Nanoscale Science and Technology Division
Room B113 - Session NS1+2D+BI+SS-MoM

Combined Nanoscale Microscopy

Moderators: Adina Luican-Mayer, University of Ottawa, Canada, **Sergei Kalinin**, Oak Ridge National Laboratory

8:20am **NS1+2D+BI+SS-MoM-1 Combined Metrology at the Nanoscale: Advanced Scanning Probe Microscopy to Evaluate Complex Semiconductors***, **Fernando A. Castro,*** National Physical Laboratory, UK **INVITED**

The performance of semiconductors is strongly affected by spatial variations that can be introduced during manufacturing or due to degradation processes. In addition to the impact of microstructure and defects on electrical and optical properties, complex semiconductors, such as some compound semiconductors, perovskites or 2D materials, can present dynamic changes in properties during operation. Combining metrology methods is critical to better understand and characterise such complex samples as individual methods provide insufficient information. Ideally these combined measurements should be either co-localised or simultaneous in order to reduce uncertainty associated with post process image registration, spatial heterogeneity, or sample contamination. NPL has been developing a suite of spatially resolved measurement methods to understand critical factors that impact semiconductor performance and reliability. In this presentation, we'll focus on nanoscale methods under controlled operational or environmental conditions, including advanced modes of scanning probe microscopy (SPM) such as time-resolved scanning kelvin probe (tr-SKPM) and tip enhanced optical microscopy (TEOS). After introducing the challenges and recent results from the European project PowerELEC, we'll present two examples of how these combined measurements are applied. First, we'll describe the application of SPM to understand degradation mechanisms in state-of-the-art perovskite solar cells (PSCs). Time-resolved SKPM can be used to distinguish the impact of ionic and electronic charges on dynamic processes and in-situ co-localised measurements under controlled environmental conditions can identify nucleation of nanoscale grains on the perovskite film surface at the start of the degradation process, allowing us to link degradation to the local electrostatic environment. The second example will focus on 2D transition metal dichalcogenide (TMD), which present promise for optoelectronic applications but are often limited by Fermi level pinning effects and consequent large contact resistances upon contacting with bulk metal electrodes. A potential solution for near-ideal Schottky–Mott behavior and concomitant barrier height control has been proposed in the literature by contacting TMDs and (semi-)metals in van der Waals heterostructures. We will show how combined nanoscale measurements allows to directly access interface parameters relevant to the Schottky–Mott rule on a local scale and how we use SKPM and TEOS measurements under simulated operational conditions (e.g. electrostatic doping induced Fermi levels) to enable decoupling and quantification of contributions from the interface dipole and electrode work function.

9:00am **NS1+2D+BI+SS-MoM-3 Correlated Functional Imaging of Printed and Ferroelectric 2D Devices for Ubiquitous Sensing and Neuromorphic Computing***, J. Kim, Z. Zhu, T. Chu, H. Choi, M. Moody,* ***Lincoln Lauhon,*** Northwestern University

The unique properties of 2D materials stimulate the design of devices that exhibit useful new behaviors. However, the correspondence of expected and actual operating principles of devices cannot always be established from simple analysis of temperature-dependent current-voltage characteristics. As a result, the rational optimization of even simple devices such as thin-film transistors, as well as the successful realization of novel neuromorphic devices, benefits from spatially resolved characterization of nanoscale structure and properties to discern the relative contributions of device geometry and 2D material structure and chemistry to device performance. This talk will describe case studies in which Kelvin probe force microscopy (KPFM) and scanning photocurrent microscopy (SPCM) are used to investigate the operating principles of thin-film transistors (TFTs) and source-gated transistors (SGTs) fabricated from MoS_2 and In_2Se_3. In the case of n-type semiconducting 2H MoS_2, model devices constructed from overlapping exfoliated flakes are analyzed to identify factors limiting the performance of printed thin-film transistors (*ACS Nano* 2023, **17**, 575). KPFM analysis is used to isolate the contact, channel, and junction resistances and calibrate a resistor network model of printed thin films. Simulations of the effective mobility and on-current dependence on flake thickness, size, and degree of overlap suggest that the performance of printed TFTs are limited by resistance arising from unpassivated edge states.

In the second use case, KPFM, SPCM, and piezoresponse force microscopy (PFM) are used to pinpoint the origin of resistance modulation in α-In_2Se_3 transistors that exhibit tunable non-volatile channel conductance. Memristive behavior in In_2Se_3 TFTs has been attributed to switching of the channel polarization, but the lack of an obvious threshold for switching raises questions about the evolution of domain structure and the contribution of trap states. Furthermore, the presumed modulation of the Schottky barrier has yet to be confirmed experimentally. We address this gap in understanding through correlated PFM, KPFM, and SPCM measurements. We then fabricate MoS_2-In_2Se_3 transistors with a geometry that induces depletion at the source electrode, i.e. a source-gated transistor, and observe non-volatile switching of the low output current. KPFM, SPCM, and finite element simulations are used to confirm source pinch-off and non-volative multi-level modulation of the effective source resistance. The quantitative correlation of device behaviors with the changes in channel potential at key interfaces usefully constrains the interpretation of the operating principles and builds a foundation for rational design of novel neuromorphic devices and systems.

9:20am **NS1+2D+BI+SS-MoM-4 A Unique New Correlative Microscopy Platform for Combined Nanoscale Microscopy by Combination of AFM and SEM***, **Chris Schwalb,*** Quantum Design Microscopy GmbH, Germany*; K. Arat,* Quantum Design, Inc.*; H. Alemansour, A. Alipour,* Quantum Design, Inc., Iran (Islamic Republic of)*; A. Amann,* Quantum Design, Inc., Germany*; L. Montes,* Quantum Design, Inc., Colombia*; J. Gardiner,* Quantum Design, Inc.*; H. Frerichs, L. Stuehn, S. Seibert,* Quantum Design Microscopy GmbH, Germany*; S. Spagna,* Quantum Design, Inc.

The combination of different analytical methods into one instrument is a powerful technique for the contemporaneous acquisition of complementary information. This is especially true for the in-situ combination of atomic force microscopy (AFM) and scanning electron microscopy (SEM), two of the most powerful microscopy techniques available. This combination gives completely new insights into the nanoscale.

In this work, we introduce a highly integrated new corelative microscopy platform, the FusionScope, that seamlessly combines AFM and SEM within a unified coordinate system. The self-sensing piezoresistive cantilever technology used for the AFM scanner results in a purely electrical measurement of the cantilever deflection signal. This allows for concurrent, correlated acquisition of both SEM and AFM images at the region of interest. In addition, a three-axis sample stage and a trunnion provide unique experimental capabilities such as profile view – an 80-degree tilt of the combined sample stage and AFM giving full SEM access to the cantilever tip region.

We will present a variety of novel case studies to highlight the advantages of this new tool for interactive, correlative, in-situ nanoscale characterization for different materials and nanostructures. First results will focus on hard-to-reach samples. FusionScope allows for fast and easy identification of the area of interest and precise navigation of the cantilever tip for correlative SEM and AFM measurements. We demonstrate that approach for analysis of blade radius of razor blades and the characterization of lacunae structures on bone surfaces.

In addition, we will present first results for the in-situ characterization of individual nanowires that will be used for energy harvesting applications. The SEM enables the easy location of individual or multiple nanowires, whereas the in-situ AFM allows the characterization of topography, surface roughness, mechanical, and electrical properties of the nanowire.

Based on the broad variety of applications regarding the inspection and process control of different materials and devices, we anticipate that this new inspection tool to be one of the driving characterization tools for correlative SEM and AFM analysis in the future.

9:40am **NS1+2D+BI+SS-MoM-5 Correlative *in-Situ* Nanoscale Microscopy Using AFM and FIB-SEM for Nanomechanical Property Mapping Throughout a 3D Volume***, **Prabhu Prasad Swain**, M. Penedo, N. Hosseini, M. Kangül, S. Andany, N. Asmari, G. Fantner,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

In this work, we present results obtained with an atomic force microscope (AFM) integrated in a focused ion beam- scanning electron microscope (FIB-SEM). The FIB-SEM is a powerful instrument, capable of automated structural analysis and prototyping at nanometer resolution, while the AFM is a well-established versatile tool for multiparametric nanoscale characterization. Combining the two techniques allows unprecedented *in-situ* correlative analysis at the nanoscale. Nanoprototyping and enhanced multiparametric analysis can be performed without contamination of the sample or environmental changes between the subsequent processing steps. The power of the combined tool lies in the complementarity of the two techniques. The AFM offers nanomechanical property mapping with electrical and magnetic characterization of the sample, while SEM offers elemental analysis and FIB enables thin slicing of the of the sample for block face imaging. This enables 3D tomographic imaging of complex samples mapping composition and mechanical properties throughout the 3D volume. Controlling both these instruments with open-hardware controller (OHC), allows us to perform automated *in-situ* AFM-FIB-SEM characterization. The setup is aimed to provide true 3D correlative information and mapping, with increased resolution for a larger volume. We will demonstrate the capabilities of correlative AFM/SEM/FIB imaging through a series of correlative experiments on polymers, 2D materials, nanowires and rock sediments.

10:00am **NS1+2D+BI+SS-MoM-6 Anisotropic Friction Effects of Perovskite Nanoplatelets on a vdW Substrate**, ***Sidney Cohen,*** *N. Itzhak, I. Rosenhek-Goldian, O. Brontvein, E. Joselevich,* Weizmann Institute of Science, Israel

Interest in 2D materials can be attributed to their unique properties such as electrical, optical, and mechanical characteristics, which can be harnessed in small devices. Assembly of these materials can be challenging. vdW epitaxy is a promising approach, in which nano-sized crystalline structures are grown on a 2D vdW substrate which has minimal interaction energy, resulting in low strain. The epitaxial growth still provides sufficient interaction to favor specific geometries according to lattice directions. In this presentation, the system is $CsPbBr_3$ platelets grown on vdW $ReSe_2$.This combination is of fundamental and applied interest due to special optoelectronic properties of these 2D-3D mixed semiconductor systems. The mechanism of the nanoplatelet growth leading to their shape and orientation on the surface remains to be fully revealed . Here, we present tribological studies performed by monitoring the force required to push the platelets along the surface. We observed a significant directional effect expressed in the lateral forces required to slide the platelets along the surface. In particular, forces 4-5 times those required to push rectangular platelets along the $ReSe_2$ surface along the long axis were insufficient to move the same platelets along their short axis. STEM images showed that this correlated with commensurability of the two lattice structures.Some of the experiments were performed in an ambient AFM system. Because sliding along the surface can be hindered by atomic steps and defects, unbiased analysis of this effect requires searching for small steps of atomic height along the sliding path. Scanning electron microscopy is a convenient way to search for these defects: thus, comparative experiments were performed in-situ in a combined AFM-SEM system. This combination had the additional advantage of allowing rapid overview of the surface to locate regions of interest.

In the process of evaluating the measurements, those performed in vacuum requiredmuch higher (by as much as an order of magnitude) forces to support pushing along the surface in comparison with comparable measurements made in the ambient AFM system.These measurements will be presented in the context of the characterization of the 2D substrate and platelet nanostructure as revealed by the two correlative measurement techniques.

Nanoscale Science and Technology Division
Room B113 - Session NS2+2D+BI+EL+SS-MoM

Chemical Identification with Scanning Probe Microscopy

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, **Harald Plank**, Graz University of Technology

10:40am **NS2+2D+BI+EL+SS-MoM-8 Nanoscale imaging with photo-induced force microscopy**, ***Eric Potma,*** University of California Irvine **INVITED**

Imaging with molecular contrast at the nanoscale is important for a myriad of applications, yet it remains a technical challenge. Over the past two decades, various flavors of optical spectroscopy combined with atomic force microscopy have been developed, each offering hope for a more routine nanospectroscopy technology. One of these approaches is photo-induced force microscopy (PiFM), a non-contact scan probe technique that is sensitive to the light-induced polarization in the material. PiFM has been used to generate molecular maps with 5 nm resolution, based on absorption contrast or on contrast derived from nonlinear optical interactions. Nonetheless, questions remain about the origin of the signal, in particular the possible contribution of forces that result from the thermal expansion of the sample. In this presentation, we will discuss various physical mechanisms that contribute to the PiFM signal and highlight several applications that are unique to the PiFM technique.

11:20am **NS2+2D+BI+EL+SS-MoM-10 Near-field Optical Microscopy Imaging and Spectroscopy at 10nm Spatial Resolution**, ***Artem Danilov,*** Attocube Systems Inc.

Fourier-transform infrared (FTIR) spectroscopy is an established technique for characterization and recognition of inorganic, organic and biological materials by their far-field absorption spectra in the infrared fingerprint region. However, due to the diffraction limit conventional FTIR spectroscopy is unsuitable for measurements with nanoscale spatial resolution. Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) allows to overcome the diffraction limit of conventional light microscopy or spectroscopy enabling optical measurements at a spatial resolution of 10nm, not only at IR frequencies but also in the whole spectral range from visible to terahertz. s-SNOM employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample and detection of the elastically tip-scattered light yields nanoscale resolved near-field images simultaneous to topography.Use of material-selective frequencies in the mid-IR spectral range can be exploited to fully characterize polymer blends or phase change polymers with nanometer-scale domains. Quantification of free-carrier concentration and carrier mobility in doped semiconductor nanowires, analysis of 2D (graphene) nanostructures, or study phase propagation mechanisms in energy storage materials is achieved by amplitude- and phase-resolved near-field imaging. Furthermore, here we introduce correlative tip-enhanced nanoscopy, enables complete collocal vibrational analysis of both IR- and Raman-active modes at the same spatial scale. Our instrument allows for a straight-forward implementation of nano-PL measurements using background suppressing provided by the demodulation of detector signal utilized in nano-FTIR detection scheme. Combining Raman, TERS, nano-FTIR and nano-PL measurements in the same instrument significantly reduces the effort of correlating the resulting datasets, enabling complete optical analysis at nanoscale, which has not been possible so far.

11:40am **NS2+2D+BI+EL+SS-MoM-11 Correlative Nanoscale Chemical, Mechanical and Electrical Property Mapping on a Single AFM-IR Platform**, *C. Li,* ***Martin Wagner,*** *C. Phillips,* Bruker Nano Surfaces Division

Chemical identification on the nanoscale is a long sought after capability from the inception of AFM. AFM-IR has proven to be uniquely successful in achieving this among all other attempts. It uses a mid-IR laser that is focused onto the AFM tip. Light absorption by the sample results in photothermal expansion that causes a detectable cantilever deflection change of the AFM probe. The obtained IR spectra correlate with conventional FTIR spectroscopy but are associated with sub-10nm spatial resolution.

However, a single data set rarely tells the full story and multiplexed analysis is essential to fully understand a material. We use an AFM-IR microscope with image registration and overlay capability to return to the same position on a sample when changing AFM probes, enabling extensive multimodal analysis. Data on a two-component polymer sample PS-LDPE comprising polystyrene and polyethylene reveals nanoIR spectra that correlate well with FTIR, while nanoIR maps at different IR wavenumbers provide the spatial distribution of each component. Further, we show that they are directly correlated at the nanometer level through PeakForce QNM elastic modulus and adhesion maps, as well as work function (surface potential) and dielectric maps with FM-KPFM (frequency-modulated Kelvin probe force microscopy). Many of the properties can be conveniently obtained simultaneously, while others are preferably obtained sequentially in a colocalized manner with the optimal probe choice and parameter settings for each AFM mode. Data on real-world industrial samples is then discussed, e.g. SBR (styrene-butadiene rubber) with carbon-black additives for car tires, exemplifying how ratio-map and multimodal property mapping unravel information not seen through one technique alone. In another use case chemical identification is complemented by nDMA, a mode where viscoelastic nanoscale sample properties are measured that match bulk dynamic mechanical analysis (DMA) data.

2D Materials Technical Group
Room C123 - Session 2D-TuM

2D-Materials: Heterostructures and Functionalization

Moderators: Xiangfeng Duan, UCLA, **Kai Xiao**, Oak Ridge National Laboratory

8:00am **2D-TuM-1 A Wafer Scale Approach to Synthesize Targeted Metastable Heterostructures*, David Johnson,*** University of Oregon **INVITED**

Heterostructures consisting of two or more compounds with different crystal structures interleaved with targeted layer thicknesses and sequences of constituents have been the focus of intense interest due to the discovery of emergent properties of interest for a number of applications. My group has pioneered a synthesis approach to these materials based on repeated deposition of a sequence of elemental layers where the number of atoms in each layer correspond to the amount need to form each of the targeted constituent structures. These designed layered precursors self-assemble at low temperatures into the targeted heterostructures because phase segregation into separated bulk constituents is disfavored by low interdiffusion rates. Since this self-assembly is independent of the substrate structure, this synthesis approach is compatible with lithography. The ability to precisely control constituent layer thicknesses and layer sequences provides opportunities to systematically probe structure-function relationships. We discovered that monolayers of VSe_2 in $(MSe)_m(VSe_2)$ heterostructures have a charge density wave whose onset temperature depends on both the identity and the thickness of the MSe (m) constituent. We found that the chemical potential difference between constituent layers is compensated by charge donation, leading to systematic changes in electrical transport properties as the relative thickness of constituent layers are varied. We have also discovered that the interaction between constituent layers can stabilize constituent layer structures that are not known as isolated compounds. We have prepared magnetic Pb_2MnSe_3 layers in $(Pb_2MnSe_3)(VSe_2)_n$heterostructures and a new 1T structured transition metal dichalcogenide, $FeSe_2$, in $(PbSe)_1(FeSe_2)_n$. Since this synthesis approach is compatible with lithography, we have been able to develop an approach to measure both cross plane and in plane electrical properties on the same structure. The ability to prepare families of heterostructures with a variety of constituent layers from designed precursors creates a new "thin film metallurgy" where nanostructure, interfacial phenomena and interlayer interactions can be systematically exploited to manipulate physical properties.

8:40am **2D-TuM-3 Simple Approach to Demonstrate the Van Der Waals Heterostructure Composed of Different Kinds of MoS_2 Phase for Photodetector Application***, K. Aydin, T. Kim,* Sungkyunkwan University (SKKU), Republic of Korea*; **Chisung Ahn,*** Korea Institute of Industrial Technology, Republic of Korea

The 2D materials have considered as noticeable candidates to demonstrate photodetector because of their excellent optical and electronic properties. Especially, inherent phase dependent tunable optical band gap properties of 2D-MoS_2 (Molybdenum Disulfide) have significant advantages for versatile optoelectronic applications. Therefore, development the easy phase controlling methodology of 2D-MoS_2 could be considered as an important factor to figure out its applicability for photodetector. In this study, innovative procedure is suggested to synthesis the Van der Waals heterostructure by stacking the different phase of MoS_2 (1T and 2H) based on plasma assisted sulfurization process through only process temperature control under the optimized other variables. It allowed to prepare 4 kinds of different MoS_2 structures (1T/2H, 1T/1T, 2H/1T and 2H/2H) by stacking the homo or hetero phase, and photocurrents for each also measured to explore the relevant correlation.

9:00am **2D-TuM-4 TaS_x Prepared by Atomic Layer Deposition: Two-Dimensional Crystalline Films as Cu Diffusion Barrier***, **Sanne Deijkers,** H. Thepass,* Eindhoven University of Technology, The Netherlands*; H. Sprey, J. Maes,* ASM, Belgium*; E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

As transistors in leading-edge nanoelectronics are becoming smaller and smaller, the challenge of scaling the interconnect becomes very prominent. In this scaling, we need a replacement for the Cu diffusion barrier in the back-end-of-line, since conventionally used TaN/Ta barriers fail if they are thinner than 3 nm [1]. Tantalum sulfide (TaS_x) is a versatile Ta-based two-dimensional transition metal dichalcogenide (2D-TMD) that can function as Cu diffusion barrier as has been recently shown for films prepared by chemical vapor deposition [2]. In this work we report on the diffusion barrier performance of TaS_x synthesized by atomic layer deposition (ALD). ALD offers the desired control and conformality required for thin layers in demanding structures. In our previous work, we have shown that 2D-TMD MoS_2 films synthesized by ALD can outperform MoS_2 films deposited by other techniques [3].

TaS_x films were deposited using a plasma-enhanced ALD process using tert-butyliminotrisdimethylaminotantalum (TBTDMT) as Ta precursor and an H_2S / Ar / H_2 plasma mixture as co-reactant at 300 °C. It is demonstrated that the crystallinity and stoichiometry can be altered by changing the plasma composition. Addition of H_2 to the Ar and H_2S plasma mixture leads to crystalline TaS_2 films, instead of amorphous TaS_3 films, as measured by x-ray diffraction and x-ray photoelectron spectroscopy.

The barrier performance of the TaS_x films against Cu diffusion was characterized by time-dependent dielectric breakdown (TDDB) tests. Amorphous TaS_3 films do not function as Cu diffusion barrier, while the crystalline TaS_2 films show a median time to failure ($TTF_{50\%}$) of 530 ± 14 s, where the longest observed breakdown time is 93 hours. This is a substantial improvement compared to barrierless structures ($TTF_{50\%}$ = 201 ± 5 s), which reveals the potential of ALD-grown TaS_x as Cu diffusion barrier.

