalating Transition Metals*, Vimukthi Pathirage,* *K. Lasek, J. Li, I. Ponomareva, M. Batzill ,* University of South Florida

Transition metal dichalcogenides (TMDs) are prototypical van der Waals materials that can be grown as ultrathin films and/or van der Waals heterostructures. While TMDs exhibit a variety of properties, they are usually non-magnetic.[1] Metal intercalation in between TMDs may be a process to introduce magnetism and thus design magnetic van der Waals materials.

Here we explore the possibility of controlling the intercalation of transition metals into ultrathin VSe_2 films in an attempt to modify their magnetic properties and to design magnetic van der Waals heterostructures. VSe_2 mono- to few-layer films are grown by van der Waals epitaxy on HOPG or MoS_2. These films are subsequently modified by post-growth deposition of transition metals, such as Cr. Our scanning tunneling microscopy (STM) studies indicate that the deposited Cr reacts with monolayer VSe_2 and forms complex ad-atom structures. In contrast, for bi- and multilayer VSe_2 the Cr-deposition maintains an atomic corrugation of the VSe_2 layer, however, the periodicity changes to a 2x1 structure with respect to VSe_2 lattice. This additional superstructure is interpreted as caused by the intercalation of Cr in between two VSe_2 layers and the superstructure at the surface is related to the periodicity of the intercalated Cr layer. The experimental results are supported by DFT calculations that suggest that Cr-intercalation is favored over Cr adatoms in bilayer structures.

Our study presents successful incorporation of dissimilar metal atoms into the van der Waals gap of TMDs by post growth intercalation. This opens new opportunities for engineering of layered materials. This intercalation process may be combined with van der Waals epitaxy and thus creates a new direction for modifications of van der Waals heterostructures.

[1] K. Lasek, J. Li, S. Kolekar, P. M. Coelho, L. a. Guo, M. Zhang, Z. Wang and M. Batzill, *Surface Science Reports***76** (2) (2021).

2D-ThP-7 Quantum Confinement in Topological Semimetal Nano-Platelets*, Margaret Brown,* *R. Laing, T. Muratore,* University of Dayton*; K. Burzynski, J. Brown,* Wright Patterson Air Force Base*; J. Corbett,* Miami University*; K. Eyink,* Wright Patterson Air Force Base*; S. Elhamri,* University of Dayton*; A. Reed,* Wright Patterson Air Force Base

Topological insulators (TI) have shown widespread excitement in the development of spintronic devices and quantum computers. Despite their revolutionary properties, the small band gaps of many TIs severely limit their potential applications. Investigations which involve increasing the bandgap are vital in supporting the implementation of this material class. One route to do so uses nano-sized grains of the material to employ quantum confinement. Quantum confinement in TIs increases in bandgap and quantizes the Dirac cone as a function of nano-particle size. Inspired by such, this presentation consists of two parts: nano-platelet growth and resulting bandgap characterization. A study of the topological semimetal, Bi_4Se_3, grown via direct current magnetron sputtering revealed the nucleation process across a variety of growth pressures using atomic force microscopy. All films began as island-type nucleation and transitioned to layered growths at varying transition thicknesses which depend on pressure. During the initial nucleation period, prior to the layering transition, the morphology is composed of many nano-platelets dispersed with nearest neighbor ordering. The sizes of the nano-platelets are controlled by deposition time and growth pressure. Ultra-violet to visible light spectroscopy was used to investigate the dependence of the optical bandgap on the dimensionality of these nano-platelets. Variation of the optical bandgap was observed over a range from 1.55 eV to 2.21 eV with decreasing average platelet volume of 200,000 nm^3 to 30,000 nm^3. Using these data, fine tuning of the nano-platelet bandgaps to meet a range of needs for optical applications becomes possible.