[1] Li *et al., Materials* **13**, 5049 (2020)

[2] Lo *et al., J. Appl. Phys.* **128**, 080903 (2020)

[3] Deijkers *et al., Adv. Mater. Interfaces***10**, 2202426(2023)

9:20am **2D-TuM-5 Hybrid Epitaxial Heterostructures for Topological Spintronics*, Nitin Samarth,*** Pennsylvania State University **INVITED**

The confluence of fundamental symmetries and spin-orbit coupling is known to produce emergent electronic states in crystalline solids that are accurately described using the language of topology [1]. This talk describes how recent developments in the synthesis and study of epitaxially grown topological quantum materials and their heterostructures yield new insights into the interplay between spin and charge transport, providing an attractive path toward topological spintronic technologies that work under ambient conditions [2-9].

Sponsored by SMART, a funded center of nCORE, an SRC program sponsored by NIST, the Institute for Quantum Matter under DOE EFRC grant DE-SC0019331, the Penn State Two-Dimensional Crystal Consortium-Materials Innovation Platform (2DCC-MIP) under NSF Grant No. DMR-2039351, and the Penn State MRSEC Center for Nanoscale Science via NSF award DMR2011839

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9. A. Vera, W. Yanez, et al., "Emergent spin phenomena in air-stable, atomically thin lead," arXiv:2205.06859

11:00am **2D-TuM-10 Designer Quantum Matter in Van Der Waals Heterostructures*, Peter Liljeroth,*** Aalto University, Finland **INVITED**

Van der Waals (vdW) heterostructures have emerged as a playground for realizing and engineering exotic quantum states not found in naturally occurring materials. Materials with very different physical properties can be combined essentially at will. As the layers interact only through weak vdW forces, the individual layers retain their intrinsic properties. However, proximity effects cause properties to “leak” between the adjacent layers and allow creating exotic quantum mechanical phases that arise from the interactions between the layers. These key features have recently made it possible to realize exotic quantum phases by design.

I will highlight these concepts through our results on realizing topological superconductivity and heavy-fermion physics in vdW heterostructures [1-3]. We use molecular-beam epitaxy (MBE) in ultra-high vacuum for the sample growth and characterize the resulting samples using low-temperature scanning tunneling microscopy (STM). Topological superconductivity requires combining out of plane ferromagnetism, Rashba-type spin-orbit interactions and s-wave superconductivity, and we use monolayer ferromagnet $CrBr_3$ on a superconducting $NbSe_2$ substrate to realize this [1,2]. I will discuss how the moiré pattern due to the lattice mismatch between $CrBr_3$ and $NbSe_2$ is an essential ingredient in this system as it profoundly modifies the topological phase diagram and enables the realization of a topological superconducting state that would not be accessible in the absence of the moiré. As another example of a designer system, I will introduce 1T–TaS_2 / 1H-TaS_2 heterostructures as a platform for realizing heavy fermion physics in a vdW heterostructure [3]. These results highlight the versatility of vdW heterostructures in realizing quantum states that are difficult to find and control in naturally occurring materials.

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11:40am **2D-TuM-12 2D Hybrids Based on Graphene Oxide and Palladium Nanozymes for Multimodal Theranostics***, A. Foti, L. Calì, S. Petralia, A. Fraix, G. Forte, R. Fiorenza, S. Scirè, L. D'Urso, C. Bonaccorso, C. Fortuna,* ***Cristina Satriano,*** University of Catania, Italy

Graphene oxide (GO)/palladium (Pd) nanocomposites have shown a great potential asmultifunctional nanoparticles with plasmonic, photothermal and enzyme-like behavior for multimodal theranostics.

In this work, different types of hybrid 2D GO/Pd nanosystems were synthesized, with the size of the 2D nanomaterials being controlled by the precursor concentrations as well as different chemical functionalities, including GO vs. reduced-thiolated GO (rGOSH), N-doped reduced GO (rGO-N_X),mixed organic/inorganic matrix. The physicochemical properties were scrutinized by using UV-visible and Raman spectroscopies, atomic force microscopy, zeta-potential and hydrodynamic light scattering. Theoretical DFT calculations paralleled the experimental studies. The GO/Pd hybrids were tested in terms of photocatalysis experiments of H_2 evolutionand photothermal response.

The assessment of nanozyme features for theGO/Pd nanoplatforms unveiled a strong enhancement of hydrogen evolution and broad antioxidant activities, as scrutinized respectively by photocatalysis experiments and MitoSOX and SOD-like activity, respectively.The bio-interface response of systems was evaluated on both tumor cells and healthy cells. Proof-of-work in vitro cell experiments on human prostate cancer cells (PC-3 line) and mouse embryonic fibroblast cells (3T3 line) cells were carried out in terms of cytotoxicity (MTT assay), inhibition of cell migration (wound scratch test) and organelle perturbation (colocalization studies by confocal microscopy). The MTT assay and wound scratch test confirmed the antitumor efficiency of all Pd-based samples in inhibiting tumor growth and monitoring cell migration, respectively. In particular, cells treated with GO-PdNP hybrids with larger sizes showed higher cell viability and migration rate in healthy cells (3T3 line). This makes them promising candidates as nanozyme-theranostic platforms for cancer treatment.The results pointed to a significant reduction of tumor growth and thus the promising potential of the developed GO/Pd hybrid nanozymes in cancer therapy.

This work has been partially funded by the European Union (NextGeneration EU), through the MUR- PNRR project SAMOTHRACE (ECS00000022) and by the University of Catania (PIAno di inCEntivi per la RIcerca di Ateneo 2020/2022 GRABIO_Linea di intervento 2).

12:00pm **2D-TuM-13 Hybrid Molecule/Quantum Material van Der Waals Heterostructures***,* ***Emanuele Orgiu,*** Institut national de la recherche scientifique (INRS), Canada

2D materials are held together by weak interplanar van der Waals (vdW) interactions. The incorporation of molecules in such materials holds an immense potential to understand and modify the fundamental physical properties of the pristine materials while creatin new *artificial materials*. Whilst nature offers a finite number of 2D materials, an almost unlimited variety of molecules can be designed and synthesized with predictable functionalities. The possibilities offered by systems in which continuous molecular layers are interfaced with inorganic 2D materials to form hybrid organic/inorganic van der Waals heterostructures (H-vdWH) are emphasized. Similar to their inorganic counterpart, the hybrid structures have been exploited to suggest novel device architectures. Moreover, specific molecular groups can be employed to modify intrinsic properties and confer new capabilities to 2D materials. In particular, I will highlight how molecular self-assembly at the surface of 2D materials can be mastered to achieve precise control over position and density of (molecular) functional groups, paving the way for a new class of hybrid functional materials.

In particular, within such vdW heterostructures, currently assembled by mechanical superposition of different layers, *periodic potentials* naturally occur at the interface between the 2D materials. These potentials significantly modify the electronic structure of the individual 2D components within the stack and their alignment, thus offering the possibility to build up hybrid and novel materials with unique properties.

Also, I will show how the presence of ordered supramolecular assemblies bearing different functional groups can *modify the pristine Shubnikov-De Haas oscillations* occurring in graphene.

Nanoscale Science and Technology Division
Room B113 - Session NS+2D+EM+MN+SS-TuM

Scanning Probe Microscopy

Moderators: Aubrey Hanbicki, Laboratory for Physical Sciences, **Fernando Castro**, National Physical Laboratory, U.K.

8:00am **NS+2D+EM+MN+SS-TuM-1 AVS Medard W. Welch Award Talk: Microscopy is All You Need: The Rise of Autonomous Science***,* ***Sergei Kalinin***[1]*,* University of Tennessee Knoxville **INVITED**

Making microscopes automated and autonomous is a North Star goal for areas ranging from physics and chemistry to biology and materials science – with the dream applications of discovering structure-property relationships, exploring physics of nanoscale systems, and building matter on nanometer and atomic scales. Over the last several years, increasing attention has been attracted to the use of AI interacting with physical system as a part of active learning – including materials discovery and optimization, chemical synthesis, and physical measurements. For these active learning problems, microscopy arguably represents an ideal model application combining aspects of materials discovery via observation and spectroscopy, physical learning with relatively shallow priors and small number of exogenous variables, and synthesis via controlled interventions. I introduce the concept of the reward-driven experimental workflow planning and discuss how these workflows can be implemented via domain-specific hyper languages. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. The real-time image analysis allows spectroscopic experiments at the predefined features of interest and atomic manipulation and modification with preset policies. I further illustrate ML methods for autonomous discovery, where the microstructural elements maximizing physical response of interest are discovered. Complementarily, I illustrate the development of the autonomous physical discovery in microscopy via the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed. These concepts and methods can be extended from microscopy to other areas of automated experiment.

8:40am **NS+2D+EM+MN+SS-TuM-3 Dielectric Constant Measurement Sensitivity in Electrostatic Force and Force Gradient Microscopy-Based Modes***,* ***Gheorghe Stan,*** National Institute of Standards and Technology (NIST)*; C. Ciobanu,* Colorado School of Mines

Understanding of the nanoscale electrostatic interaction between a conductive atomic force microscopy (AFM) probe and a dielectric film is central to the operation of various nanoscale dielectric microscopies and

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

determination of dielectric properties of the film. There is no simple analytical description of the electrostatic interaction generated in the confined probe-sample geometry of neither the static nor dynamic AFM modes used for dielectric measurements. An accurate description of the involved physics is obtained only by means of a finite element analysis modeling of the system. However, the alternative of using numerical analysis is not very popular being slower and requiring relatively high computation resources. In this work we revised the contributions from different parts of the AFM probe to the probe-sample capacitance by both analytical and numerical methods. We tried to reconciliate the two approaches and observed the differences as a function of geometry and material parameters. Under various noise levels, the efficiency of an analytical model was tested against finite element analysis that captures in detail the electrostatic interaction in AFM-based dielectric measurements. The investigation was performed in both spectroscopic force-distance curves and constant height scans with measurements for the deflection and frequency of the AFM probe. The obtained measurement sensitivities are relevant in selecting the optimal scanning mode and its operational parameters for given film thicknesses and dielectric constants but are also showing the critical role of the numerical analysis to the correct interpretation of the measurements.

9:00am **NS+2D+EM+MN+SS-TuM-4 Measuring and Understanding the Nanomechanical Properties of Halide Perovskites and Their Correlation to Structure***, I. Rosenhek-Goldian,* Dept. of Chemical Research Support, Weizmann Inst. of Science, Israel*; I. Buchine, N. Prathibha Jasti,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ., Israel*; D. Ceratti,* Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel & CNRS, UMR 9006, IPVF, Institut Photovoltaïque d'Ile-de-France*; S. Kumar,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ. Ramat Gan Israel. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel*; D. Cahen,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel*; **Sidney R. Cohen**,* Dept. of Chemical Research Support, Weizmann Inst. of Science., Israel

Halide perovskites, HaP, and especially Pb-based ones exhibit a plethora of remarkable properties. Of these, their photovoltaic properties are the most widely studied due to the proven potential these materials hold for significant technological impact. In addition to photoresponse, this material class is characterized by interesting physical properties, of which mechanical properties enjoy special attention, not only because of potential use in flexible devices, but also from a fundamental science point of view. The mechanical response can shed light on the materials' behavior including dynamic processes and strain-related effects on optoelectronic behavior.

In the context of these studies, particular emphasis has been placed on environmental factors which can alter, especially degrade, material functionality and device performance. Exposure to humidity, light, and oxygen rank prominently amongst these factors.

In this study we measure the humidity influence on the mechanical properties, i.e., elastic modulus (E) and hardness (H), for two series of lead halide perovskite single crystals, varying either by cation or by anion type. Our conclusions are based on comparing results obtained from several different nano-indentation techniques, which separate surface modulus from that of the bulk, and probe different manifestations of the hardness. These studies reveal the different crystalline parameters governing influence of humidity on the mechanics at the surface and in the bulk.

An atypical inverse correlation between E and H was measured (as seen in the supplementary figure a). Furthermore, humidity influenced these two properties in opposite fashion – humidity exposure led to lower H, but to higher E (supplementary figure b). This trend is opposite to that found in most materials where hydration lowers both E and H. We suggest a link between dynamic disorder, self-healing, and the intriguing relation between E and H.

9:20am **NS+2D+EM+MN+SS-TuM-5 3D Nanoprinting of Advanced AFM Nano-Probes***, **Harald Plank**, M. Brugger-Hatzl, R. Winkler, L. Seewald,* Graz University of Technology, Austria

The demand for correlative microscopy is still increasing, as it enables a superior ensemble of information by using various methods to combine individual strengths. The highest level of that approach are hybrid microscopes, which enable individual characterization at the very same spot in a consecutive or even parallel way. With that, however, comes the demand of a conflict-free integration of different microscopes, which require a radical redesign of the instrumentation. A major step in that direction is a recently introduced dual system called FUSIONScope, which is a deeply integrated scanning electron microscopy (SEM) and atomic force microscopy (AFM) solution. While the former enables high-resolution guidance towards the region of interest, the latter complements SEM capabilities by true quantitative 3D surface information, which together exploit their full potential by the possibility to precisely land the AFM tip on highly exposed regions. Even more importantly, advanced AFM modes such as conductive AFM (CAFM), magnetic force microscopy (MFM), electrostatic / Kelvin force microscopy (EFM/KFM), scanning thermal microscopy (SThM) or mechanical mapping, provide functional information beyond SEM capabilities. For that, special nano-probes are required, which typically achieve their intended functionality by additional thin film coatings, which contains two main disadvantages. First, they increase the apex radii and limit the lateral resolution, which is in conflict with the still decreasing feature sizes. Secondly, coatings are prone to delamination during operation, which affects resolution, lateral correlation and reliability. Therefore, to exploit the full potential of advanced AFM modes, it is of great interest to develop new approaches for the fabrication of functional nano-probes. Following that motivation, we joined forces with industry and apply the additive direct-write technology focused electron beam induced deposition (FEBID) for the development of novel 3D nano-probe concepts with industrial relevance. In this contribution, we briefly discuss the 3D nano-printing process and then go through a variety of advanced, FEBID-based tip concepts for CAFM, EFM, MFM and SThM. The joint element for all probes is the coating-free character, which eliminates the aforementioned risks during operation. Additionally, the apex regions are routinely in the sub-10 nm regime, which allows for high-resolution imaging. Aside of comparisons to traditionally used nano-probes, which reveal the superior performance of FEBID-based nano-tips, we discuss on currently ongoing research towards multi-functional AFM tips, based on FEBIDs flexibility.

11:00am **NS+2D+EM+MN+SS-TuM-10 Chemical, Mechanical, and Morphological Evolution of Nanostructures on the Surfaces of Asphalt Binders***, L. Lyu, J. Pei,* Chang'an University, China*; E. Fini,* Arizona State University*; L. Poulikakos,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; **Nancy Burnham**,* Worcester Polytechnic Institute

Bitumen (asphalt binder) holds roads together. It is a complex, dynamic, nanostructured material that comes from the bottom of an oil refinery stack—a non-renewable resource. It ages, and it ages more quickly under the influence of heat and light. Can additives made from waste materials increase the longevity of bitumen, and thus roads?

In this study, atomic force microscopy (topography, phase imaging, PF-QNM) and its combination with infrared spectroscopy (AFM-IR) were used to explore the chemical, mechanical, and morphological evolution of the surface of bitumen without and with additives. Aging is assumed to begin at the surface.

Samples of bitumen were made with and without introducing bio-modified rubber additives. Each sample was exposed to several thermal and UV aging protocols. Evolution of surface under aging was studied. Depending on the additive and type of aging (thermal, UV, or combined), the nanostructures changed their chemistry, mechanical properties, and size. Furthermore, the matrices and phases immediately surrounding the nanostructures evolved differently upon aging than the included nanodomains. In general, carbonyl and sulfoxide IR bands became more prevalent, the samples became stiffer and less adhesive, and the phase immediately surrounding the nanostructures became smaller. One additive made from two different waste materials was found to enhance the stability of the surfaces.

By understanding the evolution of asphalt binders and which additives promote their stability, longer lasting roads might be designed and built, thereby lowering the need for a non-renewable resource.

11:20am **NS+2D+EM+MN+SS-TuM-11 Identifying Potential Carbon Sources for Direct Carbon Material Production by AI Assisted HR-AFM***, **Percy Zahl**,* Brookhaven National Laboratory*; Y. Zhang,* ExxonMobil Technology and Engineering Company*; S. Arias,* Brookhaven National Laboratory

High-resolution Atomic Force Microscopy (HR-AFM) has proven to be a valuable and uniquely advantageous tool for studying complex mixtures such as petroleum, biofuels/chemicals, and environmental or extraterrestrial samples. However, the full potential of these challenging and time-consuming experiments has not yet been fully realized. To overcome these bottlenecks and enable further research into solutions for the energy transition and environmental sustainability, automated HR-AFM in conjunction with machine learning and artificial intelligence will be crucial [1].

In this study, we focus on identifying potential carbon sources suitable for more direct carbon material production by analyzing various pitch fractions based on their solubility in toluene. Specifically, we present the first comprehensive AI-assisted study of hydrocarbon fractions derived from petroleum and coal tar pitch, using and refining our previously introduced "Automated HR-AFM" tools. We explored four classes derived from Petroleum Pitch (PP) and Coal Pitch Tar (CPT), separated into toluene soluble (TS) and toluene insoluble (TI) fractions. Our analysis revealed differences in the structural characteristics of the molecules, which we binned based on the number of aromatic rings.

(Please see also the in our supplemental document included figures 1 and 2)

Overall, our results demonstrate the potential of automated HR-AFM and AI-assisted analysis for understanding complex mixtures and identifying potential carbon sources for direct carbon material production. This work represents an important step towards more sustainable and environmentally-friendly energy solutions.

Reference:

[1] Yunlong Zhang, Energy & Fuels 35(18), 14422 (2021)

11:40am **NS+2D+EM+MN+SS-TuM-12 Automated Microscopy for Physics Discovery: From High-Throughput to Hypothesis Learning-Driven Experimentation***, **Yongtao Liu**, R. Vasudevan, M. Ziatdinov, S. Kalinin,* Oak Ridge National Laboratory

In this work, we explore the ferroelectric polarization switching in relation to the applied pulse bias including bias voltage and time in scanning probe microscopy (SPM). We perform two types of automated and autonomous experiments. First, we conduct automated high-throughput experimentation to gain a comprehensive understanding of the relationship between pulse biases and ferroelectric domain growth. Second, we employ an autonomous experimentation driven by machine learning (ML) algorithm to optimize experimental conditions based on real-time experiment results.

SPM has proven to be a powerful tool for manipulating and visualizing ferroelectric domains at the nanoscale. Investigations of ferroelectric domain size and stability can advance our knowledge of ferroelectrics application in memory devices, such as operating time, retention time, and bit size. However, conventional SPM measurements have been time-intensive and dependent on experienced researchers to perform repetitive tasks and make real-time decisions regarding measurement parameters. For example, researchers determine and manually tune the parameters for next iteration of experiment according to the previous results.Here, we perform automated and autonomous experiments in SPM to explore the mechanism of ferroelectric polarization. The first experiment is a high-throughput experiment of applying various bias pulse conditions to write ferroelectric domains followed by imaging domain structure using piezoresponse force microcopy. In this automated experiment, we systematically adapt the bias pulse parameters to gain a comprehensive understanding of their relationship with the resulting domain structures. We discovered different polarization states that show up upon different bias conditions. In the second experiment, we implement a hypothesis active learning (HypoAL) algorithm based on structured Gaussian process to control the SPM for ferroelectric domain writing. The HypoAL analyzes the relationship between the bias pulse conditions and the written domain size in real-time experiments, and determines the bias pulse parameters for the next iteration. The goal of HypoAL is to establish the best physical hypothesis for the material's behaviour within the smallest number of experiment step.The HypoAL identifies that the domain growth in a $BaTiO_3$ film is governed by kinetic control. The approaches developed here have the potential to be extended to other experiments beyond SPM in the future to accelerate the discovery of new materials and advances in physics.

Surface Science Division

Room D136 - Session SS+2D+AS+HC-TuM

Oxide and Chalcogenide Surfaces and Interfaces

Moderators: Rachael Farber, University of Kansas, **Gareth Parkinson**, TU Wien

8:00am **SS+2D+AS+HC-TuM-1 ViPErLEED: LEED-*I*(*V*) Made Easy***, **Alexander Michael Imre**[1]*, TU Wien, Austria*; F. Kraushofer,* TU Munich, Germany*; T. Kißlinger, L. Hammer,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; M. Schmid, U. Diebold, M. Riva,* TU Wien, Austria

Most surface science laboratories are equipped with a low-energy electron diffraction (LEED) setup. LEED patterns provide quick, qualitative insight into surface structure and ordering. However, the diffracted electron beams contain a large amount of additional structural information which is often ignored. By studying the diffraction intensities as a function of incident electron energy [LEED-*I*(*V*)], it is possible to quantitatively compare experimentally observed surfaces with structural models.

Despite the clear need for such a direct experiment-to-theory comparison, LEED-*I*(*V*) is only routinely used by few specialized groups. A main obstacle for widespread adoption is that existing solutions for LEED-*I*(*V*) analysis and simulation are time-consuming and hard to use for scientists who are not already experts in the field.

To resolve this issue, we have developed the Vienna Package for Erlangen LEED (ViPErLEED) – a package of three independent but complementary tools for easy LEED-*I*(*V*) acquisition and analysis. All parts of ViPErLEED will be released as open source at the time of publishing:

1. **Electronics:** We provide schematics and control software for electronics, which allows users to easily and cheaply upgrade most existing LEED setups for acquiring high-quality LEED-*I*(*V*) data. These ViPErLEED electronics are based on an Arduino microcontroller and can be home-built from off-the-shelf components. The associated control software synchronizes with the camera and automates the experiment.
2. **Spot-tracker:** ViPErLEED provides a plugin for the public-domain image processing program ImageJ, for spot tracking and extraction of LEED-I(V) spectra from series of raw diffraction images. The automatically extracted I(V) curves can be used for further analysis or as a fingerprint of the surface surface. The plugin package also provides user-friendly options for examination, selection and smoothing of the *I*(*V*) data.
3. **Simulation software:** For structure analysis, we introduce a Python package for calculation of LEED-*I*(*V*) spectra and structure optimization. This software is based on the established TensErLEED package and extends its functionality while still making it easy for new users to get started with the technique. It uses standard file formats for the surface structure, provides automated symmetry detection, and requires just a handful of parameters for running a structure determination.

8:20am **SS+2D+AS+HC-TuM-2 Quasicrystal-like Ordering of the $La_{0.8}Sr_{0.2}MnO_3$(001) Surface***, **Erik Rheinfrank**, G. Franceschi, L. Lezuo, M. Schmid, U. Diebold, M. Riva,* TU Wien, Austria

Lanthanum-strontium manganite ($La_{0.8}Sr_{0.2}MnO_3$, LSMO) is a perovskite oxide used as a cathode material in solid oxide fuel cells, which convert chemical energy to electrical energy. To gain deeper insights into the reaction mechanisms, it is important to understand the structure of the surface at the atomic scale. To this end, we grow atomically flat single-crystalline LSMO thin films on Nb-doped $SrTiO_3$ (STO) substrates via pulsed laser deposition (PLD). Previously, this has been achieved for the (110) orientation.[1,2. Here, we use a similar approach on the (001) surface that is commonly used for oxide-based electronics and spintronics. The as-grown films have a MnO_x terminated surface that shows a 4-fold symmetric structure in low-energy electron diffraction (LEED), best explained by a set of four basis vectors reminiscent of quasicrystals. Scanning tunnelling microscopy (STM) and Q+ non-contact atomic force microscopy (nc-AFM) reveal an aperiodic arrangement of tiles with rotation angles of ±26.6° and 90±26.6°, and a Fourier transform consistent with the LEED pattern. As for quasicrystals, the surface has a sharp diffraction pattern despite the lack of translational symmetry.

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

[1] Franceschi *et al.*, J. Mater. Chem. A, 2020, **8**, 22947-22961

[2] Franceschi *et al.*, Phys. Rev. Materials, 2021, **5**, L092401

8:40am **SS+2D+AS+HC-TuM-3 AVS Graduate Research Awardee Talk: The Selective Blocking of Potentially Catalytically-Active Sites on Surface-Supported Iron Oxide Catalysts***, **Dairong Liu**[1,2], N. Jiang,* University of Illinois - Chicago

The extensive research on ultrathin ferrous oxide (FeO) islands and films over the last few decades has significantly contributed to the understanding of their structural and catalytic properties.One important aspect that has been investigated is the surface properties of ultrathin FeO islands, particularly the role played by the edges of these islands in catalytic reactions, such as CO oxidation. So far, two different types of edge, Fe-terminated edge and O-terminated edge, have been identified in the well-growth FeO island. However, despite this significant progress, the local chemical properties of these two types of edges, including their metal affinity, have remained largely unexplored. Here, we used scanning tunneling microscopy (STM) to study the interaction of Pd and Pt with FeO grown on Au(111). Different Fe affinities for Pd and Pt are demonstrated by the preferential growth of Pd on the Fe-terminated edge and Pt on the O-terminated edge of FeO nanoislands, resulting in selectively blocked FeO edges. In addition to revealing the different metal affinities of FeO edges, our results provide new insights into the edge reactivity of FeO/Au(111) and suggest an approach for controlling the selectivity of FeO catalysts. By comparing the behavior of different edges in the catalysis reaction, the catalytic activity of these edges can be studied solely, thereby sheds light into the future modification of ferrous-based catalysts.

9:00am **SS+2D+AS+HC-TuM-4 Unraveling Surface Structures of Ga-Promoted Transition Metal Catalysts in CO_2 Hydrogenation***, **Si Woo Lee**, S. Shaikhutdinov, B. Roldan Cuenya,* Fritz Haber Institute of the Max Planck Society, Germany

Gallium-containing alloys with transition metals (TM) have recently been reported to be reactive in the selective hydrogenation of CO_2 for methanol synthesis. However, a full understanding of the Ga-promoted catalysts is still missing due to the lack of information about the *surface* structures formed under reaction conditions. In this respect, studies using surface-sensitive techniques applied to well-defined model systems can provide key information to elucidate the reaction mechanism and provide the basis for the rational design of Ga-promoted catalysts.

In this work, we employed *in-situ* Near Ambient Pressure Scanning Tunneling Microscopy (NAP-STM) and X-ray Photoelectron Spectroscopy (NAP-XPS), which make it possible to study surfaces in the reaction conditions, for monitoring the structural and chemical evolution of the Ga-covered Cu surfaces in the CO_2 hydrogenation reaction. NAP-STM images recorded in the reaction mixture revealed temperature- and pressure-dependent de-alloying of the initially formed, well-ordered $(\sqrt{3}\times\sqrt{3})R30°$-Cu(111) surface alloy and the formation of Ga-oxide islands embedded into the Cu(111) surface, exposing GaO_x/Cu(111) interfacial sites. Notably, in our atomically-resolved STM image of Ga-oxide/Cu(111), it is clearly observed that Ga-oxide grows into an ultrathin oxide layer form with $(4\sqrt{3}\times4\sqrt{3})R30°$ superstructure. From NAP-XPS studies on Ga/Cu(111) in the presence of CO_2 and H_2, the formation of formate was observed, and this reaction intermediate was eventually transformed into methoxy at elevated temperatures, representing the final surface-bound intermediate for methanol synthesis. In contrast to Ga-containing Cu catalyst, on the other hand, there was no reaction intermediate at high temperature on the Ga-free Cu(111) surface, demonstrating that further reactions do not occur anymore from chemisorbed $CO_2^{\delta-}$ on Cu surface alone. Therefore, the GaO_x/Cu interface formed under reaction conditions may expose catalytically active sites never considered for this reaction before. We believe that our experimental results shed light on the complex surface structure of Ga-containing catalytic systems, which is only possible to obtain using state-of-the-art experimental techniques under reaction conditions. Only by establishing the atomic structure of the Ga-oxide layer(s) and its interface to the transition metal under working conditions can one bring insight into the reaction mechanism of this methanol synthesis catalyst.

9:20am **SS+2D+AS+HC-TuM-5 Ultrathin Metal Oxide, Nitride and Sulfide Films: Bringing the Well-Known Compounds to a Unit-Cell Thickness***, **Mikołaj Lewandowski**,* NanoBioMedical Centre, Adam Mickiewicz University in Poznań, Poland **INVITED**

Bringing the well-known materials from bulk size to a unit-cell thickness may significantly influence their structure and physicochemical properties. As an example, ultrathin (< 1-nanometer-thick) films of metal/non-metal compounds, such as metal oxides, nitrides or sulfides epitaxially grown on single-crystal supports, are characterized by unique electronic, catalytic and magnetic properties not observed for their bulk counterparts. Such films also exhibit superior structural flexibility, undergoing phase transitions upon exposure to external factors (such as reactive gases or high temperatures) [1,2]. All this makes them promising candidates for applications in various technological fields, including nanoelectronics, spintronics and heterogeneous catalysis.

Within the lecture, I will address the growth, structure and properties of ultrathin metal oxide, nitride and sulfide films, with compounds of iron as exemplary cases. The scanning tunneling microscopy and spectroscopy (STM/STS), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), low energy electron microscopy (LEEM) and density functional theory (DFT) results – obtained by my group and our collaborators – provide universal guidelines for designing ultrathin films with desired structure and properties [1–3].

[1] Y. Wang, G. Carraro, H. Dawczak-Dębicki, K. Synoradzki, L. Savio, M. Lewandowski, Applied Surface Science 528 (2020) 146032.

[2] N. Michalak, T. Ossowski, Z. Miłosz, M. J. Prieto, Y. Wang, M. Werwiński, V. Babacic, F. Genuzio, L. Vattuone, A. Kiejna, Th. Schmidt, M. Lewandowski, Advanced Materials Interfaces 9 (2022) 2200222.

[3] P. Wojciechowski, W. Andrzejewska, M.V. Dobrotvorska, Y. Wang, Z. Miłosz, T. Ossowski, M. Lewandowski, submitted (2023).

The author acknowledges financial support from the National Science Centre of Poland (through SONATA 3 2012/05/D/ST3/02855, PRELUDIUM 11 2016/21/N/ST4/00302 and M-ERA.NET 2 2020/02/Y/ST5/00086 projects), as well as the Foundation for Polish Science (First TEAM/2016-2/14 (POIR.04.04.00-00-28CE/16-00) project co-financed by the European Union under the European Regional Development Fund).

11:00am **SS+2D+AS+HC-TuM-10 Optimized Infrared Reflection Absorption Spectroscopy for Metal Oxides: Overcoming Challenges of Low Reflectivity and Sub-Monolayer Coverage***, **Jiri Pavelec**, D. Rath, M. Schmid, U. Diebold, G. Parkinson,* Vienna University of Technology, Austria

Infrared reflection absorption spectroscopy (IRAS) is a wide-spread technique in heterogenous catalysis, and it is an ideal tool for the comparison of real and model catalysts [1]. Most surface science groups perform IRAS studies either directly on metal single crystals, or on (ultra-)thin metal oxide films grown on such samples [2]. Achieving high-quality data from metal-oxide single crystal surfaces is difficult because their low reflectivity necessitates averaging many individual measurements with long acquisition times [3]. The goal of this work was to develop an IRAS setup for studying the adsorption of molecules on model “single-atom” catalysts. Here, the low reflectivity of oxide support is exacerbated by the sub-monolayer coverage of adsorbates on single adatoms. In the contribution, I will present the novel IRAS system we have developed to overcome these two challenges.

The main improvements over commonly-used setups are a high numerical aperture, an optimized optical path, control of the incidence angle range, and high mechanical stability. The high numerical aperture of the optical system leads to an increase in the amount of light reflected from a small single crystal sample. This is achieved by placing both the illumination and collector mirrors inside the UHV chamber close to the sample. To minimize the loss of signal, optimization of the optical path was performed using a ray tracing program. The other limit is the small area on the sample that is covered with adsorbates: in our setup, a molecular beam delivers adsorbates with a spot diameter of 3.5 mm [4]. Infrared light is reflected only from this area.

The reflectivity and absorbance of non-metallic samples varies strongly with incidence angle, and can even change a sign, leading to cancellation. The optimum angle ranges are different for every material. As our setup has a large range of incident angles, we can use this to our advantage: Using two adjustable aperture plates, we can vary the minimum and maximum incidence angle from 49° to 85° to maximize the signal for each single crystal sample. Angle control also allows us to optimize the signal for both p-polarized and s-polarized light independently.

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[1] **AVS Graduate Research Awardee**

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

We successfully executed and compared D_2O and CO absorbance measurements on a rutile $TiO_2(110)$ surface, and our results agree with the established literature [3]. By properly selecting the incidence angle range, we achieved a signal-to-noise ratio of ~16 for 1 ML CO adsorbed on TiO_2 with only 150 seconds of measurement time.

[1] F. Zaera, Chem. Soc. Rev., 43, 2014
[2] J. Libuda et al., J. Chem. Phys., 114, 10, 2001
[3] N. G. Petrik et al., The Journal of Physical Chemistry C, 126 (51), 2022
[4] J. Pavelec et al., J. Chem. Phys., 146, 2017

11:20am **SS+2D+AS+HC-TuM-11 VO Cluster-Stabilized H_2O Adsorption on a TiO_2 (110) Surface at Room Temperature**, ***Xiao Tong***, Brookhaven National Laboratory

We probe the adsorption of molecular H_2O on a TiO_2 (110)-(1 × 1) surface decorated with isolated VO clusters using ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) and temperature-programmed desorption (TPD). Our STM images show that preadsorbed VO clusters on the TiO_2 (110)-(1 × 1) surface induce the adsorption of H_2O molecules at room temperature (RT). The adsorbed H_2O molecules form strings of beads of H_2O dimers bound to the 5-fold coordinated Ti atom (5c-Ti) rows and are anchored by VO. This RT adsorption is completely reversible and is unique to the VO-decorated TiO_2 surface. TPD spectra reveal two new desorption states for VO stabilized H_2O at 395 and 445 K, which is in sharp contrast to the desorption of water due to recombination of hydroxyl groups at 490 K from clean TiO_2(110)-(1 × 1) surfaces. Density functional theory (DFT) calculations show that the binding energy of molecular H_2O to the VO clusters on the TiO_2 (110)-(1 × 1) surface is higher than binding to the bare surface by 0.42 eV, and the resulting H_2O-VO-TiO_2 (110) complex provides the anchor point for adsorption of the string of beads of H_2O dimers.

11:40am **SS+2D+AS+HC-TuM-12 Synthesis and Multimodal Characterization of Thin-Film Oxides**, ***Dario Stacchiola***, Brookhaven National Laboratory

Thin films of metal oxides exhibit a variety of unique physical and chemical properties leading to broad applications in optics, microelectronics, optoelectronics, superconducting circuits, gas sensors, thermal catalysis, electrocatalysis, and solar energy harvesting. Many metal oxides can form stoichiometric and non-stoichiometric alloys and compounds with each other, commonly known as complex metal oxides. Alloy and compound formation, including growth and process conditions, offer great flexibility for manipulating the lattice, atomic scale structure motifs, and electronic structure to realize desired properties. In order to exploit this potential, knowledge about fundamental processes and atomic level structural information is required. We present here the synthesis and multimodal characterization of mixed-oxide films based on silica and titania, from single layers to complex metal oxides.

1. "Deciphering phase evolution in complex metal oxide thin films via high-throughput materials synthesis and characterization", Nanotechnology 34, 125701 (2023)

2. "Resolving the evolution of atomic layer deposited thin film growth by continuous in situ X-ray absorption spectroscopy", Chem. Mat. 33, 1740-1751 (2021)

3. "First-Principles Study of Interface Structures and Charge Rearrangement at the Aluminosilicate / Ru(0001) Heterojunction" J. Phys. Chem. C 123, 7731–7739 (2019)

12:00pm **SS+2D+AS+HC-TuM-13 Atomic Structure of Reconstructed Al_2O_3(0001) Surface**, *J. Hütner, A. Conti,* TU Wien, Austria*; D. Kugler,* CEITEC, Czechia*; F. Mittendorfer, U. Diebold, M. Schmid,* ***Jan Balajka***, TU Wien, Austria

Corundum α-Al_2O_3 is an important ceramic widely used in electronics, optical applications, or as catalyst support. Despite its importance, the atomic structure of the most stable (0001) termination has not been conclusively determined. Detailed studies of Al_2O_3 surfaces have been stymied by its insulating nature, preventing the use of many surface science methods.

Structural models based on surface X-ray diffraction (SXRD) [1], and atomic force microscopy (AFM) [2], concluded the $(\sqrt{31} \times \sqrt{31})R\pm 9^\circ$-reconstructed Al_2O_3(0001) surface formed upon high-temperature annealing is terminated by one or two layers of metallic Al strained to lattice-match the oxide substrate.

We imaged the reconstructed Al_2O_3(0001) surface with noncontact AFM (nc-AFM) using specifically functionalized tips for chemically-sensitive contrast. In particular, CuO_x terminated tips [3], enabled us to directly identify oxygen and aluminum atoms in the topmost layer.

With the aid of *ab-initio* calculations, we propose a structural model of the $(\sqrt{31} \times \sqrt{31})R\pm 9^\circ$-reconstructed Al_2O_3(0001) surface consistent with atomically resolved nc-AFM images and area-averaging spectroscopic data. Unlike prior models, the surface does not contain a metallic Al layer but consists of oxygen and aluminum atoms arranged in similar structural units as reported in thin AlO_x films [4,5].

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2D Materials Technical Group
Room C123 - Session 2D+TF-TuA

2D-Materials: Synthesis

Moderators: David Johnson, University of Oregon, **Peter Liljeroth**, Aalto University

2:20pm **2D+TF-TuA-1 High-Order Van Der Waals Superlattices and Artificial Quantum Solid Beyond Mechanical Exfoliation and Restacking*, Xiangfeng Duan,*** UCLA **INVITED**

The advent of two-dimensional atomic crystals (2DACs) and van der Waals heterostructures (vdWHs) has inspired a new thinking on heterostructure construction beyond the limits of lattice matching requirement. However, the vdWHs explored to date have been largely limited to relatively simple systems with a small number of building blocks. The preparation of high-order vdW superlattices with a larger number of alternating units is exponentially more challenging due to the limited yield and scalability of the commonly used exfoliation-and-restacking strategy. Here I will discuss strategies to create high-order vdW superlattices (vdWSLs). First, by exploiting a capillary-force-driven rolling-up process, we show a series of synthetic VDWHs can be transformed into high-order vdWSLs with alternating atomic layers of widely variable material compositions, electronic band offset dimensions, chirality and topology. Alternatively, we further discuss a molecular intercalation approach to prepare a new family of hybrid superlattices consisting of alternating layers of covalently bonded 2D atomic layers and self-assembled molecular layers, which opens the door to exploit highly versatile molecular design strategies to tailor solid-state materials, enabling artificial materials with designable structural motifs and tunable electronic properties beyond the reach of conventional crystalline solids. We will particularly highlight a recent example of a new class of chiral molecular intercalation superlattices with robust chiral-induced spin selectivity. The formation of high-order vdW superlattices defines a rich artificial materials platform to unlock previously inaccessible physical limits and enable new device concepts beyond the reach of the existing materials.

3:00pm **2D+TF-TuA-3 Understanding the Sequential Growth of Bilayer MoS2 on SiO2 Substrate by Mo Isotope Labeling*, Kai Xiao,*** Center for Nanophase and Materials Sciences Oak Ridge National Laboratory*; Y. Yu,* School of Physics and Technology, Wuhan University, China*; J. Hachtel,* Center for Nanophase and Materials Sciences Oak Ridge National Laboratory*; M. Yoon,* Material Science and Technology Division, Oak Ridge National Laboratory*; A. Puretzky, A. Ievlev, C. Rouleau, D. Geohegan,* Center for Nanophase and Materials Sciences Oak Ridge National Laboratory

Bilayer 2D materials and heterostructures with different stacking configurations have attracted interest due to their emerging optical and quantum properties. Usually, it can be synthesized by the two-step chemical vapor deposition (CVD) method. Here we utilized isotope labeling method to study the CVD growth of bilayer MoS_2 on SiO_2/Si substrates. The stacking configuration and growth sequence were characterized by Raman spectroscopy, time-of-flight second ion mass spectroscopy (ToF-SIMS), and scanning transmission electron microscopy (STEM). We found that the growth of bilayer MoS_2 follows a sequential growth process which the second growth layer of MoS_2 goes underneath the fist growth layer. The AB and AA stacked bilayer MoS_2 are formed by templating the first growth single crystal MoS_2 layers. The embedded antiphase grain boundaries were characterized by atomic-resolution z-contrast STEM. Density functional theory (DFT) with molecular dynamic (MD) simulation were performed to understand the sequence growth pathway of bilayer MoS_2. This new understanding of the growth mechanism for bilayer MoS_2 can provide a new strategy for synthesis of 2D materials with controllable layer numbers and stackings.

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.

4:20pm **2D+TF-TuA-7 The Transformation from Dendritic to Triangular Ws_2 Growth via Nacl-Assisted Low-Pressure Chemical Vapor Deposition*, Himal Pokhrel,*** *J. Duncan, S. Pollard,* The University of Memphis

Monolayer tungsten disulfide (WS2) is one of the promising two-dimensional materials in the transition metal dichalcogenide family due to its remarkable optical, electronic, and electrocatalytic behavior. However, the structure of this material varies significantly with growth conditions. In this work, we use the salt-assisted low-pressure chemical vapor deposition (LPCVD) method to grow monolayer WS_2 crystals reaching over 50 µm in size on the SiO2/Si substrates. We observe a transition from large, dendritic to triangular growth by systematically varying the amount of promotor material (NaCl), growth temperature, and source-substrate distance. The synthesized material is characterized by Raman spectroscopy, scanning electron microscopy, and X-ray photoemission spectroscopy in order to understand the role of each parameter during the growth process. The results of this work provide a framework for the synthesis of large-area WS_2 growth with variable morphology through salt-assisted LP-CVD.