2D-ThP-8 Characterizing the Low-Symmetry Crystallographic Axis in Atomically Thin WTe2 Layers Using Raman Spectroscopy for Spin-Orbit Torque Studies*, Anh Ramirez,* *I. Kao, R. Muzzio, J. Katoch, S. Singh,* Carnegie Mellon University, USA

Low-symmetry crystal structure and topological electronic structure in WTe_2, which is a Weyl semimetal candidate, can be used to generate spin current with controllable spin polarization. Spin-orbit torques (SOT) exerted on a nearby magnetic thin film by the spin current in WTe_2, is appealing for an energy efficient field-free magnetization switching[1]. For the field-free SOT switching, it is essential to distinguish the crystallographic orientation in mesoscopic flakes of WTe_2 a so that charge current can be applied along the low-symmetry axis for generating out-of-plane oriented spin currents. We will present our polarized Raman spectroscopic studies on WTe_2 flakes that we use to prepare SOT switching devices. Raman spectra are collected by rotating the polarization of the incident laser for different angles relative to the a-axis of WTe_2. The polarization angle dependence of the Ag Raman peak at 212 cm^{-1} exhibits minimum intensity when the excitation laser polarization is along the straight edge of the WTe_2 flake, which allows us to characterize the crystallographic axis in WTe_2.

[1]. Kao et al., Nature Materials 21, 1029–1034 (2022)

2D-ThP-11 Designing a Green Synthesis Route and a Green Solvent to Exfoliate Graphene for Cost-Efficient Supercapacitors*, S. Kittur, J. Zhang, A. Pangal, I. Agrawal, S. Raj,* ***Abhiram Hanumanchi****, N. Sangeneni,* ASDRP

Graphene, the two dimensional counterpart of graphite, is a novel hexagonal lattice structured, single layer sheet of carbon atoms. The material exhibits unique and suitable properties for applications in supercapacitors—notably, high electrical conductivity, lightweight structure, and high tensile strength, The main challenge of producing graphene lies in discovering a process that is green, scalable, and cost-effective. Other processes such as mechanical or electrochemical exfoliation, oxidation/reduction, chemical synthesis, and chemical vapor deposition fall short in at least one of these categories. Instead, our research turns to a more promising method—liquid-phase exfoliation. Refinement of the LPE method included comparisons of bath and probe sonication in their effects on yield. Additionally, we explored the supplementation of magnetic stirring and centrifuging to the process, and the effects of these additions on the end yield. The end yield of graphene was free of trapped oxygen atoms, as confirmed by XRD characterization. Moreover, our experiment did not involve any toxic solvents that pose environmental risks during disposal. Previous research indicates that solvents' properties determine the quality and amount of graphene produced. Solvents with similar surface tensions to graphene are better able to permeate in between the graphite layers during the sonication process. Ethanol in particular is suitable due to its low boiling point, low toxicity, and mix of polar and nonpolar properties. Ethanol's low surface tension in comparison to graphene was remedied by adding water so that the mixture's surface tension was similar to graphene's. We calculated the ratio of water and ethanol to be used based on their surface tensions, which are 73 and 21 mJm-1 respectively. Adding materials like curcumin to the solvent also decreases the amount of defects in graphene, and gives us a better yield. In addition curcumin also acts as a reducing and stabilizing agent, which helps in avoiding agglomeration and keeping the graphene sheets apart. UV-Vis, XRD, and FTIR spectroscopy were used to characterize impurities in the exfoliated graphene. We prepared inks from the exfoliated graphite and performed cyclic voltammetry and galvanostatic charge discharge to test the energy capabilities of graphene electrodes. To further our research, we plan on conducting characterization with Raman spectroscopy and SEM. A green solvent and synthesis process remains desirable in the field of electrochemistry, providing sustainable storage for electricity without a massive loss in yield.

2D-ThP-12 Chemical Vapor Deposition of Large Grain and Continuous Mos$_2$ Layers on Catalyzed SiO$_2$/Si Substrate, *Z. Graham,* ***Matara Indika,*** *M. Williams,* Clark Atlanta University

MoS$_2$ has shown to be remarkable in its electrical and optoelectrical capabilities. Studies exemplify that with its modulating band gap and other properties, it can be useful as an excellent semiconductor material in devices such as field-effect transistors, photodetectors, solar cells. A uniform, continuous, monolayer growth of MoS$_2$ has still been regarded as a challenge in 2-D transition metal dichalcogenide growth. Here in this study, using a conventional CVD (chemical vapor deposition) growth method under particular growth parameters, large-grain and continuous MoS$_2$ layers can be achieved based on the synergistic reaction of precursor and Na2SO$_4$catalysis on a SiO$_2$/Si substrate with no powder transition metal precursors. Experimental studies have proven that rather than the Na interfering with the growth process between molybdenum and sulfur, it does in fact act as a catalyst in this reaction and bonds with the SiO$_2$/Si substrate instead. Confocal laser microscopy, Raman and Photoluminescence techniques will be utilized to study the uniformity/surface morphology, size, thickness, strain, stress, band gap, spin–orbit coupling, etc. of these layers.