Kay words: Chemical vapor deposition, dendrites, WS_2

4:40pm **2D+TF-TuA-8 Hybrid Pulsed Laser Deposition Growth of Layered Chalcogenides*, Mythili Surendran,*** *H. Chen, J. Ravichandran,* University of Southern California

Mythili Surendran[1], Huandong Chen[1],Shantanu Singh[1], Boyang Zhao[1] and Jayakanth Ravichandran[1]

1. Mork Family Department of Chemical Engineering and Materials Science, University of Southern California

Chalcogenides, especially layered transition metal dichalcogenides, have emerged as an exciting class of materials that host several novel physical phenomena suitable for a broad range of electronic and photonic applications. High-quality thin film growth of these chalcogenides is critical to enable investigations into their fundamental properties and also for device applications. The thin films of layered chalcogenides are mostly grown using chemical vapor deposition, although molecular beam epitaxy, metal-organic vapor deposition, pulsed laser deposition (PLD) and several other techniques have been exploited. However, large area and high-quality growth with precise and uniform thickness control and low defect densities still remain a challenge due to a large cation-chalcogen vapor pressure mismatch, corrosive and reactive nature of most chalcogen precursors, high synthesis temperatures and the propensity to oxidize easily in the presence of oxygen at these high temperatures. In case of metal disulfides, most growth techniques utilize H_2S as the sulfur source. However, H_2S is a toxic, hazardous, and flammable gas and require high temperatures for efficient decomposition and sulfurization, resulting in high defect densities.

Here, we report an alternative hybrid PLD approach wherein we employed organo-sulfur precursors as sulfur source to grow chalcogenide thin films. This novel method enables low temperature growth (~500°C) of chalcogenides as the precursors decompose at a lower temperature (~250-400°C) to provide dissociated sulfur species. To demonstrate the efficacy of this approach, we have demonstrated large area epitaxial growth of Group IV 2D chalcogenides such as TiS_2 (metallic), ZrS_2 and HfS_2 (semiconducting). Structural and electrical characterization, along with low temperature transport studies reveal low defect densities and high carrier mobilities in these thin films. These results emphasize the importance of development of low temperature growth techniques for high mobility refractory metal-based chalcogenides for electronic applications, especially with back-end-of-line (BEOL) compatibility. The potential of these chalcogenides as suitable candidates for transparent and conducting layers in chalcogenide-based optoelectronic devices will be discussed. Further, we will also briefly discuss about the epitaxial growth of a variety of other chalcogenides such as 3D metal chalcogenides, chalcogenide perovskites, thus establishing the versatility of this novel method to grow chalcogenides for next-generation electronics and photonics.

5:00pm **2D+TF-TuA-9 Effect of Several Growth Parameters on Graphene Growth on Four Types of Supported Cu Films Using Cold Wall Cvd and Perspective on Growth Mechanism of Graphene from Scaling Functions of Graphene Island Size Distribution*, Shantanu Das,*** Intel Corporation

Graphene growth was explored on solid electrodeposited, recrystallized, sputter deposited and liquid Cu films supported on W or Mo refractory substrates under ambient pressure using Ar, H2 and CH4 mixtures using a custom-automated LabVIEW controlled graphene growth method in a custom-modified multi-chamber UHV chamber transformed into a cold wall CVD system. Among these films, electrodeposited Cu film was chosen to study the effect of total flow rate, CH4:H2 ratio and dilution of the CH4/H2 mixture by Ar at a fixed substrate temperature of 1000 °C and total pressure of 700 Torr, on the nucleation density and average size of graphene crystallites. The resulting morphological changes correspond with those that would be expected if the precursor deposition rate was varied at a fixed substrate temperature for physical deposition using thermal evaporation. The evolution of graphene crystallite boundary morphology with decreasing effective C deposition rate indicates the role of edge diffusion of C atoms along the crystallite boundaries, in addition to H2 etching on graphene crystallite shape. The results indicate that graphene grown on Cu films using cold wall CVD follows a classical two-dimensional nucleation and growth mechanism. Following nucleation at the earliest growth stages, isolated crystallites grow, impinge and coalesce to form a continuous layer. During the pre-coalescence growth regime, the size distributions of graphene crystallites exhibit scaling which is a function of island area, graphene coverage, average island area and areal density. For graphene grown on Cu surfaces that have been annealed in a reducing Ar+H2 ambient, excellent data collapse onto a monotonically decreasing universal Avrami scaling function is observed irrespective of graphene coverage, surface roughness or Cu grain size. This result is interpreted to indicate attachment limited growth and desorption of C-containing species. Graphene grown on Cu surfaces that were annealed in a nonreducing environment exhibits a qualitatively different bimodal scaling function indicating diffusion-limited growth with a lower attachment barrier combined with C detachment from the graphene edges. Graphene growth on molten Cu films supported on custom-designed Mo substrates demonstrate a similar 2D nucleation and growth mechanism. The roles of temperature gradient, chamber pressure and rapid thermal heating in C precursor-rich environment on graphene growth morphology on thin sputtered Cu films are explained. I anticipate that applying the study of pre-coalescence size distribution method to other 2D material systems may be useful for elucidating atomistic mechanisms of film growth that are otherwise difficult to obtain.

5:20pm **2D+TF-TuA-10 Decoupling of Graphene from Metal Substrate via Interface Epitaxy***, **Abdullah Al-Mahboob**, J. Sadowski,* Center for Functional Nanomaterials, Brookhaven National Laboratory

The research on two-dimensional quantum materials (2DQM) received significant attention in both, theoretical and experimental physics. Among 2DQM systems, graphene (Gr) remains a material of special interest since its discovery three decades ago. The interest in 2DQM research further evolved beyond Gr and its analogs (called Xenes) as these materials have potential for technological applications including quantum computing and quantum information.

The interest on Gr originated not only from well-known Gr stability in ambient conditions, massless Dirac carrier characteristics and feasibility of roll-to-roll production, but also successful use of Gr as a template for other 2DQMs. Despite the interest in Xenes other than Gr, such as silicene, antimonene, borophene, these materials are generally unstable at ambient conditions. In order to protect reactive Xenes and stabilizing their structure, Gr can also be also used as a protective inert coating. In the present study we explored a method of interfacial 2D growth under the inert overlayer, graphene.

We employed in-situ real-time low-energy electron/photoemission electron microscopy (LEEM/PEEM), micro-beam LEED, XPS/UPS and micro-spot ARPES for the study of interface chemistry of silicon allotropes and 2D silica structures grown at the Gr/Ru interface.

In this report, we show how the Si interface epitaxy can decouple Gr electronically from the catalyst Ru substate, and a successful scalable synthesis of Gr/√3-Silicene and Gr/Si/SiO_2 heterostructures can be realized. Tuning the growth conditions also provided means to control the growth of 2DQM at large scale. The strategy of interface epitaxy could be more general and opens the avenue of growing and stabilizing other atomically thin 2D materials.

Research was carried out at the Center for Functional Nanomaterials and the National Synchrotron Light Source II at Brookhaven National Laboratory under Contract No. DE-SC0012704.

5:40pm **2D+TF-TuA-11 Wafer-Scale, Phase-Selective Growth of Two-Dimensional Indium Selenides by Metal-Organic Chemical Vapor Deposition***, **Seunguk Song**, S. Jeon, M. Rahaman, J. Lynch, D. Rhee, P. Kumar, S. Chakravarthi, G. Kim, X. Du,* University of Pennsylvania*; E. Blanton,* KBR Inc.*; K. Kisslinger,* Brookhaven National Laboratory*; M. Snure,* Air Force Research Laboratory, Sensors Directorate*; N. Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA*; E. Stach, R. Olsson III, D. Jariwala,* University of Pennsylvania

The two-dimensional (2D) indium selenides (InSe and In_2Se_3) have garnered attention as a highly desirable ultrathin III-VI semiconductor, possessing favorable qualities akin to III-V semiconductors and 2D van der Waals transition metal dichalcogenides. However, due to the complexity of the In-Se system and challenges related to promoting lateral growth, large-area, phase-selective synthesis of 2D InSe and In_2Se_3 has proved difficult. Here, our work presents a successful method for the growth of high-quality and thickness-controlled 2D InSe and In_2Se_3 thin films using vertical, cold-walled metal-organic chemical vapor deposition. By interrupting the Se source periodically, we create an environment deficient in Se that favors the nucleation of InSe over In_2Se_3. Additionally, pulsing the Se precursor promotes lateral growth of InSe at low temperatures (360-500 °C), allowing us to produce highly stoichiometric, crystalline thin films on 2-inch sapphire substrates. Importantly, these growth temperatures are compatible with back-end-of-line integration in Si microelectronics. The resulting 2D domains are oriented along the crystal structure of the substrate, and the thickness can be controlled by growth time. We also demonstrate the fabrication of few-layer InSe transistors with high on-to-off current ratios (~10^4-10^5) and field-effect mobility (~2.8 $cm^2V^{-1}s^{-1}$) comparable to that of mechanically exfoliated single crystals of InSe. In the case of a few-layer In_2Se_3, its inherent ferroelectric nature allows us to evaluate its potential as a ferroelectric semiconductor field-effect transistor with non-volatile memory. Our work offers a promising approach for creating phase-pure 2D InSe and In_2Se_3 films at the wafer scale, which can be adapted for other material systems with multiple polymorphs.

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP1+2D+EM+PS+TF-TuA

Atomic Layer Processing: Integration of Deposition and Etching

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

2:20pm **AP1+2D+EM+PS+TF-TuA-1 Combination of Plasma-Based Atomic-Scale Deposition and Etching Processes for Advanced Patterning***, **Marceline Bonvalot**,* LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY College of Nanoscale Science and Engineering*; r. gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France*; N. Possémé,* STmicroelectronics, France **INVITED**

Selective Deposition processes have gained increased research interest in recent years, because they enable the accurate placement of a thin film on a specific substrate surface (in the case of area selective deposition ASD) or on specifically oriented surfaces (in the case of topographical selective deposition TSD). Such processes require atomic-scale precision, and usually involve Atomic Layer Deposition techniques, with possibly plasma assistance. Several pathways have been proposed in the literature for ASD, most commonly implying surface inhibition treatments with dedicated chemical treatments (self-assembled molecules or small molecule inhibitors for instance) to increase the nucleation delay during the subsequent ALD growth. However, the dedicated inhibition behavior eventually deteriorates when exposed to a few ALD cycles, which requires that on the one hand, nuclei formed on non-growth surfaces be removed and on the other hand, the inhibitor be systematically regenerated.

In this presentation, we will show how the insertion of an *in situ* etching step in the overall ALD process can serve as an effective corrective treatment for this purpose. The etching periodicity in conventional deposition/etching duty cycles will be investigated in details. We will show that the etching step should preferentially be carried out before the transition from the Volmer-Weber 1D island growth mode to the 2D layer by layer growth mode on non-growth surfaces, to limit plasma-induced surface defects. Moreover, the 1D island growth mode seems to coincide with the onset of degradation for the surface inhibition treatment. In this context, it will be shown that the etching periodicity is a determining parameter for the successful development of a selective bottom-up growth strategy.

3:00pm **AP1+2D+EM+PS+TF-TuA-3 Application of Etching Reaction Models to Deposition Processes***, **Nobuyuki Kuboi**,* Sony Semiconductor Solutions Corporation, Japan **INVITED**

Advanced CMOS devices require highly intricate 3D stacked structures with varying aspect ratios such as FinFETs and GAAs [1]. Understanding the process properties of plasma etching [2] and deposition [3] processes based on their mechanism and combinations has become increasingly important in addressing this challenge. Additionally, microfabrication properties should be stably suppressed within a specific range during mass production. However, the monitoring system equipped in the process chamber is limited for mass production. Therefore, we propose predictive models for plasma etching and deposition that consider the physical and chemical aspects of the plasma and surface.

First, we briefly introduce simulations for fluctuations in the SiN etching rate influenced by the chamber wall condition, critical dimensions during Si gate etching caused by $SiBr_x$ by-products dependent on open area ratios on wafer/chip/local-pattern levels, damage distribution affected by local-pattern structure, ion energy, and hydrogen concentration in the SiO_2 and SiN films, and selectivity during SiO_2-ALE [4][5][6].

We then present a modeling and simulation of the deposition process as a motif of the SiN-PECVD process using a 3D voxel method that can be associated with the previous process, such as plasma etching [7]. The model can predict film properties as well as the coverage on a large-scale pattern. Reactions among voxels are considered pseudo treatments for atomistic interactions on the surface. A statistical ensemble method involving probabilities is used to express physical and chemical phenomena such as sticking, migration, and bond formation on the deposited surface. The sticking and bond probabilities are affected by surface damage and IEADFs, respectively. Our model can successfully reproduce the experimental characteristic relationship between the morphology and film density dependent on the SiH_4 flow rate during the low temperature (120 ºC) SiN-PECVD process considering different gas residence times that affect surface reactions. Furthermore, we discuss the issue of modeling the ALD process.

These simulation technologies can aid in optimizing the chamber wall condition, pattern design, and etching/deposition combination process.

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4:20pm **AP1+2D+EM+PS+TF-TuA-7 Recent Advancements for Atomic Layer Advanced Manufacturing Processes: Microreactor Direct Atomic Layer Processing (µDALP™)***, **Maksym Plakhotnyuk**, A. Varga, I. Kundrata,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* ATLANT 3D Nanosystems; Friedrich-Alexander Universität Erlangen-Nürnberg, Denmark **INVITED**

As the demand for miniaturized and complex devices continues to grow across various industries, the need for innovative and precise atomic layer advanced manufacturing (ALAM) technologies becomes increasingly apparent[1]. Our company, utilizing proprietary Microreactor Direct Atomic Layer Processing (µDALP™), is at the forefront of pushing sALD's capabilities and broadening its application horizons. The µDALP™ process undergoes the same cyclic ALD process but only in a spatially localized area.[2] The microreactor or micronozzle confines the flows of gases used for ALD within a defined µm-scale centric area on the substrate to deposit the desired material.[3]

ATLANT 3D's recent advancements in our novel µDALP™ technology have enabled innovation within the thin film deposition field ranging from ALD material development to rapid prototyping and manufacturing. The µDALP™ process enables multiple depositions e.g., depositions with varying film thicknesses, to be deposited onto a single wafer used to calculate a given processes growth rate within only a few hours, compared to days for a traditional ALD process. In Addition, innovation of applications including optics and photonics, quantum devices, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage are possible and have been demonstrated using µDALP™ technology.

Discussing the improvements to the µDALP™ process, we have decreased the process resolution, increased material compatibility, and accessible morphologies. Giving one example of the recent development in morphologies, films deposited with µDALP™ have conformal coverage of gratings, microchannels, and trenches up to a depth of 25 µm using a Platinum deposition process. **Fig. 1** demonstrates how a given ALD material process (in this case, Pt) can be used with ATLANT 3D technology to deposit localized area conformal coatings of complex surfaces with an aspect ratio of 1:25. Hence demonstrating the versatility and potential of our technology for achieving inherently selective ALD for processing on complex surface morphologies.

This talk aims to shed light on how our breakthroughs in spatial ALD and µDALP™ technology contribute to the advancement of ALAM and scale-up. Fostering a deeper understanding of our technology's capabilities and exploring the possibilities it opens up for various industries.

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Nanoscale Science and Technology Division
Room B113 - Session NS1+2D+EM+MN-TuA

Nanofabrication and Characterization of Low-Dimensional Materials

Moderator: Georg Fantner, EPFL

2:20pm **NS1+2D+EM+MN-TuA-1 Atomic-Scale Design and Defect Networks at the 2D/3D Interface***, **Kate Reidy**,* MIT **INVITED**

'Mixed dimensional' 2D/3D van der Waals heterostructures, where 3D metallic nanostructures are integrated with suspended two-dimensional (2D) van der Waals materials, show unique functionalities including light-matter coupling, charge transfer, and enhanced catalytic activity. To enable such integration, an understanding of how structure and defects at the 2D/3D interface affect heterostructure properties is required. Moreover, 2D/3D heterostructures display fluctuations of opto-electronic properties in nanometer spatial range; and it is advantageous to probe position-dependent properties at the same spatial scales. In this seminar, I will share work exploring the local properties of the 2D/3D interface using a combination of atomic resolution scanning transmission electron microscopy (STEM), in situ ultra-high vacuum (UHV) TEM, and monochromated high-energy resolution electron energy-loss spectroscopy (EELS). We demonstrate epitaxial, single-crystalline metallic nanoisland growth of technologically relevant metals (Au, Ti and Nb) with with ultra-low defect density interfaces and facetted morphologies on several thin suspended 2D materials. We then explore the key parameters of 2D/3D growth, including the role of temperature, defects, moiré, surface chemistry, and thermodynamic equilibrium shapes. Lastly, we fabricate more complex heterostructure stacks with defect densities controlled by the compliance of the 2D material substrate. Through fundamental understanding of the structure-property-performance relationship, we suggest that future electronic, magnetic, and optical nanodevices will utilize versatile fabrication of 2D/3D heterostructures with well-characterized interfaces and morphologies.

3:00pm **NS1+2D+EM+MN-TuA-3 Highly Asymmetric Doping of Epitaxial Bilayer Graphene by Targeted Bonding of the Intercalated Gadolinium***, **Marek Kolmer**,* Ames National Laboratory*; J. Hall,* Ames National Laboratory and Department of Physics and Astronomy, Iowa State University*; S. Chen, M. Tringides,* Ames National Laboratory, Department of Physics and Astronomy, Iowa State University

Heterostructures consisting of vertically stacked two-dimensional (2D) materials have recently gained large attention due to their highly controllable electronic properties. Particularly, mechanically stacked multilayered systems offer exceptional control over a stacking sequence or interlayer twist angles. On the other hand, epitaxially grown 2D materials express unprecedented quality and stability over wafer-scale lengths. In both cases controlling the interlayer coupling can generate novel electronic and topological phases and its effective implementation is commonly done with a transverse electric field. However, phases generated by high displacement fields are elusive.

Here, we introduce an exceptionally large displacement field by structural modification of a model system: AB-stacked epitaxial bilayer graphene (BLG) on a SiC(0001) surface. We show that upon intercalation of gadolinium with two specific interlayer locations, electronic states in the top two graphene layers exhibit a significant difference in the on-site potential energy (~1 eV), which effectively breaks the interlayer coupling between them. As a result, for energies close to the corresponding Dirac points, the BLG system behaves like two electronically isolated single graphene layers. We prove this fact by a comprehensive multi-technique methodology based on low-temperature scanning tunneling microscopy/spectroscopy (STM/S) and angle-resolved photoelectron spectroscopy, which are corroborated by density functional theory, tight binding, surface diffraction and multiprobe STM transport. The work presents charge transfer from intercalated metal atoms as a promising approach for the synthesis of 2D graphene heterostructures with electronic phases generated by giant displacement fields.

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4:20pm **NS1+2D+EM+MN-TuA-7 AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient Talk: Exfoliated 2D Nanosheets for Large-Area, Solution-Processed Optoelectronics***, **Lidia Kuo**[1], S. Rangnekar, V. Sangwan, M. Hersam,* Northwestern University

Two-dimensional (2D) materials exhibit thickness-dependent optoelectronic properties due to their atomically thin nature, unlike their bulk layered crystalline counterparts. In particular, semiconducting MoS_2 undergoes an indirect to direct bandgap transition as the thickness is decreased to the monolayer limit, leading to enhanced optical absorption and emission at the atomically thin scale. Liquid-phase exfoliation (LPE) is a scalable and cost-effective method for obtaining 2D materials from bulk crystals. However, the yield of monolayer sheets by LPE has been impractically low in previous work. The resulting LPE-processed optoelectronic devices have fallen short compared to nanosheets derived from mechanical exfoliation or chemical vapor deposition. Here, we demonstrate that LPE coupled with megasonic exfoliation – i.e., processing at megahertz frequencies compared to the kilohertz frequencies commonly utilized for LPE – yields an unprecedentedly high fraction of monolayer MoS_2. As a result, megasonic exfoliation enables ultrahigh responsivity in printed MoS_2 photodetectors as well as the first demonstration of electroluminescence for large-area, solution-processed MoS_2 films. This work establishes megasonic exfoliation as a scalable and generalizable approach for achieving optoelectronic-grade 2D semiconductors via LPE.

Nanoscale Science and Technology Division
Room B113 - Session NS2+2D+EM-TuA

Light-Matter Interactions at the Nanoscale

Moderator: Nancy Burnham, Worcester Polytechnic Institute

4:40pm **NS2+2D+EM-TuA-8 Highly Tunable Room-Temperature Exciton-Polariton Strong Coupling from Monolayer WSe_2 in Nanocavities***, P. Schuck, **Thomas Darlington**,* Columbia University **INVITED**

In the interaction of light and matter, strong coupling occurs when exchange between a photon and electronic transitions exceeds the relative loss rate leading to hybridization of the optical and electronic states. The behavior is well known in cavity quantum electrodynamics (QED), and is a fundamental ingredient in single photon quantum logic gates. In solid-state systems, many strong coupling phenomena have been explored between different material excitations. Plasmons in particular have attracted great interest owing to their small mode volumes, allowing for strong coupling of a plasmon and single quasi-particles excitations such as excitons, potentially recreating in the solid-state, at the nanoscale, and at elevated temperatures many of the phenomena previously studied in traditional trapped atom QED.

Here, I describe our investigations of strong coupling between TMD excitons and a tunable plasmonic nanocavity formed between a plasmonic tip and gold substrate. Strong coupling between plasmons and excitons has been observed in excitons systems: e.g., J-aggregates, and colloidal quantum-dots. While these systems offer large coupling strengths, the exciton transition energies are largely fixed, and vary randomly depending on variations in growth conditions. By contrast, TMDs offer strong exciton emission and large tunability of exciton energy by applied strain. We utilized this tunability to control coupling strengths in nanocavities in a proof-of-principle nano-electro-mechanical system (NEMS) platform, demonstrating the ability to continuously tune, between weak and strong coupling conditions where we observe both upper and lower polariton bands.

5:20pm **NS2+2D+EM-TuA-10 Surface Plasmon Characterization in Ag Nanotriangles for Evaluation of Fano Resonance Conditions***, **Nabila Islam**,* Department of Physics, Portland State University*; R. Word,* Department of Physics, Portland State University, Portland, Oregon*; E. Abdul, S. Rananavare,* Department of Chemistry, Portland State University*; R. Könenkamp,* Department of Physics, Portland State University

Surface plasmon resonances in metal nanostructures allow confinement of the electromagnetic field well below the light diffraction limit and have attracted research interest for a broad range of sensing applications [1]. The comparably broad spectral width of surface plasmon based sensors can be improved by coupling the plasmon resonance to other resonances to generate Fano resonances with the distinctive and sharp asymmetric Fano line-shape. We used photoemission electron microscopy to explore the spectral and spatial behavior of plasmon resonances in structures consisting of a single nanoscale triangular platelet on a substrate providing coupling to a waveguide layer or to an optically active excitonic layer. In our experiments stationary and propagating surface plasmons are optically excited in the nano-triangle at wavelengths around 820-900nm, and multi-photon electron-emission is used to obtain images of the lateral surface plasmon distribution. An aberration-corrected photoemission microscope allowed us to obtain a spatial resolution of ~15nm and a femtosecond pulsed Ti-sapphire laser provided the photon intensities needed for the 3-photon photoemission imaging process [2]. The analysis of the obtained images is done in optical simulations of the same experimental set-up and by calculating the plasmon electric field distribution which is then used to analyze and interpret the photoemission micrographs. The analysis allows to identify the prominent surface plasmon modes and to analyze their interaction to form stationary resonance patterns and propagating modes. Fano-resonances are established in the simulation by placing the triangles in the vicinity of an optical waveguide using an appropriate spacer layer [3]. The simulation then allows to optimize this type of arrangement and to determine locations where the Fano-resonance amplitudes are most pronounced. Simulations of this kind were also applied to the case of gold triangles on substrates provided with exciton and spacer layers. Our results indicate that both the high plasmon field strengths typical for single nanoparticle structures and the sharp spectral features available in Fano-resonances can be combined in these single nano-particle structures, thereby allowing improved resolution in sensor applications.

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5:40pm **NS2+2D+EM-TuA-11 Interconnected Plasmonic Nanogap Antennas for Photodetection via Hot Carrier Injection***, **John Grasso**, R. Raman, B. Willis,* University of Connecticut

Modern integrated circuits have active elements on the order of nanometers; however, optical devices are limited by diffraction effects with dimensions measured in wavelengths. Nanoscale photodetectors capable of converting light into electrical signals are necessary for the miniaturization of optoelectronic applications. Strong coupling of light and free electrons in plasmonic nanostructures efficiently confines light into sub-wavelength volumes with intense local electric fields. Localized electric fields are amplified in nanogap regions between nanostructures where enhancements can reach over 1000. Hot carriers generated within these high field regions from nonradiative decay of surface plasmons can be injected into the conduction band of semiconductors at room temperature, enabling sub-bandgap photodetection. The optical properties of these plasmonic photodetectors can be tuned by modifying antenna materials and geometric parameters like size, thickness, and shape. Electrical

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

interconnects provide connectivity to convert light into electrical signals. In this paper, we will describe the optical properties of plasmonic nanostructures with electrical interconnects and compare experiment and theory using finite-difference time-domain (FDTD) simulations. We will present experimental extinction data and FDTD simulations to elucidate how geometric structure and dielectric properties influence optical properties. We will present sub bandgap photodetection for nanostructures integrated with ALD deposited TiO_2, and investigate both wavelength and polarization dependence. We will also discuss how plasmonic heating effects contribute to photocurrent generation. These plasmonic nanogap antennas are subwavelength, tunable photodetectors with sub-bandgap responsivity for a broad spectral range.

2D Materials Technical Group
Room C123 - Session 2D-WeM

2D-Materials: Defects, Dopants, and Modifications

Moderators: Jin Myung Kim, University of California, Irvine, **Stuart Parkin**, MPI Halle

8:00am **2D-WeM-1 Developing Quantum Photon Sources from 2D Semiconductor Materials**, ***Xuedan Ma***, Argonne National Laboratory **INVITED**

Optical photons are ubiquitous in quantum communication and storage applications due to their long coherence times and ease to travel over long distances. On-demand quantum photon sources that may emit single photons as quantum information carriers are especially sought after for quantum-related applications. In this talk, I will present our recent effort in the development of solid-state quantum photon sources based on low-dimensional semiconductor materials. By atomic defect creation [1,2] and local strain field engineering,[3-7] we demonstrate versatile approaches for efficient single photon generation and modulation.

References:

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[6] W. Wang et al. *ACS Photon*. 7, 2460 (2021)

[7] L. Peng et al. *Nano Lett*. 20, 5866 (2020)

8:40am **2D-WeM-3 Bandgap Modulation of Graphene by Boron Nitride Doping**, ***Sergi Campos Jara***, Leiden University, The Netherlands; *L. Caputo,* Université Catholiqué de Louvain, Belgium; *T. Roorda, T. Benschop, A. Mozes,* Leiden University, The Netherlands; *V. Calvi, R. van Rijn,* Delft University of Technology, Netherlands; *M. P. Allan, I. M.N. Groot,* Leiden University, The Netherlands

Since its discovery, graphene has shown to exhibit remarkable electronic properties.[1] Numerous techniques have been devised to create high-performance devices by manipulating the bandgap in order to enhance their semiconducting properties.[2]

Doping has proven to be one of the most effective methods for bandgap engineering. Experimental and theoretical studies on graphene doping show the possibility of making p-type and n-type semiconducting graphene by substituting C atoms. Boron and nitrogen have been specifically studied during the last years due to the interesting insulating behavior of h-BN. Boron, nitrogen, and carbon can be atomically mixed to form various semiconducting, hexagonal, layered structures. Experimental and theoretical studies have indicated that BNC nanostructures show semiconducting properties with small bandgaps.[2,3] Low concentrations of borazine rings within the graphene structure can modify graphene's electronic properties to form a 2D semiconductor material with homogeneous patterns.[4,5]The intercalation of hexagonal BN (h-BN) within the graphene lattice has already been successfully achieved, however, segregation of both materials has been the main issue. Recent research has demonstrated that incorporating borazine-like molecules with carbon structures into graphene can result in reduced segregation of h-BN domains.[5,6] Herrera Reinoza et al. demonstrated a notable example by depositing hexamethylborazine onto Ir(111), which yielded numerous boron-nitrogen-carbon (BNC) domains exhibiting low BN segregation and an estimated bandgap ranging between 1.4 and 1.6 eV.[6]

To grow our boron nitride-doped graphene nanomaterial (Figure 1a) we first synthesized graphene via chemical vapor deposition (CVD) by cyclic exposures to 10^{-5} mbar of ethylene for 10 minutes with subsequent annealing at 1100 K for 10 minutes. We have successfully doped our graphene by exposing it to hexamethylborazine right after the 3rd cycle of graphene synthesis. Auger electron spectroscopy depicted in Figure 1b demonstrated the presence of B, C and N in the sample. As depicted in Figure 1c, a bandgap was opened on our BN-doped graphene, forming a semiconductor material.

9:00am **2D-WeM-4 Wafer-Scale Photoluminescence Enhancement for MoS_2 Monolayers Through Simple Wet-Chemical Defect Passivation in Acidic Hydrogen Peroxide Solution**, ***Dennis H. van Dorp***, IMEC Belgium; *L. van der Krabben,* Radboud University Nijmegen, Netherlands; *A. Brady-Boyd,* Aberystwyth University, UK; *C. Gort,* TU Darmstadt, Germany; *S. Arnauts, T. Nuytten, H. Medina Silva, E. Altamirano Sanchez,* IMEC Belgium; *J. Hofmann,* TU Darmstadt, Germany; *S. Brems,* IMEC Belgium

It is expected that in the 2030 timeframe, CMOS technology nodes could include not only Si based transistors, but also possible 'Beyond-CMOS' devices that are co-integrated with the classical CMOS-based solutions. The alternative devices could be used along CMOS for specific functions. For instance, devices are being explored that have two-dimensional transition-metal dichalcogenides (2D TMDCs) as their conduction channel.

While device processing strategies for conventional CMOS technologies are well established, the use of TMDCs as atomic channel material poses new problems. In such applications, both dry and wet etching are essential processing steps for nanodevice fabrication, e.g. for patterning, contacting, layer selective etching, and surface engineering purposes. In contrast to dry etching, that may induce surface damage in the form of chalcogenide vacancies, wet-chemical methods provide an attractive alternative that avoids the problem of surface damage. However, the atomic scale dimensions of the 2D layer require ultimate selectivity and control to maintain and or improve the electronic and optical properties at wafer-scale level. To meet these goals, in-depth insight is needed in the compatibility of TMDC's with wet-chemical solutions.

In this work, we will show the first semiconductor ICP-MS results on the atomic-scale etching kinetics of MoS_2 in acidic solutions. Despite the very small dimensions of TMDC atomic layers, a surprisingly high chemical stability is demonstrated for both multilayer and monolayer MoS_2. Controlled wet etching of the layers was achieved for dilute HCl/H_2O_2 solutions without significantly modifying the surface chemistry. In addition, it was found that wet-chemical treatment of MoS_2 can dramatically enhance the photoluminescence properties on wafer-scale level using simple acidic solutions that contain a strong oxidizing agent.

We will show that wet-chemical processing can be utilized to significantly lower defect related non-radiative decay in the monolayers through passivation of sulphur vacancies. Room temperature PL measurements were used to optimize the passivation step. PL enhancements of up to 3 orders of magnitude were consistently achieved. Wafer-scale PL mapping showed good uniformity across the 2-inch wafer. Cryo-PL measurements confirmed effective defect passivation through the quenching of the bound exciton peaks.

The data presented indicate a good wet-chemical compatibility of the atomic layer TDMC material which is highly relevant for future developments in the CMOS industry.

9:20am **2D-WeM-5 Metal-to-Semiconductor Transition Observed in the Surface Density of States of Ti-Te Layered Monoclinic Crystals via Forced Atmospheric Exposure**, ***Bishal Pokhrel***, *J. Quarnstrom, S. Shrestha, H. Helfrich, E. Echeverria, D. McIlroy, M. Borunda, A. Yost,* Oklahoma State University

Transition metal chalcogenides are promising 2D materials due to their unique properties and emerging phenomena such as charge density waves, superconductivity, ferroelectricity and ferromagnetism. Specifically the transition metal trichalcogenides of the form AX_3 (A=Ti, Zr, Hf, X=S, Se, Te) exhibit a quasi 1-D nature with anisotropic bandstructure which leads to preferential charge transport along the chain direction and minimal edge scattering effects suitable for fabricating high-performance devices. In this study, we examine the surface sensitivity of a high pressure grown Ti-Te transition metal chalcogenide using the chemical vapor transport (CVT) technique and study the surface changes in the sample upon exposure to air. The high-pressure growth results in the formation of silvery mirror-like sheets and nanowhiskers atypical of bulk 1T-$TiTe_2$ growth, which is usually black and non-reflective. The silvery materials are capable of mechanical exfoliation via the scotch tape method and if left in atmosphere turn a darker color within a few hours. The crystal structure and size of the sheets are examined using X-Ray Diffraction (XRD), transmission electron microscopy (TEM), and select area electron diffraction (SAED). The material adopts a preferential (001) single crystalline nature with monoclinic structure and P2 1/m space group symmetry. Additionally, the SAED patterns show signs of a superlattice formation at the surface of the exposed layer. The local density of states (LDOS) of the in-situ exfoliated sample surface, measured using scanning tunneling spectroscopy (STS), exhibits a metallic to semi-conducting transition, with narrow gap, when exposed to atmosphere, suggesting the surface rapidly decomposes. The STM topography indicates a decrease in surface roughness after exposure to atmosphere reminiscent of ad-layer/s formation at the surface. X-ray photoemission spectroscopy confirms the surface of the exposed sample contains -OH, O_2, -H, H_2O ad-atom species. Stability and reactivity of such layered materials has been a field of interest to researchers lately as these materials have the ability for extreme sensitivity when incorporated into a gas sensor device. In the interest of optical and gas sensing we fabricate simple FET devices and measure the opto-electronic properties while exposing to different wavelengths of light and gases (CO_2, H_2, H_2O, and N_2).

9:40am **2D-WeM-6 Correlated KPFM and TERS Imaging to Elucidate Defect-induced Inhomogeneities in Oxygen Plasma Treated 2D MoS_2 Nanosheets***, **Sanju Gupta**,* Penn State University

Modulating physical and chemical properties of two-dimensional (2D) transition metal dichalcogenides (TMDC) by defect-engineering induced by oxygen plasma is actively pursued. In this work, exfoliated 2D MoS_2 layers treated by medium power oxygen plasma for different times (0, 10, 20, 40, and 60 s) are investigated using Kelvin Probe Force microscopy and tip-enhanced Raman spectroscopy (TERS) besides micro-Raman and photoluminescence (PL) spectroscopy. Under oxygen plasma, defects (mono- and di-sulfur vacancies) and chemical oxidation is predominant from 0s (native defects) up to 40s, while etching becomes dominant beyond 40 s, for mono- (1L), bi- (2L), and tri- (3L) layer MoS_2 with optimal defect density for four- (4L) and more layers. While Raman spectra exhibited lattice distortion (broadening of phonon bands) and surface oxidation by the presence of sub-stoichiometric molytrioxide MoO_3 (*i.e.,* MoO_{3-x} or MoS_xO_{2-x}) the increased spectral weight of trions and quenching in PL spectra are observed with treatment time. The localized nanodomains (~20-40 nm) and aggregated vacancies as nanovoids and intermixed MoS_2/MoO_{3-x} alloy are identified in near-field Raman spectra. The atomic force microscopy also showed defects aggregation and Kelvin probe force microscopy revealed the work function (WF) increase from 4.98 eV to 5.56 eV, corroborating the existence of MoO_{3-x} phase which enables doping and shift Fermi level. We also highlight the unique interaction between the gold substrate and the formed MoO_{3-x} facilitating Mo^{6+} cation reduction to lower oxidation (*i.e.*, Mo^{4+}) thereby yielding intermediate oxidation states responsible for lower WF (*ca.* theoretical 6.3 eV for stoichiometric MoO_3). Strong correlations among the work function, vibrational and optical responses are established while exploring the oxygen plasma-induced defects and changing the landscape on oxygen doping at the nanoscale with varying MoS_2 layers, which are useful for heterogeneous electrocatalysis and applicable to other 2D TMDCs.[1]

[1] S. Gupta, A. Johnston, and S. Khondaker, J. Appl. Phys. **131**, 164303 (2022) and references therein.

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11:00am **2D-WeM-10 Imaging Carrier Motion in Graphene Using Scanning Tunneling Potentiometry***, V. Brar, **Zachary Krebs**,* University of Wisconsin - Madison **INVITED**

In this talk I will show how scanning tunneling potentiometry (STP) can be used to directly image the motion of charge carriers in graphene, revealing the manner that they scatter off defects, pass through potential barriers, and generate Hall voltages. In the ballistic regime, STP imaging allows for the semi-classical motion of graphene quasiparticles to be visualized over large lengthscales, and for their incoming/scattered wavefunctions to be imaged locally. Near potential barriers, this allows for the direct observation of Landauer residual resistivity dipoles and scattering processes involving quasibound states. When magnetic fields are applied, the carriers generate a Hall field that can be quantified using STM, and near potential barriers they are observed to take a spiral-like trajectory in low fields, and form bound states around the potentials in the quantum hall regime. We also probe the carrier motion as the graphene is heated and the electrons enter a hydrodynamic phase. In this regime, STP can be used to image the new fluid-like flow patterns of the electrons and quantify how those new flow properties reduce the macroscopic resistivity of the sample.

11:40am **2D-WeM-12 Interfacial Design of 2D Materials for Energy-Efficient Nanoelectronics***, **Huamin Li**,* University at Buffalo

With the rise of graphene (Gr) since 2004, two-dimensional (2D) have been extensively explored for energy-efficient nanoelectronics due to their novel charge transport properties compared to conventional three-dimensional (3D) bulk materials. However, there are still challenges and issues for the practical implementation of 2D materials. Here from the perspective of interfacial design, we take 2D semiconducting MoS2 as an example to review our recent research on energy-efficient nanoelectronics, ranging from synthesis, metal contact, and device demonstration. First, at the interface between MoS2 and substrates, an interfacial tension can be induced during high-temperature chemical vapor deposition (CVD) synthesis. Due to a mismatch of thermal expansion coefficients, the interfacial tension creates an anisotropy of in-plane charge transport and leads to a self-formed nanoscroll structure [DRC 2019]. Second, at the interface between MoS2 and metal contact, a monolayer h-BN decoration can enable novel manipulation of charge transport through quantum tunneling, in contrast with conventional thermionic emission [IEEE NMDC 2018; Adv. Mater. 2019]. Third, at the interface between MoS2 and other 2D materials, band-to-band Zener tunneling and cold-source charge injection can be enabled, giving rise to a superior transport factor (<60 meV/decade) in transistor configurations. These novel charge transport can overcome the fundamental limitations of “Boltzmann tyranny”, and realize tunnel transistors and cold-source transistors with sub-60-mV/decade subthreshold swings [IEEE IEDM 2020; ACS Nano 2020]. Fourth, at the interface between MoS2 and ferroelectric or ionic dielectrics, excellent electrostatic gating leads to a superior body factor (<=1), and also improves the energy efficiency for transistor operation [Nano Express 2023].

12:00pm **2D-WeM-13 Substrate Van Der Waals Force Effect on the Stability of Violet Phosphorous***, **Sarabpreet Singh**,* University of Georgia*; M. GhafariAsl,* University of georgia*; H. Ko,* Cornell University*; S. Gamage,* University of Georgia*; R. Distasio Jr.,* Cornell University*; M. Snure,* Air Force Research Laboratory*; Y. Abate,* University of Georgia

The weak van der Waals (vdWs) forces between monolayers has been a unique distinguishing feature of exfoliable materials since the first isolation of graphene. However, the vdWs interaction of exfoliable materials with the substrate and how this interface force influences the interaction of vdWs materials with the surroundings have yet to be well understood. Here, we experimentally and theoretically unravel the role of vdWs forces between the recently rediscovered wide band gap p-type vdW semiconductor violet phosphorus (VP), with various substrates (including, SiO_2, mica, Si, Au) and quantify how VP stability in air and its interaction with its surroundings is influenced by the interface force. Using a combination of infrared nanoimaging and theoretical modeling we find the vdWs force at the interface to be a main factor that influences how VP interacts with its surroundings. In addition, the hydrophobicity of the substrate and the substrate surface roughness modify the vdWs force there by influencing VP’s stability. We found that VP can maintain its stability for a prolonged period if it is exfoliated on SiO_2 substrate, followed by mica and Au substrates, and is least stable when placed on a Si substrate. Our results could guide in the selection of substrates when vdW materials are prepared and more generally highlight the key role of interface force effects that could significantly alter physical properties of vdWs materials. Our findings can assist in the choice of substrates to exfoliate vdWs materials and emphasize the crucial impact that interface forces can have on altering the physical properties of exfoliable materials.