2D Materials Technical Group
Room 303 - Session 2D+AS+BI+HC+SS-FrM

2D Materials: Biological, Electronic, Energy, and Other Applications

Moderators: Robert Hovden, University of Michigan, **Jyoti Katoch**, Carnegie Mellon University

8:20am **2D+AS+BI+HC+SS-FrM-1 Printable Electrochemical Biosensors based on 2D and 3D Graphene***, A. Ebrahimi, **Derrick Butler**, V. Kammarchedu, K. Zhou,* Penn State University **INVITED**

The increasing demand for low-cost and field-deployable biosensors has driven researchers to explore robust and scalable biochemical sensor materials and fabrication strategies. Compared to more complicated and expensive photolithography methods, printing techniques – including inkjet and direct laser writing – can enable tailorable and easily-prototypable sensors that are conducive to testing at the point of need. Electrochemical sensors have the potential to meet these criteria and integrate well with printing methods.[1] In recent years, graphene has emerged as a key material in the area of electrochemical biosensors due to high conductivity, wide electrochemical window, biocompatibility, tunability, and excellent surface sensitivity.[2] In particular, advances in preparation of solution-phase graphene suspensions (such as inks containing 2D graphene sheets) have brought about breakthroughs in printed electronics, while the advent of laser-induced graphene (LIG) has enabled the direct writing and integration of 3D porous graphene patterns in various low-cost substrates.Over the past few years, our group has developed different facile functionalization methods to enhance the sensitivity and specificity of printed devices based on graphene ink and LIG, with special attention to sensor performance in complex biological fluids (such as serum, saliva, sweat).[3,4] We have investigated application of the sensors for *in vitro* detection of small molecules involved in neurological functions, kidney disease, and wound infection as well as real-time monitoring of drug-induced response of cancer cells and biofilm biomarkers. Interfacing of the printed sensors with low-cost readout electronics and smartphone has been also demonstrated to showcase the sensor applicability for remote sensing at the point of need. Convergence of machine learning with electrochemical sensing has been also investigated, demonstrating a significant enhancement of sensitivity, while enabling reliable multiplexing of example biochemical markers in saliva and sweat. This talk will highlight our recent progress and ongoing work on advancing printable graphene biosensors in more detail.

[1] K. Yamanaka, M. C. Vestergaard, E. Tamiya, *Sensors (Switzerland)***2016**, *16*, 1761.

[2] A. Bolotsky, D. Butler, C. Dong, K. Gerace, N. R. Glavin, C. Muratore, J. A. Robinson, A. Ebrahimi, *ACS Nano***2019**, *13*, 9781.

[3] R. Muralidharan, V. Chandrashekhar, D. Butler, A. Ebrahimi, *IEEE Sens. J.***2020**, *20*, 13204.

[4] D. Butler, D. Moore, N. R. Glavin, J. A. Robinson, A. Ebrahimi, *ACS Appl. Mater. Interfaces***2021**, *13*, 11185.

9:00am **2D+AS+BI+HC+SS-FrM-3 A Large Area Selective Emitter for Thermophotovoltaic Applications***, **Minsu Oh**, K. Grossklaus, D. DeMeo, Z. Kranefeld, T. Vandervelde,* Tufts University

Thermophotovoltaic (TPV) devices enable energy harvesting from waste heat. In a TPV system, photons radiated by a selective emitter are converted into electricity by a photodiode due to the photovoltaic effect. The total photon flux available for power conversion is determined by the temperature, emission spectrum, and size of the emitter. Due to the engineerability of metamaterial's optical properties, they have been widely used to create TPV emitters with a desired emission spectrum for varying heat source temperatures. However, the difficulties in fabricating nano- or micrometer-sized metamaterial features that are two-dimensional over large areas pose challenges to realizing a large emitter. This fundamentally limits the output power of a TPV system due to power density restrictions. Therefore, achieving large area emitters with engineerable optical properties are critical for utility of TPV devices at scale with a reasonable power output. In this work, we experimentally demonstrate a 4-inch diameter selective emitter fabricated from one-dimensionally patterned Si and Cr. The selective emission of the emitter peaks at 3.75 µm, which targets 773K blackbody temperature, with a bandwidth of less than 1.5µm. The emission bands of this structure can also be engineered for varying source temperatures owing to the interference effects. Moreover, due to the fabrication ease, our emitter can easily be scaled up to any size of the substrate. We also present the impact of temperature and oxidation on the emission band when heated up to 1000K.

9:20am **2D+AS+BI+HC+SS-FrM-4 Advanced Two-Dimensional Nanohybrids for Efficient Electrocatalytic Hydrogen Evolution***, **Fei Yao**,* University at Buffalo-SUNY

Hydrogen (H_2) shows great potential in reducing greenhouse gas emissions due to its environmentally friendly nature and high gravimetric energy density. It can be generated via electrochemical water splitting based on the hydrogen evolution reaction (HER). It is well known that Pt-group metals (PGMs) are excellent catalysts for HER, but their broad adoption is limited by high cost and scarcity. Recently, two-dimensional (2D) molybdenum disulfide (MoS_2) is regarded as a promising alternative to PGMs due to its large surface area, rich active sites, and ideal hydrogen adsorption energy. However, its practical application is hindered by the intrinsically low electrical conductivity arising from the semiconducting nature of 2H phase MoS_2. On the other hand, 2D Ti_3C_2 MXene with high electrical conductivity, excellent hydrophilicity, and large interlayer distance has been intensively investigated in energy storage devices lately. Compared with charge-neutral graphene, MXene exhibits a negatively charged surface due to the existence of numerous surface functional groups (-OH, -O, -F, *etc.*), which not only enhances the dispersion of MoS_2 precursors but also promotes MoS_2 nucleation, making it a superior template for MoS_2 synthesis. Nevertheless, undesired oxidation of MXene occurs in aqueous solutions, reducing the overall catalyst stability.

To address the above issues, we employed a one-step solvothermal method using DI water/DMF as bisolvent and constructed a metallic 1T phase-enriched MoS_2/MXene/CNT composite as HER catalyst. A low overpotential (169 mV) and Tafel slope (51 mV/dec) along with the highest turnover frequency ($7\ s^{-1}$ at - 0.23V vs. RHE) and an ultralong lifetime (72 hours) was successfully achieved. The origin of the outstanding HER performance of the ternary composite can be ascribed to: (i) the prevention of 2D layer restacking as well as the enlarged surface area due to the 2D/2D MoS_2/MXene integration and ion intercalation; (ii) the vertical growth of MoS_2 flakes on the MXene template which increases the exposure of MoS_2 edge planes, maximizing the total number of active sites; (iii) the synergistically enhanced conductivity because of the formation of hybrid 1D/2D conductive network via the integration of 1T-phase metallic MoS_2, conductive MXene backbone with suppressed oxidation along with the CNT crosslinks, minimizing the charge transfer resistance at the electrode/electrolyte interface. This work demonstrated an effective strategy for two-dimensional material structure-property engineering with the aim of optimizing the HER performance which will shed light on the development of the next-generation PGM-free HER electrocatalysts.

9:40am **2D+AS+BI+HC+SS-FrM-5 Bandstructure Engineering in Two-Dimensional Semiconductors***, **Keun Su Kim**,* Yonsei University, Republic of Korea **INVITED**

The tunable band structure of two-dimensional quantum mater is not only interesting in itself, but also useful for the fundamental study of condensed matter physics. As example, surface chemical doping can be used to reduce the band gap of black phosphorus over the energy range greater than its intrinsic band gap [1]. This could be used to deliberately induce a topological phase transition to a Dirac semimetal phase protected by spacetime inversion symmetry [2]. It could also be used to trace the evolution of quantum phases (pseudospin) order across the topological phase transition [3]. In this talk, I will introduce our recent study on the band renormalizations and pseudogap of black phosphorus doped by alkali metals [4]. Using angle-resolved photoemission spectroscopy (ARPES), we found that the simple quadratic band dispersion of doped black phosphorus anomalously bends back towards zero wavenumber, which can be explained by Anderson-McMillan's framework developed for the band structure of liquid (or disordered) metals in the 1960s. This is a natural consequence of resonance scattering by the potential of dopant ions with short-range order. The depth of scattering potential tuned by different kinds of alkali metal (Na, K, Rb, and Cs) allows us to classify the pseudogap of p-wave and d-wave resonance.