Applied Surface Science Division
Room B117-119 - Session AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM

Multi-Modal & Multi-Dimensional Analysis

Moderators: Gustavo Trindade, National Physical Laboratory, UK, **Paul Mack**, Thermo Fisher Scientific, UK, **Tim Nunney**, Thermo Fisher Scientific, UK

8:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-1 Growth and Characterization of Large-Area 2D Materials***, **Glenn Jernigan**,* US Naval Research Laboratory **INVITED**

Nothing could be more coupled than Growth and Characterization. When two dimensional (2D) materials appeared on the radar of the scientific community (with the amazing properties of graphene), it was immediately obvious that large area samples would be needed. Exfoliating flakes was insufficient for the demands of scientific studies, in addition to not being viable should a commercial application be developed. Thus, the search began for growth methods to produce large-area 2D materials for large scale testing and development.

The Naval Research Laboratory has, over the past 15 years, pursued research programs in producing large areas of graphene, transition metal dichalcogenides (TMDs), boron nitride (BN), and other 2D materials. In every one of those programs, they began with surface analysis of composition, chemistry, and morphology of the grown films. The uniquely sensitive nature of x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and scanning tunneling and atomic force microscopy (STM and AFM) to 2D materials was necessary to measure the electrical, chemical, and physical properties obtained in the large area films and to understand what was observed in the exfoliated flakes. The production of large areas allowed "mass-scale" optical and electrical characterization, which then became a feedback loop in the search for new and interesting properties and relevant applications. In this presentation, I will show how we developed large-area graphene, by both epitaxial growth and chemical vapor deposition methods, TMDs, and other 2D materials for characterization and device utilization.

8:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-3 Using a Correlative Approach with XPS & SEM to Measure Functionalized Fabrics for Antimicrobial Applications***, **Tim Nunney**, H. Tseng,* Thermo Fisher Scientific, UK*; D. Marković, M. Radetić,* University of Belgrade, Serbia

Medical textiles are an indispensable component for a wide range of hygienic and healthcare products, such as disposable surgical gowns and masks, or personal protection equipment, with opportunities to provide further protection by engineering textiles with suitable medical finishing. While antibiotics are considered a viable option for their efficiency in treating bacterial infections, their abuse can result in adverse effects, e.g., bacteria resistance. Nanocomposites have emerged as a promising alternative to antibiotics, as the large surface-to-volume ratio and high activity helps attain the targeted antimicrobial efficiency by using tiny amounts of nanocomposites, and their biocompatibility and scalability are particularly advantageous for medical applications [1]. Thus, developing processing methods to integrate nanocomposites in the fabrics is essential for exploiting their properties for medical textiles.

In this study, polypropylene fabrics, alginate and copper oxides, were selected to develop novel antimicrobial nanocomposites based on various surface treatments, i.e. corona discharge and alginate impregnation, which led to improved fabrics hydrophilicity with functional groups introduced as binding sites for Cu(II), a precursor that formed Cu nanoparticles when reacted with reducing agents, i.e. NaBH4 and ascorbic acid. The composition of the fabrics after being treated with corona discharge and impregnation observed by XPS indicates the materials formed mainly consisted of C and O, attributed to the presence of a thin, hydrophilic layer and alginate, respectively, consistent with depth profiling measurements. Following Cu reduction, XPS mapping of the fabrics finds that, reacting with ascorbic acid resulted in formation of nanocomposites containing a mixture of Cu and Cu (II) oxides across the surface, which could be visualised by using SEM in the same locations. Excellent anti-microbial activity against Gram-negative bacteria E. coli, Grampositive bacteria S. aureus and yeast C. albicans was observed for the treated fabrics[2]. This result not only demonstrates a cleaner, and healthier approach for developing novel nanocomposites, but more importantly highlights the role of surface techniques in uncovering challenges in designing and engineering functional textiles.

References:

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[2] D. Marković, H.-H. Tseng, T. Nunney, M. Radoičić, T. Ilic-Tomic, M. Radetić, Appl. Surf. Sci., 527, 146829, (2020)

9:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-4 Multi-Modal Analysis in Photoelectron Spectroscopy: From High-Resolution Imaging to Operando Experiments***, **Olivier Renault**,* CEA-Leti, France*; A. Benayad,* CEA, France*; N. Gauthier,* CEA-Leti, France*; R. Charvier,* ST Microelectronics, France*; E. Martinez,* CEA-Leti, France

Over the past years, the field of surface and interface analysis has been greatly expanded by new developments made possible by lab-scale instruments enabling higher excitation energies. These new developments are directly serving technological advances especially in the area of technologies in renewable energies and nanoelectronics, which are adressing more and more complex system requiring to go beyond traditional ways of characterizing surfaces and interfaces. Different dimensions are to be explored in multi-modal surface analysis : the depth dimension, the lateral dimension, and the dynamic dimension.

After a short review of some of the achievements towards enhancing the depth dimension by lab-scale hard X-ray photoelectron spectroscopy (HAXPES) and the lateral dimension using X-ray PEEM, we will present different application cases of *operando* HAXPES. Here, the material is analyzed as being part of a device operated *in situ* during the experiment, in conditions that are as close as possible to the final applications and where the interfaces can be studied in dynamic conditions. We will first review some results of *operando* HAXPES on resistive memories obtained with synchrotron radiation [1, 2] before presenting various lab-scale experiments [3, 4] and the current limitations to such approaches.

[1]B. Meunier, E. Martinez, O. Renault et al. *J. Appl. Phys*. **126**, 225302 (2019).

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[4]A. Benayad et al., *J. Phys. Chem. A* 2021, 125, 4, 1069-81.

9:20am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-5 Multi-Modal Analyses of Ultrasonic-Spray-Deposited Ultrathin Organic Bathocuproine Films***, J. Chen, **Juliet Risner-Jamtgaard**, T. Colburn, A. Vailionis, A. Barnum, M. Golding,* Stanford University*; K. Artyushkova,* Physical Electronics*; R. Dauskardt,* Stanford University

Bathocuproine (BCP) is a small organic molecule that is typically used as an ultrathin hole blocking interlayer (< 10 nm thickness) in organic solar cells and perovskite solar cells. The film is typically deposited via low-throughput vacuum thermal evaporation with an *in-situ* Quartz Crystal Monitor to measure film thickness. Open-air ultrasonic spray deposition for low-cost and large-scale deposition is an attractive alternative method for solution processing of BCP films, but the process lacks a comparable *in-situ* metrology. Given that the BCP film is transparent to visible light and ultrathin, it is important to utilize a multi-modal approach to evaluate optoelectronic and physical properties of the sprayed film.

A suite of characterization techniques that span a range of equipment complexity, measurement time, and measurement sensitivity are used to analyze the BCP films. We begin by demonstrating the limitations of the singular ellipsometry model[1] for BCP found in literature and motivate a need to rely on other techniques. Multi-modal analyses including X-Ray Reflectivity, Angle-Resolved X-ray Photon Spectroscopy (AR-XPS), Auger Spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy with EELS are then performed on the sprayed BCP film. The advantages and disadvantages of each characterization technique are compared and discussed. We conclude that AR-XPS provides the most distinctive determination of individual layer thicknesses for a sample architecture consisting of silicon substrate/native SiO_x/BCP across the applicable range of AR-XPS from ~ 1-10 nm.

[1] Liu, Z.T., *et al*. The characterization of the optical functions of BCP and CBP thin films by spectroscopic ellipsometry. *Synthetic Materials*. 150(2):159-163. (2005)

9:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-6 Combinatorial Synthesis and High-Throughput Characterization of Pt-Au Thin Films Fabricated by Confocal Magnetron Sputter Deposition***, **David Adams**, R. Kothari, M. Kalaswad, C. Sobczak, J. Custer, S. Addamane, M. Jain, E. Fowler, F. DelRio, M. Rodriguez, R. Dingreville, B. Boyce,* Sandia National Laboratories

A few binary metal alloys are predicted to form thermally stable, compositionally segregated structures owing to the thermodynamic preference for minority species to collect and remain at grain boundaries established within the solid.(J.R. Trelewicz et al., PRB, 2009) When produced as a nanocrystalline thin film, these stable structures afford the potential to maintain excellent mechanical properties (e.g., high hardness) even after annealing to elevated temperature. Indeed, several systems, including $Pt_{.9}Au_{.1}$ thin films, are reported to develop thermally-stabilized, hard, nanocrystalline structures attributed to solute segregation at grain boundaries.(P. Lu et al., Materialia, 2019)

Future studies that seek optimal stoichiometry and/or preferred synthesis processes require access to a wide range of composition as well as an ability to vary key deposition parameters. Toward this end, our team reports on the challenges and the benefits of combinatorial synthesis for expediting the discovery of improved binary metal thin films. Our study utilized confocal sputter deposition wherein Pt and Au targets were individually sputtered via pulsed DC magnetron methods. Substrates (150 mm diameter wafers) were fixed in order to gain access to a wide compositional range for each deposition. The sputter power and cathode tilt orientation were then varied in subsequent depositions to access the nearly full binary metal compositional range. The binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films 2012), which simulates the transport of sputtered atoms within the process gas, helped guide the selection of these process parameters in order to achieve compositional goals in relatively few depositions. Notably, the binary compositions predicted by SiMTra closely matched (within a few molar %) the measured compositions determined by Wavelength Dispersive Spectroscopy completed in 112 different areas across each wafer. The various combinatorial Pt-Au films were further characterized by high-throughput Atomic Force Microscopy, automated X-ray Diffraction, fast X-ray Reflectivity, mapping four-point probe sheet resistance, and automated nanoindentation. These studies reveal how hardness, modulus, film density, crystal texture, and resistivity of combinatorial films varied with composition as well the atomistics of film deposition. Attempts to correlate key film characteristics with the kinetic energies and incident angles of arriving metal species (estimated by SiMTra) are discussed with a goal of improving fabrication processes.

Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

11:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-10 Optical and X-Ray Characterization and Metrology of Si/Si(1-X)Ge(X) Nanoscale Superlattice Film Stacks and Structures***, Alain Diebold,* SUNY Polytechnic Institute **INVITED**

As traditional scaling of transistors comes to end, transistor channels and capacitors are being stacked to form new 3D transistor and memory devices.Many of these devices are fabricated using films stacks consisting of multiple Si/Si(1-x)Gex layers known as superlattices which must be fabricated with near atomic precision.In this talk, we discuss how Optical and X-Ray methods are used to measure the feature shape and dimensions of these structures.The use of X-Ray methods such as ω-2θscans and reciprocal space maps provide layer thickness and stress characterization. We will use simulations to show how a buried layer with a different thickness or Ge concentration alters the data. Recent electron microscopy studies have quantified the stress at the interfaces of these superlattices.We will also discuss how Mueller Matrix spectroscopic ellipsometry (MMSE) based scatterometry is used to measure feature shape and dimension for the nanowire/nanosheet structures used to fabricate nanosheet transistors and eventually 3D DRAM.The starting point for optical scatterometry is determining the optical properties of stressed pseudomorphic Si(1-x)Gex.MMSE can be extended into the infra-red and into the EUV.In addition, small angle X-Ray scattering has been adapted into a method knows as CDSAXS which can be used to characterize these structures.This talk will be an overview of these methods.

11:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-12 Non-Destructive Depth Differentiated Analysis of Surfaces Using Ion Scattering Spectroscopy (ISS), XPS and HAXPES***, Paul Mack,* Thermo Fisher Scientific, UK

Recently there has been renewed interest in probing deeper into surfaces using HAXPES in addition to the more surface sensitive (soft X-ray) XPS. On modern XPS systems, with high sensitivity, the total sampling depth may be somewhere between 10nm and 15nm but HAXPES enables the analyst to look deeper, without having to destructively sputter the surface with ions. For a complementary, more comprehensive analysis, XPS and HAXPES can be combined with Ion Scattering Spectroscopy (ISS). ISS is far more surface sensitive than XPS, typically being thought of as a technique to analyse the top monolayer of a sample for elemental information.

In this work, the combination of XPS, HAXPES and ISS on a single tool has been used to give a non-destructive depth differentiated analysis of a range of samples, including a perovskite and an industrially relevant material containing multiple transition metals. The combination of all three techniques provides insight into the depth distributions of elements and chemical states, from the top monolayer to beyond 20nm into the surface.

12:00pm **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-13 Towards Measurement of Molecular Shapes Using OrbiSIMS***, Gustavo F. Trindade, J. Vorng, A. Eyres, I. Gilmore,* National Physical Laboratory, UK

An OrbiSIMS [1] instrument features a dual analyser configuration with a time-of-flight (ToF) mass spectrometer (MS) and an Orbitrap^{TM} MS, which confer advantages of speed and high-performance mass spectrometry, respectively. The ability to combine the MS performance usually found in a state-of-the-art proteomics and metabolomics MS with 3D imaging at the microscale and from nanolayers of <10 nm of material has proved popular in a broad field of application from organic electronics to drug discovery. For secondary ions to be efficiently transferred to the Orbitrap analyser, the sample is biased by a target voltage V_T necessary to match the acceptance window of the Orbitrap. Furthermore, the ions kinetic energy from the SIMS collision process must be reduced. Therefore, in the OrbiSIMS, a transfer system with helium gas at a pressure P_{He} slows the ions and reduces their kinetic energy distribution through inelastic collisions with gas atoms. Usually, an Orbitrap is used with an ambient pressure ion source and so here an extra gas flow of nitrogen is introduced that leads to an increase of pressure P_{N2} to compensate.

We conducted a systematic assessment of V_T and P_{He} and P_{N2} on the transmitted secondary ion intensities [2] and revealed a complex behaviour, indicating the possibility for additional separation of ions based on their shape, stability, and kinetics of formation. We showed that the V_T for maximum transmission of secondary ions will not be the same for all molecules of the same material and that sometimes multiple maxima exist. Here, we present recent progress towards the understanding of these phenomena and how we are leveraging it to measure molecular shape by using reference trisaccharides raffinose, maltrosiose and melozitose [3].

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Surface Science Division
Room D136 - Session SS+2D+AS+HC-WeM
Surface Science of 2D Materials

Moderators: Irene Groot, Leiden University, The Netherlands, **Bo-Hong Liu**, National Synchrotron Radiation Research Center

8:00am **SS+2D+AS+HC-WeM-1 Heterogeneous Photocatalysis: Alcohols on Bare and Metal-loaded TiO_2(110) and Fe_2O_3(012)***, Moritz Eder,* TU Wien, Austria*; P. Petzoldt, M. Tschurl,* Technical University of Munich, Germany*; J. Pavelec, M. Schmid, U. Diebold,* TU Wien, Austria*; U. Heiz,* Technical University of Munich, Germany*; G. Parkinson,* TU Wien, Austria

We investigated the (photo)chemistry of alcohols on TiO_2(110) and Fe_2O_3(012) in ultra-high vacuum. Our studies focused on the role of the metal co-catalyst in the photocatalytic reaction by comparing the reactivity of bare and metal-loaded surfaces. We show that photocatalytic reactions are not merely a couple of redox reactions, but an interplay of thermal and photon-driven surface reactions.

Our results demonstrated that the co-catalyst plays a crucial role in the outcome of the reaction. On TiO_2(110), alcohols are oxidized to the aldehyde/ketone and hydrogen surface species upon illumination. The hydrogen surface species were thermally converted to H_2 by the co-catalyst, allowing for a steady-state photocatalytic conversion of alcohols and the continuous production of molecular hydrogen. Using mass spectrometry, we determined turnover frequencies and rate constants. The identification of surface mechanisms on Fe_2O_3 is less advanced, but there seem to be strong parallels in the photochemistry.

Our studies shed light on the fundamental processes involved in photocatalytic reactions on metal-loaded surfaces and contribute to the development of sustainable energy technologies.

8:20am **SS+2D+AS+HC-WeM-2 Factors Governing the Reactivities of Transition Metal Carbides at Vapor/Solid and Liquid/Solid Interfaces***, S. Alhowity, A. Ganesan, M. Gharaee, O. Omolere,* ***Qasim Adesope****, K. Balogun, P. Chukwunenye, F. D'Souza, T. Cundari, J. Kelber,* University of North Texas

Transition metal carbides are of broad interest for both heterogeneous and electro-catalysis. However, fundamental understanding of chemical factors governing reactivities and selectivities at the vapor/solid and liquid/solid interfaces remain sparse. Herein, *in situ* XPS results, electrochemical measurements, and DFT-based calculations are presented regarding the reactivities of NbC and TaC in the presence of O_2 vapor, and reactivity in solution towards the reduction of N_2 to NH_3. NbC and TaC films were prepared by DC magnetron sputtering deposition, then exposed to O_2 vapor at room temperature, and analyzed by *in situ* XPS without exposure to ambient. Similarly prepared samples were also analyzed by *ex situ* XRD. These data show that, although Nb and Ta have similar oxophilicities, (a) deposited NbC films contain significant amounts of Nb oxide phases throughout the film, whereas TaC films deposited under similar conditions do not, and (b) the exposure of NbC films to O_2 at 300 K results in significant Nb oxide formation, but that TaC films remain inert towards O_2 under these conditions. DFT calculations indicate that this significant reactivity difference towards O_2 is due in large part to the greater Ta-C bond strength compared to Nb-C, and in part due to the relative energetic stabilities of the corresponding oxides. Electrochemical studies show that ambient-exposed NbC, with a Nb_2O_5 surface layer, becomes reactive towards N_2 reduction to NH_3 under acidic conditions, but only after etching in NaOH to remove the surface oxide layer. Additionally, chronoamperometric data indicate that this reactive NbC surface is eventually modified under electrochemical conditions and becomes relatively inert towards N_2 reduction with time. Experiments involving *in situ* sample transfer between UHV and electrochemistry environments demonstrate that electrochemically active NbC surfaces in solution comprise Nb sub-oxide surface layers, in line with previous studies showing that effective NRR catalysts contain surface transition metal ions in intermediate oxidation states, supporting both N_2 lone pair attraction and pi-backbonding to bind and activate the NN triple bond.

Acknowledgement This work was supported in part by the UNT College of Science through COS grants 1600089 and RSG-2023-002 and and in part by the NSF under grant no. DMR 2112864.

8:40am **SS+2D+AS+HC-WeM-3 Tunable Interfacial Electrochemistry at Moiré Material Interfaces***,* ***D. Kwabena Bediako****,* University of California at Berkeley **INVITED**

At electrode–electrolyte interfaces, crystallographic defects are frequently implicated as active sites that mediate interfacial electron transfer (ET) by introducing high densities of localized electronic states (DOS). However, conventional defects can be challenging to deterministically synthesize and control at an atomic level, challenging the direct study of how electronic localization impacts interfacial reactivity. Azimuthal misalignment of atomically thin layers produces moiré superlattices and alters the electronic band structure, in a manner that is systematically dependent on the interlayer twist angle. Using van der Waals nanofabrication of two-dimensional heterostructures, scanning electrochemical cell microscopy measurements, and four-dimensional scanning transmission electron microscopy, we report a strong twist angle dependence of heterogeneous charge transfer kinetics at twisted bilayer and trilayer graphene electrodes with the greatest enhancement observed near the 'magic angles'. These effects are driven by the angle-dependent engineering of moiré flat bands that dictate the electron transfer processes with the solution-phase redox couple, and the structure of the relaxed moiré superlattice. Moiré superlattices therefore serve as an unparalleled platform for systematically interrogating and exploiting the dependence of interfacial ET on local electronic structure.

9:20am **SS+2D+AS+HC-WeM-5 Growth of Ultrathin Silica Films on Pt(111) and Rh(111): Influence of Intermixing with the Support***,* ***Matthias Krinninger****,* Technical University of Munich, Germany*; F. Kraushofer,* Technical University of Munich, Austria*; N. Refvik,* University of Alberta, Canada*; F. Esch,* Technical University of Munich, Germany*; B. Lechner,* Technical University of Munich, Austria

Silica is a widely used catalyst support material for clusters and nanoparticles. Understanding the relationship between these clusters and the support is challenging, however, because SiO_2 is insulating, and in most applications not crystalline which drastically limits the use of experimental techniques to those that work on insulating samples and are not diffraction-based. Several previous studies have investigated ultrathin, quasi-2D silica films on a variety of metal supports [1], which can then be measured by scanning tunneling microscopy (STM), XPS and most other surface science methods. Previous work on Pt(111) did not result in closed films, which was attributed to lattice mismatch [2]. We show that closed films can in fact be grown on Pt(111) when silica is deposited in excess, likely due to formation of a platinum silicide layer with slightly expanded lattice constant at the interface. We also report results of film growth on Rh(111), which is a near-perfect match to the lattice constant of freestanding SiO_2 films as calculated by theory. However, no high-quality films were achieved on Rh due to thermodynamic competition with a surface silicide.