1. J. Kim et al., Science 349, 723 (2015).
2. J. Kim et al., Phys. Rev. Lett. 119, 226801 (2017).
3. S. W. Jung, S. H. Ryu et al., Nature Mater. 19, 277 (2020).
4. S. H. Ryu, M. Huh, D. Y. Park et al., Nature 596, 68 (2021).

10:20am **2D+AS+BI+HC+SS-FrM-7 Graphene – Ferritin Interface Unpins Fermi-Level and Induces Temperature Dependent Coherent Tunneling Across Biomolecular Junctions***, **Ayelet Vilan,*** Weizmann Institute of Science, Israel*; N. Kumar Gupta,* National University of Singapore*; S. Kumar Karuppannan,* National Quantum Fabless Foundry, Singapore*; R. Reddy Pasula,* Nanyang Technological University Singapore*; J. Martin, W. Xu,* National University of Singapore*; E. May,* Nanyang Technological University, Singapore*; A. Pike,* Newcastle University, UK*; H. Astier, T. Salim,* National University of Singapore*; S. Lim,* Nanyang Technological University, Singapore*; C. Nijhuis,* University of Twente, Netherlands

Molecular electronics is one road to ultimate miniaturization: can we reduce the size of an electronic element to a size of a single molecule? However, as the size reduces to few-atoms level, it becomes harder to distinguish the role of the molecular core from that of the contacts. Here we show the prominent role of graphene interfaces with Fe storing proteins in the net charge transport across their tunnel junctions. Here, ferritin (AfFtn-AA) is adsorbed on graphene by non-covalent amine-graphene interactions. In contrast to junctions with metal electrodes, graphene has a vanishing density of states toward its intrinsic Fermi-level ("Dirac point"), which increase away from the Fermi-level. Therefore, the amount of charge carriers is highly sensitive to temperature and electrostatic charging (induced doping), as deduced from a detailed analysis of charge transport as a function of temperature. Moreover, increasing the iron loading of ferritin, changes the graphene from n- to p-doping. Remarkably, the temperature dependence can be fully explained within the coherent tunneling regime due to excitation of hot carriers. The sensitivity of graphene (and 2D materials in general) to electrostatic charging opens rich possibilities in employing interface electrostatics in tuning the electronic properties of molecular junctions and is important for 2D / biomolecules hybrids in general.

10:40am **2D+AS+BI+HC+SS-FrM-8 The Influence of Selenium Incorporation on the HER Catalytic Activity of Electrodeposited Se-MoS$_x$ Electrocatalysts***, **Lee Kendall**, G. Zangari , S. Mc,* University of Virginia

With the increase in the global consumption of energy, the need to meet the growing energy demands has put significant pressure on the current means of energy production and storage.To meet this demand, water splitting has seen substantial efforts in developing catalytically active materials that replace costly materials, such as Pt, to allow for economically viable implementations.MoS$_2$ has attracted significant attention over the past decade due to its low cost and availability. Additionally, MoS$_2$ is one of the most promising materials for electrocatalytic hydrogen evolution as its Gibbs free energy of hydrogen adsorption, $\Delta G^{H}_{0,ads-}$, is the closest to Pt, a state-of-the-art catalyst, when compared to other metallic materials. However, due to the limited number of accessible edge sites, as well as high kinetic barriers for H$_2$ evolution, the catalytic performance of MoS$_2$ is still far from the needed requirements. To address this, researchers have investigated amorphous MoS$_x$ due to its increased structural heterogeneity that increases catalytic site density. Combined with short-range atomic arrangements that enable adequate electronic conductivity, amorphous MoS$_x$ is an attractive candidate for electrochemical processes.This can be further improved, however, as the bridging bonds are the most catalytically active while the terminal and apical are significantly less active.To increase their activity, we investigated incorporating selenium into MoS$_x$ due to the success in crystalline, selenium alloyed MoS$_2$. This success centered on obtaining a more thermoneutral ΔG^{H}_{ads} for the sulfur edges and basal plane, similar motif to terminal and apical bonds in the amorphous system, respectively.To accomplish this, we used an electrodeposition technique that allows for the incorporation of selenium into the MoS$_x$ polymeric chains. We will report on this investigation of the electrodeposition of Se-MoS$_x$ and its effect on the physical, electronic, and catalytic properties towards the hydrogen evolution reaction. Through electrodepositing catalytically active Se-MoS$_x$ thin films, this effort demonstrates improved HER efficiency over current, low-cost materials.

11:00am **2D+AS+BI+HC+SS-FrM-9 Two-Dimensional Skintronics***, **Dmitry Kireev**, D. Akinwande,* The University of Texas at Austin **INVITED**

Modern healthcare displays a significant shift from hospital-based medicine towards a personalized, ambulatory, and wearable approach. In this regard, the development of skin-wearable electronics (*skintronics*) is an essential step toward mobile health monitoring, the healthcare Internet of Things, and eventually preventive medicine. Continuous long-term monitoring of brain activity, heart activity, body hydration, or temperature, is vital for better comprehension of human physiology, understanding systematic disease risk factors, and building preventative care solutions. In this work, we utilize *graphene* and other *2D materials* such as platinum diselenide (PtSe$_2$) and platinum ditelluride (PtTe$_2$) to construct the thinnest elements of skintronics - electronic tattoos. The PtSe$_2$ and PtTe$_2$ e-tattoos that can be grown at comparably low temperatures (400ºC) were found to have superior sheet resistance and electrode-skin impedance compared to monolayer graphene e-tattoos. On the other hand, we also report on the significant advancement of the classic graphene electronic tattoos by introducing graphene nanoscrolls and stacking multiple graphene monolayers. Moreover, we show that graphene tattoos can be made insusceptible to sweat by introducing microholes into their structure. Significantly, we show that graphene electronics tattoos can be used for deep tissue monitoring, detecting complex analytes such as blood pressure and respiration rate in a continuous and entirely non-invasive manner. Beyond the simple use of graphene tattoos as passive electronic elements, we have discovered that the semimetallic 2D material can be used as transistors, biased electrostatically through the body itself, creating transistor tattoos. The body-gated graphene tattoo transistors can function as biosensors or small-signal amplifiers, contributing to the development of higher-fidelity electrophysiology measurements and decreased susceptibility to movement-related artifacts.

11:40am **2D+AS+BI+HC+SS-FrM-11 Ultrasonic-Assisted Assembly of Metal Nanoparticles within Graphene Oxide for Tailoring Stem Cell Response***, J. Jaiswal ,* Indian Institute of Technology (Banaras Hindu University) , India*; **Marshal Dhayal,*** Indian Institute of Technology (Banaras Hindu University) , India

Recently 2D material-assisted stimulation for cellular functions has gained significant attention. In this paper, we will be presenting the methodology used for preparing tunable properties of 2D surfaces incorporating metal nanoparticles (NP) within graphene oxide sheets. The study will report the use of mechanical forces generated through an ultrasonication-assisted method for increased diffusion of metal ions in graphene oxide (GO). The transmission electron microscopy (TEM) analysis has been used to confirm the distribution of metal particles in GO sheets whereas Raman spectra were used to identify the relative changes in the Raman bands. The study presents a correlation of these observations with corresponding confirmation in the distortion of multilayer assembly of thin layers of GO by the nucleation of metal nanoparticles. The X-ray diffraction (XRD) spectra of GO-NP also demonstrated similar outcomes in Raman spectra. UV-visible spectra and X-ray photoelectron spectroscopy (XPS) analysis were used to determine optical activity and relatively % proportions of their atomic concentrations. These unique combinations of functionally graded GO-NP were used to study the response of human mesenchymal stem cells. This method may be helpful to address the challenges associated with developing metallic assembly within graphene oxide without chemical functionalization of their inert surface for their application in the biomedical field.

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