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9:40am **SS+2D+AS+HC-WeM-6 CO_2 Adsorption on Graphitic-Like Bilayer ZnO Film Studied by NAP-XPS***,* ***Bo-Hong Liu****, S. Cheng,* National Synchrotron Radiation Research Center, Taiwan

CO_2 activation is a fundamental process in heterogeneous catalysis. ZnO-based catalyst has been extensively used in commercial methanol synthesis from CO_2 gas and the reverse water gas shift reaction. The adsorption behavior of CO_2 on the catalyst surface is pivotal to the reactivity. Whereas ZnO(0001)-Zn physisorbed or weakly chemisorbed CO_2,[1] strong chemisorption of the molecule happens on non-polar surfaces, such as ZnO(10-10), resulting in a tridentate carbonate.[2] In Operando TEM investigation during methanol synthesis shows that ZnO single atomic layer stacks distortedly around Cu nanoparticles via strong metal-support interaction. The lake of interlayer ordering between the layers suggests a weak interlayer interaction; therefore, each layer resembles a free-standing sheet.[3] DFT modeling concluded that free-standing ZnO(0001) layer adopts an graphitic-like co-planner structure. The co-planner feature was verified experimentally for the bi-layer ZnO(0001) supported on Ag(111) and Au(111).[4] On Au(111) substrate, TPD shows that CO_2 adsorbs on the low coordinate sites at the layer edges.[5] In the present study, we investigate the CO_2 adsorption on bi-layer ZnO/Ag(111) film using NAP-XPS to extend the pressure condition towards reality. We found a more considerable CO_2 chemisorption at elevated pressure. The presentation will also address how the surface hydroxyl group influences CO_2 adsorption.

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11:00am **SS+2D+AS+HC-WeM-10 Investigation of Nitride Spintronic and Kagome-Structured Intermetallic Topological Materials Using Molecular Beam Epitaxy and Scanning Tunneling Microscopy***,* ***Arthur R. Smith****,* Ohio University Physics and Astronomy Department

Owing to the overwhelming interest in topological [1] and spintronic materials [2], it is imperative to investigate these down to the atomic scale for their possible use in advanced devices. Many promising properties discovered among nitride materials, such as chemical stability and wide band gaps [3], may be combined with the equally promising aspects of topological materials, such as the topological Hall and Nernst effects [4]. Very recent work illustrates that spin-polarized scanning tunneling microscopy is a powerful tool for exploring topological band-structured Kagome antiferromagnets [5]. In our current work, we investigate both nitride material systems grown using molecular beam epitaxy as well as the growth of topological systems such as Kagome antiferromagnetic materials. Ongoing work in our group encompasses the investigation of Mn_3Sn, FeSn, CrSn, Mn_3Ga, and as a spintronic and topological nitride, Mn_3GaN. These materials are grown in combined UHV MBE and scanning tunneling microscopy chamber systems in which the grown samples are first fabricated using MBE and after that investigated for their structural, electronic, and magnetic properties including using STM and tunneling spectroscopy. Our goal is also to investigate these materials using spin-polarized STM as a function of temperature and applied magnetic field. Our current results show that these materials can be fabricated effectively using molecular beam epitaxy and investigated using various *in-situ* techniques such as reflection high energy electron diffraction and STM. Results from multiple on-going investigations will be presented with a birds-eye view of the progress. Especially to be presented will be STM and STS results in these Kagome systems grown using MBE.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

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11:20am **SS+2D+AS+HC-WeM-11 Molecular Beam Epitaxial Growth and Investigations of FeSn on $LaAlO_3$,** ***Tyler Erickson,*** *S. Upadhyay, H. Hall, D. Ingram, S. Kaya, A. Smith,* Ohio University

Kagome antiferromagnetic and ferromagnetic materials provide an interesting avenue for research through the investigation of frustrated magnetism, band topology and electronic correlations [1-4]. FeSn is a layer-wise antiferromagnetic Kagome structured material with characteristic dispersion-less flat bands and Dirac cones at the Brillouin zone boundaries. Li *et al.* have presented exciting spin-polarized scanning tunneling microscopy results revealing surface electronic and magnetic properties of *in-situ* cleaved bulk FeSn [1]. Zhang *et al*. reported strain engineering of FeSn on $SrTiO_3$ (111) with precise control of the stanene layers [2]. Kawakami *et al.* reported Fe_3Sn_2 growth on Pt buffer layers on top of Al_2O_3 and studied various topological phenomena of this topological Kagome material [3,4]. Bhattarai et. al. studied the magnetotransport properties of FeSn grown on silicon substrates [5]. Here, we study the growth of FeSn directly on $LaAlO_3$ and report the successful growth of high-quality crystalline thin-films of FeSn. Reflection high-energy electron diffraction and x-ray diffraction are used to discover the *in-plane* and *out-of-plane* lattice constants, while atomic force microscopy and Rutherford backscattering provide topographical and stoichiometric characterization. Preliminary results indicate *in-plane* and *out-of-plane* lattice constants of 5.290 Å and 4.56 Å compared to the expected results of 5.297 Å and 4.481 Å, respectively. Besides discussing the thin film FeSn growth results, we also plan to present scanning tunneling microscopy results on the MBE-grown surfaces.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

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11:40am **SS+2D+AS+HC-WeM-12 AVS Graduate Research Awardee Talk: Molecular Beam Epitaxial Growth, Structural Properties, and Surface Studies of *a*-Plane-Oriented Mn_3Sn on *C*-Plane Al_2O_3**, ***Sneha Upadhyay***[1]*, T. Erickson,* Ohio University*; J. Hernandez,* Universidad Autonoma de Puebla, Mexico*; H. Hall, K. Sun,* Ohio University*; G. Cocoletzi,* Universidad Autonoma de Puebla, Mexico*; N. Takeuchi,* Universidad Nacional Autonoma de Mexico, Mexico*; A. Smith,* Ohio University

Recently, Chen *et al.* reported the observation of tunneling magnetoresistance in an all-antiferromagnetic tunnel junction consisting of $Mn_3Sn/MgO/Mn_3Sn$.[1] Furthermore, Bangar *et al.* demonstrated a technique for engineering the spin Hall conductivity of Mn_3Sn films by changing the Mn: Sn composition.[2] These works show the potential of studying this Kagome antiferromagnetic material and the importance of being able to grow smooth films. This work uses molecular beam epitaxy to investigate the growth of Mn_3Sn ($11\underline{2}0$) on Al_2O_3 (0001). The growth is monitored *in-situ* using reflection high energy electron diffraction and measured *ex-situ* using X-ray diffraction, Rutherford backscattering, and atomic force microscopy.In our previous work, we carried out a single-step growth at 450°C, which resulted in a crystalline but discontiguous *a-plane-oriented* (~43% $11\underline{2}0$) Mn_3Sn film with a mix of other orientations including 0002.[3] Leading from this work, changes were made to the growth recipe, which involved carrying out a two-step growth procedure at room temperature, resulting in a contiguous, epitaxial Mn_3Sn film with up to ~82% $11\underline{2}0$-orientation. We are also exploring the effect of varying the Mn: Sn flux ratio and the film thicknesses (in the range of 5 – 200 nm) on the film crystallinity and orientation. We observe that varying the Mn: Sn flux ratio leads to a change in the RHEED patterns from pointy to streaky, and the XRD shows that the $11\underline{2}0$ peak can be varied between~ 82 % to ~38 % of all the peaks' total intensity. We also plan to present the first results on ultra-high vacuum scanning tunneling microscopy imaging of the ($11\text{-}\underline{2}0$) Mn_3Sn surface.

Acknowledgments:

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. Eric Stinaff and his students for back-coating the sapphire (0001) substrates.

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[1] **AVS Graduate Research Awardee**

2D Materials Technical Group
Room C123 - Session 2D-WeA

2D-Materials: Electronic/Magnetic/Optical Properties

Moderators: Zachary Krebs, University of Wisconsin - Madison, **Xuedan Ma**, Argonne National Lab

2:20pm **2D-WeA-1 Josephson Diode Effect via Proximity Induced Superconductivity in 2D Materials***, **Stuart Parkin**,* Max Planck Institute for Microstructure Physics, Germany **INVITED**

Recently we have discovered a non-reciprocal Josephson diode effect in several Josephson junctions, both lateral and vertical, formed from conventional superconducting electrodes (Nb, NbSe$_2$) separated by several non-superconducting metals including the 2D van der Waals metals, NiTe$_2$ [1] and WTe$_2$[2], as well as sputtered layers of platinum that are magnetically proximitized via a magnetic insulator (YIG) [3]. Each of these materials becoming superconducting by proximity to the conventional superconducting electrodes. The superconductivity can be sustained over long distances of, in some cases, up to ~1 micron. The critical supercurrent densities for current flowing in opposite directions within the junction are distinct and can vary by up to 40% or more. For the van der Waals metals the non-reciprocity is only observed in the presence of a small magnetic field oriented perpendicular to the supercurrent, whereas for the Pt based junctions the diode effect is observed in zero field. For vertical Josephson junctions formed from WTe$_2$ we show that the non-reciprocity depends on the orientation of the magnetic field with respect to the crystal structure of the WTe$_2$, proving thereby the intrinsic origin of the Josephson diode effect. We also show how the magnitude of the asymmetry increases with the thickness of the WTe$_2$ barrier[2]. Finally, we discuss our recent work on spin-triplet supercurrent spin valves using 2D chiral Kagome antiferromagnets [4].

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3:00pm **2D-WeA-3 Behavior of Excited States in 2H and 3R Bilayer WSe$_2$***, **Kathleen McCreary**, M. Phillips, H. Chuang, D. Wickramaratne, M. Rosenberger, C. Hellberg, B. Jonker,* Naval Research Laboratory

Transition metal dichalcogenide bilayers exhibit improved stability and higher carrier mobility compared to their monolayer counterparts, and may be attractive for a variety of applications. Both 2H and 3R bilayers are energetically stable and are expected to exhibit semiconducting behavior. However, 2H has received the bulk of attention due to its ready availability in the form of mechanically exfoliated flakes. Here, we detail the energies and temperature dependent behaviors of the ground and the first excited excitonic states in both 2H and 3R WSe$_2$ bilayers. Samples are obtained through chemical vapor deposition, encapsulated with hBN, and reflectance contrast (RC) is measured to identify 1s and 2s excitonic states. At cryogenic temperatures, a splitting of approximately 17 meV is experimentally observed in both the 1s and 2s states of 3R bilayers. This splitting is consistent with our DFT calculations and is due to lack of inversion symmetry, with the two peaks corresponding to distinct excitonic transitions in the upper and lower layers of the 3R WSe$_2$. As temperatures increases, excitonic states broaden and RC intensity decreases, preventing detection of 2s states above 100 K. The 1s state is evident at all temperatures between 4 K and 300 K, and splitting of the 1s state in 3R samples is detectable to approximately 250 K. This work provides much needed insight into bilayer systems and demonstrates that interlayer interactions are strong enough to significantly modify the optical properties in WSe$_2$ samples.

3:20pm **2D-WeA-4 2D SnO/MoO$_3$ van der Waals Heterojunction with Tunable Electronic Behaviors for Multi-functional Applications: DFT Calculations***, **Junyu Lang**,* ShanghaiTech University, China*; Y. Ma,* Shanghai Jiao Tong University, China*; Y. Yang,* ShanghaiTech University, China

Introduction

Following the advent of graphene in the late 1940s, two-dimensional (2D) materials, such as MXenes, transition-metal dichalcogenides (TMDs), black phosphorene, etc., have attracted extensive attention. Among various 2D materials, transition-metal oxides (TMOs) possess exceptional advantages, such as tunable redox property, high chemical stability, environmental friendliness and earth-abundant characteristic. Metal oxide van der Waals (vdW) heterostructures have attracted extensive attention in fundamental research and new-device design. The remarkable advantage of their tunable energy band structure makes it particularly important to develop versatile metal-oxide heterojunctions and to explore their mechanisms. Herein, 2D SnO/MoO$_3$ vdW heterojunction is successfully constructed by first-principles calculations.The electronic structure of the SnO/MoO$_3$ vdW heterojunction has been systematically investigated, and the underlying physical mechanism responsible for its band alignment has been further revealed. A Z-scheme charge transfer mechanism has been demonstrated in SnO/MoO$_3$ with remarkable photocatalytic CO$_2$ reduction capability. Most importantly, the band alignment can be efficiently tuned by varying the external electric field, indicating its multifunctional potential. Furthermore, the CO$_2$ reduction reaction pathway and product selectivity occurring at the surface of 2D SnO/MoO$_3$ vdW heterojunction can be optimized by adjusting the applied electric field.

Results and Discussion

The vdW heterojunction, SnO/MoO$_3$ has been designed by first-principles calculations. The formation of 2D SnO/MoO$_3$ vdW heterojunctions is not limited by the relative horizontal displacements between the different layers, which greatly facilitates fabrication processes and functional applications. In addition, a Z-scheme charge transfer mechanism has been demonstrated in SnO/MoO$_3$, exhibiting remarkable photocatalytic CO$_2$ reduction capability. Possible reduction reaction pathways for CO$_2$ on the surface of the SnO/MoO$_3$ vdW heterojunction were further explored and it was shown that CH$_4$ and CH$_3$OH are the main products. Furthermore, we found that the electronic properties of 2D SnO/MoO$_3$ vdW heterojunction can be efficiently modulated by applying an external electric field, which is beneficial for optimizing the reaction path and improving the product selectivity of CO$_2$ reduction reactions. Most importantly, transitions between type-III and type-II band alignments are observed in the 2D SnO/MoO$_3$ vdW heterojunction at negative electric fields. These findings will provide a strong theoretical support for designing novel tunneling field-effect transistors and photocatalysts.

4:20pm **2D-WeA-7 2D Materials Explored Using nanoARPES***, A. Bostwick, C. Jozwiak, **Eli Rotenberg**,* Lawrence Berkeley Lab, USA **INVITED**

Angle-resolved photoemission is a premiere technique for measuring the electronic structure of materials, as represented by momentum-resolved electronic bands. Furthermore, with modern high-resolution instrumentation it is possible to access the single-particle spectral function $\boldsymbol{A}(k,\omega)$, which gives important information on the renormalization of excited state energies and lifetimes due to many-body interactions and defect scattering.

NanoARPES machines capable of spatially-resolving the ARPES spectrum on the mesoscopic scale are coming online at synchrotrons around the world, with spatial resolution in the range 100-1000nm. Combining these new small probes with arbitrary stacking orders of diverse materials assembled micromechanically, nanoARPES can obtain information on new materials far faster than in the past, when probe sizes limited us to wafer-scale, epitaxially grown heterostructures. Using small x-ray probes, nanoARPES can also study naturally or spontaneously-formed heterogenous materials. Most if not all nanoARPES machines are accessible through proposals to international user facilities, and the community specializing in these experiments is growing rapidly.

Most excitedly, nanoARPES offers the possibility to measure 2D materials and heterostructures at true device scales, and can thus enable for the characterization of materials under *in operando* conditions. In this talk I will review recent developments and pioneering experiments at the MAESTRO beamline at the Advanced Light Source in Berkeley, CA. These capabilities include the application of external fields (electrical, magnetic, and optical) and current. Prospects for the application of magnetic fields to create a new "MagnetoARPES" technique will be presented.

5:00pm **2D-WeA-9 Probing Many-body Effects in 2D Materials using nanoARPES***, **Jyoti Katoch**,* Carnegie Mellon University, United States Minor Outlying Islands (the)

Two-dimensional (2D) materials provide unprecedented opportunity to engineer their physical properties by modification to the electronic structure utilizing external perturbations- strain, gating, adsorbates, defects, twist-angle, and interface engineering. This is expected to cause changes to the Hamiltonian describing the system and has resulted in exotic phenomena such as superconductivity, bound quasiparticles, topological states as well as magnetic phases, with implications for novel electronics and spin-device applications. In this talk, I will present our work on directly visualizing (without any assumption) the electronic structure of atomically thin systems utilizing *in-operando* angle-resolved photoemission spectroscopy with nanoscale spatial resolution (nanoARPES) on 2D heterostructures and their fully functional devices [1,2,3,4,5]. I will present the experiments which demonstrate on-demand tuning of the electronic band structure in atomically thin systems, such as transition metal dichalcogenides (TMDCs) and graphene, by varying the twist-angle between the atomic layers and external dopants. Specifically, I will discuss the electric field tuning of the electronic interactions that result in van Hove singularity and flat bands in twisted bilayer graphene and twisted double bilayer graphene heterostructures. In addition, I will show our recent results where we observe the formation of quasiparticle polarons due to many-body interactions in graphene/TMDC heterostructures.

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[5] Jones, et. al., Adv. Mater., 32, 2001656 (2020).

5:20pm **2D-WeA-10 Electrical Transport of High-Quality CVD-Grown $MoSe_2$ Nanoribbons***, **Y.-J. Leo Sun,*** Laboratory for Physical Sciences*; O. Ambrozaite, Z. Zhang, T. Kempa,* Johns Hopkins University*; T. Murphy,* University of Maryland, College Park*; A. Friedman, A. Hanbicki,* Laboratory for Physical Sciences

Two-dimensional (2D) materials such as transition metal dichalcogenides are excellent candidates for creating novel nano-electronic and photonic devices. Previous research indicates that the edge states of MoS_2 could strongly influence its conductivity, and the 2D honeycomb structure enables different electronic performance along the zigzag and armchair edges. Understanding and controlling the conductivity is essential in devices like field effect transistors that use MoS_2 as the channel. To date, transport along edge states of $MoSe_2$ nanoribbons, which have substantially reduced dimensionality relative to 2D crystals, has not been explored. In this project, we used chemical vapor deposition (CVD) to synthesize $MoSe_2$ nanoribbons through a particle-seeded approach. This approach yields directed growth of monolayer $MoSe_2$ to form high aspect ratio (>7) nanoribbons. Tip-enhanced photoluminescence (TEPL) is used to probe the optical properties of the edge and surface of the $MoSe_2$ nanoribbons. To perform electronic transport measurements, we used e-beam lithography to pattern contacts on the nanoribbons in a Hall bar configuration with the side contacts at the edges and tips of the nanoribbons. The influence of edge states on the electrical performance of $MoSe_2$ nanoribbons was investigated by conductivity and Hall transport measurements. Current flow in the transverse and longitudinal directions of the nanoribbon was compared to analyze the importance of edge states on $MoSe_2$ nanoribbon conductivity.

5:40pm **2D-WeA-11 Strain-Exciton Coupling in Two-dimensional Semiconductors***, **Jin Myung Kim**, S. Nam,* University of California, Irvine, USA **INVITED**

In this talk, I will present our work on deterministic manipulation and confinement of excitons in two-dimensional (2D) semiconductors. I will discuss predictable and reconfigurable strain modulation in 2D transition metal dichalcogenides (TMDs) via wrinkle architectures. Strain exerted on wrinkled 2D TMDs was periodically modulated to tensile and compressive strain at peaks and valleys of the wrinkles, respectively. Furthermore, owing to the deformable nature of the wrinkle architecture, the applied strain can be tuned reconfigurably with the optical gap of TMDs dynamically modulated. We also observed exciton transport across apex and valley of strained TMDs as well as exciton localization at the apex due to strain gradient induced energy modulation of wrinkled TMDs. Finally, I will discuss an extension of our strain modulation approach to interlayer excitons in TMD vertical heterostructures where strain is used to tune both optical gap as well as interlayer coupling between the heterobilayers. I will share our perspectives on strain-exciton engineering toward quantum and optoelectronic devices.

Magnetic Interfaces and Nanostructures Division
Room B110-112 - Session MI+2D+TF-WeA

Special Symposium on Coupling Phenomena in Magnetism

Moderator: Hendrik Ohldag, Lawrence Berkeley National Laboratory

2:20pm **MI+2D+TF-WeA-1 Coupling Spin-Orbit and Exchange Interaction in a Low-Dimensional Magnet***, **Pascal Jona Grenz**[1], M. Donath, P. Krüger,* University of Münster, Germany

Coupling exchange interaction (SOI) and spin-orbit interaction (XCI) provides the foundation for many prospective spin-based information technology applications. For example, it was suggested that the strength of SOI at a ferromagnet/heavy-metal (FM/HM) interface is decisive for the efficiency of writing magnetic bits in spin-orbit-torque MRAM devices [1].

Exploring the electronic structure is the key to access the factors underlying the coupling of SOI and XCI. We use spin- and angle- resolved inverse photoemission to study the interplay of SOI and XCI in the unoccupied electronic structure at the interface of a low-dimensional FM on a HM substrate. The prototypical FM/HM hybrid system Ni/W(110) exhibits exchange-split Ni-related states that become strongly influenced by SOI. A balanced ratio of SOI and XCI results in a magnetization- and k-dependent quenching or enhancement of the spin splitting. This remarkably large interplay of SOI reflected in the adlayer states contrasts previous studies of the occupied electronic structure of the same system, where the observations were attributed solely to either SOI or XCI [2].

Using density-functional-theory (DFT) calculations, we investigate the underlying drivers responsible for the experimentally observed coupling of SOI and XCI. We find that hybridization between adsorbate and substrate states, along with the strongly localized wave functions at the heavy W nuclei, cause the strong influence of SOI within the Ni-related exchange-split states.

[1] I.M. Miron *et al*., Nature, **476** 189 (2011)

[2] A. Nuber, PhD Thesis (University of Würzburg, Germany, 2011)

2:40pm **MI+2D+TF-WeA-2 AVS Graduate Research Awardee Talk: Temperature Dependent Magnetic and Electronic Properties of $NiCo_2O_4$ Thin Film Surfaces***, **Arjun Subedi**[2,3],* University of Nebraska-Lincoln*; D. Yang, C. Mellinger, X. Xu,* University of Nebraska–Lincoln*; P. Dowben,* University of Nebraska-Lincoln

Although $NiCo_2O_4$ thin film is shown to possess perpendicular magnetic anisotropy [1], we have observed in-plane spin polarization of $NiCo_2O_4$ thin film in spin polarized inverse photoemission spectroscopy (SPIPES). The unoccupied states of $NiCo_2O_4$, above Fermi level, were observed to have unequal density of states for spin majority and spin minority carriers in SPIPES, and the spectra obtained from the SPIPES have spectral features that can be compared to the XMCD spectra. The in-plane spin polarization of $NiCo_2O_4$ is found to decrease with increasing temperature, as expected. In addition to the temperature dependent change in spin polarization, we observed that there is change in the surface electronic properties of $NiCo_2O_4$ from conducting to insulating when the temperature is increased. X-ray photoemission spectroscopy (XPS) studies show that there exist no appreciable binding energy changes of Ni $2p_{3/2}$ and Co $2p_{3/2}$ core levels with change in temperature (T) when the $NiCo_2O_4$ film exists in conducting phase. However, when the $NiCo_2O_4$ films became insulating, the core level binding energies changed reversibly with change in temperature during annealing and cooling cycles. The core level binding energy (BE) change with temperature (T) is found to closely follow a modified Arrhenius type model. The proposed model is also followed by Co $2p_{3/2}$ and Fe $2p_{3/2}$ core levels in temperature dependent XPS of insulating $CoFe_2O_4$ thin films.Our studies indicate that thermal effects and oxygen defects should play the roles in changing both magnetic and electronic properties of $NiCo_2O_4$ thin films with temperature.

[1] C. Mellinger et al., Phys. Rev. B 101, 014413 (2020).

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[1] **Falicov Student Award Finalist**

[2] **AVS Graduate Research Awardee**

[3] **Falicov Student Award Finalist**

3:00pm **MI+2D+TF-WeA-3 Antiferromagnetic Real-Space Configuration Probed by Dichroism in Scattered X-Ray Beams with Orbital Angular Momentum***, **Sophie Morley**, M. McCarter, A. U. Saleheen, A. Singh,* Lawrence Berkeley Lab*; R. Tumbleson,* University of California Santa Cruz*; J. Woods,* Argonne National Laboratory*; A. Tremsin,* UC Berkeley*; A. Scholl,* Lawrence Berkeley Lab*; L. de Long, J. Hastings,* University of Kentucky*; S. Roy,* Lawrence Berkeley Lab **INVITED**

X-ray beams with orbital angular momentum (OAM) are a promising tool for x-ray characterization techniques. Beams with OAM have an azimuthally varying phase, and new material properties can potentially be probed by utilizing this unique phase structure. Here, we show how OAM beams are created through resonant diffraction from an artificial antiferromagnet with a topological defect. The scattered OAM beams have circular dichroism whose sign is coupled to the phase of the beam [1]. Using magnetic scattering calculations, we show that this dichroism is related to the real-space configuration of the antiferromagnetic ground state. Thermal cycling of the artificial antiferromagnet can change the ground state, as indicated by the changing dichroism. These results exemplify the potential of OAM beams to probe matter in a way that is inaccessible using currently available x-ray techniques.

[1] M. R. McCarter et al., Phys. Rev. B 107, L060407 (2023)

5:00pm **MI+2D+TF-WeA-9 Spin-dependent Hybridization of Image-potential States with Tl States in Tl/Ag(111)***, **Sven Schemmelmann**[1],* Universität Münster, Germany*; P. Härtl,* Universität Würzburg, Germany*; P. Krüger,* Universität Münster, Germany*; M. Bode,* Universität Würzburg, Germany*; M. Donath,* Universität Münster, Germany

The BiAg$_2$ and PbAg$_2$ surface alloys exhibit giant Rashba splittings [1-4]. The related TlAg$_2$ surface alloy is expected to show states with smaller but still large Rashba splittings due to the lower atomic number of Tl. However, this alloy forms only small patches with long-range structural order [5]. For higher coverages of Tl on Ag(111), a smooth and stable wetting layer forms with a moiré superstructure due to the lattice mismatch between Tl and Ag. We present a study of the unoccupied electronic structure of this superstructure by spin- and angle-resolved inverse photoemission. The experimental results are accompanied by DFT calculations. We observe surface states and an image-potential resonance located several Å in front of the surface. Surprisingly, one surface state exhibits almost no Rashba splitting even though it is located around the Tl atoms. This result is explained by the orbital symmetry of the respective state. For the image resonance, we find hybridization with a downward dispersing Tl state leading to spin-dependent spectral intensities that vary strongly close to the hybridization point. This observation, both in experiment and bandstructure calculations, is supported by charge distribution calculations showing an expeditious change from the image resonance to the Tl-induced surface state depending on $k_{||}$.

[1] C. R. Ast *et al.*, Phys. Rev. Lett. **98**, 186807 (2007)

[2] G. Bihlmayer, S. Blügel, and E. V. Chulkov, Phys. Rev. B **75**, 195414 (2007)

[3] S. Wissing *et al.*, Phys. Rev. Lett. **113**, 116402 (2014)

[4] L. El-Kareh *et al.*, New J. Phys. **16**, 045017 (2014)

[5] P. Härtl, S. Schemmelmann, P. Krüger, M. Donath, and M. Bode, submitted to Phys. Rev. B

5:20pm **MI+2D+TF-WeA-10 Distinct Tamm and Shockley Surface States on Re(0001) Mixed by Spin-Orbit Interaction – A Photoemission Study***, **Marcel Holtmann**, P. Krüger,* University of Münster, Germany*; K. Miyamoto, T. Okuda,* HiSOR, Japan*; P. Grenz,* University of Münster, Germany*; K. Shimada,* HiSOR, Germany*; M. Donath,* University of Münster, Germany

Tamm and Shockley states, these two paradigmatic concepts are used to describe surface states not only in electronic systems but also in photonic and phononic crystals. The Re(0001) surface was found to host both types of electronic surface states in neighboring, but qualitatively different gaps [1]. Interestingly, spin-orbit interaction generates a double W-shaped energy vs $\mathbf{k}_{||}$dispersion by mixing both types of states and lifting their spin degeneracy. We employ a combination of spin- and angle-resolved photoemission, tight-binding model calculations, and density functional theory that accounts for the photoemission process to establish reliable criteria for distinguishing between the two types of surface states. Our approach leads to a coherent understanding of the mechanism of spin-orbit interaction in such a situation.

From a detailed investigation of the Re(0001) surface along the ΓM and ΓK high-symmetry directions [2], we obtain Rashba parameters of 0.32 and 0.34 eVÅ along the two respective directions. This indicates a slight warping of the surface state. Regarding the aforementioned state's spin polarization: at variance with theoretical predictions for a perfect hcp(0001) of rhenium [3], we do not find any out-of-plane spin polarization. This is attributed to monatomic steps of a real Re(0001) surface with alternating terminations, leading on average to an effective sixfold surface symmetry and vanishing net out-of-plane spin polarization.

[1] M. Holtmann *et al.,* Phys. Rev. B **105**, L241412 (2022)

[2] M. Holtmann *et al.,* Phys. Rev. B **107**, 165420 (2023)

[3] A. Urru and A. Dal Corso, Surf. Sci. **686**, 22 (2019)

5:40pm **MI+2D+TF-WeA-11 Coupling between Spin Order and Orbital Order in 2D-Superlattice Perovskite Film***, **Bin Hu**,* University of Tennessee Knoxville **INVITED**

The coupling between spin order and orbital order presents a fundamental request to develop advanced multifunctional materials. 2D-superlattice perovskite films, known as solution-processing semiconductors, possess strong orbital order within non-degenerate Rashba band structures under the concurrent influence of spin-orbital coupling and symmetry breaking. This provides a fundamental condition to dynamically couple spin order and orbital order through multiferroic interface design. Here, we combine ferroelectric 2D-suparelattice perovskite (4,4-DFPD$_2$PbI$_4$) film and ferromagnetic cobalt (Co) film to form multiferroic perovskite/Co interface. By using this multiferroic interface design, we found that the circularly polarized orbitals with right and left handedness ($\mathbf{s}^+$ and $\mathbf{s}^-$) in Rashba band structures can selectively interact with spin-up and spin-down spin dipoles on the Co surface, leading to a mutually selectivity between spin order and orbital order. Particularly, this selective interaction between spin order and orbital order can enable spin-switchable phenomena towards developing emerging functionalities in these solution-processing hybrid metal halide perovskites. When the ferromagnetic spins on the Co surface are altered between positive and negative magnetic field directions (+**B** and -**B**), the circularly polarized luminescence (CPL) in 2D-superlattice perovskite can be switched between $\mathbf{s}^+$ and $\mathbf{s}^-$polarizations, leading to spin-switchable phenomena at room temperature. More interestingly, our polarized neutron reflectometry (PNR) studies found that circularly polarized photoexcitation generates a static magnetization within 2D-superalttice perovskite film prepared on the Co surface. This presents an optically induced magnetization phenomenon. Essentially, this optically induced magnetization reveals a long-range coupling between the spin order on the Co surface and the orbital order within Rashba band structures in 2D-superlattice perovskite film. This presentation will discuss the fundamental coupling between spin order and orbital order through Rashba band structures in 2D-superlattice perovskite film.

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[1] **Falicov Student Award Finalist**

2D Materials Technical Group
Room C123 - Session 2D-ThM
2D-Materials: Microscopy

Moderator: David Cobden, University of Washington

8:00am **2D-ThM-1 In and Ex Situ (S)TEM Manipulation of 2D Materials***, J. Kotakoski, **Harriet Åhlgren**,* University of Vienna, Austria **INVITED**

Heteroatom implantation in 2D materials requires a delicate balance between being able to displace atoms from the target material while at same time stopping the incoming ion [1]. An additional problem is imposed by momentum and energy conservation, which fundamentally limits ion implantation of graphene to elements between Li and Ti. Nevertheless, some success has been made for light elements [2,3,4]. Unfortunately, even in the case of successful implantation, the samples suffer from surface contamination. Here, we describe how all of these issues can be overcome combining vacancy-mediated heteroatom implantation [5,6] with efficient sample cleaning [7] in a vacuum system shared with an atomic-resolution scanning transmission electron microscope [7].

References

1. Phys. Rev. B 83, 115424 (2011)
2. Nano Lett. 13, 4902 (2013)
3. 2D Mater. 4, 021013 (2017)
4. ACS Nano 12, 4641 (2018)
5. J. Phys. Chem. C 123, 13136-13140 (2019)
6. 2D Mater. 9, 025011 (2022)
7. Nano Lett. 21, 5179-5185 (2021)

8:40am **2D-ThM-3 Synthesis of Quantum-Confined Borophene Nanoribbons***, **Qiucheng Li**, M. Hersam,* Northwestern University

Borophene refers to synthetic two-dimensional (2D) boron, which has attracted significant attention due to its anisotropic metallicity, correlated electron phenomena, and diverse superlattice structures.[1]Reducing the dimensionality of nanomaterials imposes additional quantum confinement effects that unlock new physical phenomena, such as one-dimensional (1D) confined plasmons, spin-polarized edge states, and Luttinger liquid behavior. However, the realization of quantum-confined borophene nanoribbons (BNRs) is hampered by limited boron precursor optionsfor bottom-up synthesis. In this work, we present a substrate mediation strategy to synthesize quantum-confined BNRs onvicinal Ag(977) substrates. The resulting BNRs inherit thehigh degree of polymorphism present in borophene, resulting in $v_{1/5}$ and $v_{1/6}$-BNR lattice configurations in addition to phase intermixing.[2]Through atomic-scale imaging, spectroscopy, and first principles calculations, the edge structures of BNR polymorphs are shown to possess reconstructed armchair edges for $v_{1/6}$-BNRs and sawtooth zigzag edges for $v_{1/5}$-BNRs. The confined electron wave functions in 1D BNRs lead to the observation of energy level quantization and spatial nodes characteristic of quantum-well states.

Acknowledgement:

This work was supported by the Office of Naval Research (ONR N00014-17-1-2993) and the National Science Foundation Materials Research Science and Engineering Center (NSF DMR-1720139).

References:

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[2] Liu, X., *et al.*, Intermixing and periodic self-assembly of borophene line defects. *Nature Materials*, **2018**, *17* (9), 783-788.

9:00am **2D-ThM-4 Formation of Multilayer Bismuthene on Hexagonal Manganese Nitride***, **Ashok Shrestha**, A. Abbas, A. Smith,* Ohio University

Bismuthene, a two-dimensional (2D) topological material, has attracted considerable attention due to its large bandgap compared to other 2D topological materials [1]. The structure and electronic properties of the single layer bismuthene have been studied by many authors [2, 3], but the growth, structure, and electronic properties of multilayer bismuthene have not yet been reported. We have successfully grown the multilayer of bismuthene on the hexagonal ζ- phase Mn_2N surface using molecular beam epitaxy.

In this presentation, we will briefly discuss the growth of the thin layer of ζ-phase Mn_2N in the first part, and the formation of a multilayer of bismuthene in the second part. Initially, the Mn_2N film is prepared on MgO (001) substrate under nitrogen-rich conditions at 510 ºC. The correct phase of Mn_2N is confirmed using various *in-situ* techniques such as reflection high energy electron diffraction, scanning tunneling microscopy, and Auger electron spectroscopy. Once a high-quality Mn_2N surface is achieved, an ultra-thin layer of bismuth is deposited on its top at 150 ºC.

The STM investigations reveal atomically flat multiple terraces and steps of bismuthene with a step height of 1.60 Å, which agrees well with the height of bismuthene reported by Sun *et al.* (2022) [2], although the atomic resolution STM image shows the nearly rectangular structure. Some other interesting features of bismuthene, such as “quantum islands”, are also observed. The *ex-situ* X-ray diffraction clearly shows the Bi 0002 peak, giving an interplanar spacing of 3.20 Å. This measurement is consistent with twice the step height observed in the STM image. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

References:

[1] F. Reis, G. Li, L. Dudy, M. Bauernfeind, S. Glass, W. Hanke, R. Thomale, J. Schafer, R. Claessen, Science **357**, 287-290 (2017).

[2] S. Sun, J. Yang, S. Duan, J. Chen, and W. Chen, ACS Nano **16**, 1463-1443 (2022).

[3] J. Gou, K. Longjuan, H. Xiaoyue, Y. L. Haung, J. Sun, S. Meng, K. Wu, L. Chen, A. S. Wee, Sci. Adv. **6**, eaba2773 (2020).

9:20am **2D-ThM-5 A Combined NAP-XPS and NAP-STM Study on 2D MoS_2-based Catalysts for Hydrodeoxygenation of Organic Feedstocks***, **Lars Mohrhusen**, M. Hedevang, J. Lauritsen,* Aarhus University, Denmark

For the technological utilization of sustainable feedstocks such as pyrolysis oils from biomass, oxygen removal via hydrodeoxygenation (HDO) is one of the most essential steps.[1] Metal-promoted MoS_2-based catalysts are well-established for hydrode-sulphurization (HDS) of crude oil components, and thus a promising material for HDO catalysts.[2-4] This is already proven technology for simple feedstocks such as vegetable oils, but more complex compounds with high oxygen content and multiple oxygen functionalities such as bio-oils remain challenging, and thus gain increasing interest.

In contrast to the established use in (virtually oxygen free) HDS, the sulphide catalyst will be exposed to water or organic oxygenates in the herein desired HDO process. Thus, in the presence of oxygen, sulphur atoms may be partially exchanged. Thereby, active sites can become blocked, which triggers strong catalyst degradation on the long term. [5,6]

To gain an atomistic understanding of such processes, herein two-dimensional MoS_2 particles on Au (111) surfaces exposed to H_2 and/or oxygenate containing atmospheres were investigated combining microscopic (scanning tunneling microscopy (STM), see fig. 1) and spectroscopic insights (photoelectron spectroscopy (XPS)) under various conditions mimicking HDO from UHV level to the near-ambient-pressure regime (few mbar, NAP-STM, NAP-XPS).

9:40am **2D-ThM-6 NanoFrazor Technology - Fabricating Advanced 2D and Grayscale Structures for 2D Materials Using Thermal Scanning Probe Lithography and Direct Laser Sublimation***, **Nicholas Hendricks**, A. Ubezio, M. Käppeli, J. Vergés, J. Chaaban, E. Çağin,* Heidelberg Instruments Nano, Switzerland

Thermal scanning probe lithography (t-SPL), enabled by the NanoFrazor technology, is establishing itself as a mature and reliable direct-write nanolithography technique for generating nanoscale structures [1-4]. The NanoFrazor technology offers an alternative or complementary process for conventional lithography techniques of electron-beam lithography (EBL) or focused-ion beam (FIB). t-SPL generates patterns by scanning an ultrasharp tip over a sample surface to induce local changes with a thermal stimulus. By using thermal energy as the stimulus, it is possible to perform various modifications to the sample via removal, conversion, or addition of/to the sample surface. Along with an ultrasharp tip, the t-SPL cantilever contains several other important functions such as an integrated thermal height sensor and an integrated heating element both of which are advantageous for fabricating devices for nanoelectronics, photonics, molecular sensing, and quantum computing.

To complement the sub-100 nm patterning capabilities of t-SPL, a direct laser sublimation (DLS) module has been incorporated into the NanoFrazor platform. The DLS module allows for increased throughput by patterning larger structures, e.g. > 500 nm, with a continuous wave (CW) laser operating at a wavelength of 405 nm. Over the last several years, further developments of the NanoFrazor technology have been realized that are enhancing the application space of nanofabrication. Such developments include the integration of the t-SPL and DLS modules into gloveboxes, active field stitching to allow seamless large area patterning with both t-SPL and DLS, and automated overlay to allow for precise nano and micropatterning on top of pre-existing structures.

Within this presentation, the background and workings of t-SPL will be introduced as well as the nanolithography and processing capabilities of both t-SPL and DLS will be presented, with a focus on patterning on topography. A workflow for detecting and correcting intentional topography (flakes of 2D materials, pre-patterned contacts, nanowires), and unintentional defects (impurities, folds in 2D material flakes) will be introduced. Device performance examples achieved using the damage-free lithography techniques will be included, in order to provide a comparison between conventional and novel nanolithography methods.

[1] S. Howell et al., Microsystems & Nanoengineering, 6, 21 (2020); [2] N. Lassaline et al., Nature, 582, 506-510 (2020); [3] X. Liu et al., APL Materials, 9, 011107 (2021); [4] M. Giordano et al., Advanced Material Interfaces, 10, 2201408 (2023)

11:00am **2D-ThM-10 Phase Transformations in 2D Van der Waals Materials: Insights from Cryogenic Atomic Resolution STEM and EELS***,* ***Miaofang Chi****,* Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) van der Waals (vdW) materials and their heterostructures offer a remarkable platform for investigating intriguing physical phenomena and implementing diverse applications. A key advantage of these materials is their tunable quantum behavior, which varies with the number of layers. Notably, samples with different thicknesses, particularly in the range from monolayer to several nanometers, exhibit distinct and exotic properties such as magnetism, electronics, and optoelectronics. While it is recognized that lattice structural transformations often accompany changes in electronic and spin structures, leading to the emergence of exotic quantum phenomena, it remains uncertain whether the same structural transformations observed in bulk materials occur in thin flake samples. Consequently, a comprehensive understanding of the structure-property relationship in several-layer thick 2D vdW materials is often lacking. In this presentation, we unveil the thickness-dependent phase transformation and exciton state changes in several model 2D vdW materials using cryogenic atomic resolution scanning transmission electron microscopy (STEM) and monochromated electron energy loss spectroscopy (EELS). Through our findings, we provide precise insights into the layer-number-dependent properties that are crucial for harnessing the unique quantum characteristics of thin layer 2D vdW materials for device applications.

11:40am **2D-ThM-12 Intercalation of Transition Metals in between Bilayer-VSe2***, V. Pathirage, K. Lasek, S. Lisenkov,* University of South Florida*; I. Ponomareva,* University South Florida*;* ***Matthias Batzill****,* University of South Florida

Modifications of transition metal dichalcogenides (TMD) can be achieved by metal insertion into the van der Waals gap. Those metals covalently bond to the chalcogen atoms and thus form a 3D crystal structure. For ultrathin TMD films, however, insertion of excess metals will result in pseudo-2D nanolayers that may be incorporated with other van der Waals materials. In this talk we discuss modifications of bilayer VSe_2 by insertion of different transition metals (V, Cr, Mn) to modify its magnetic properties. The excess transition metals are inserted by sequential vapor deposition onto the VSe2 bilayer film. DFT simulations indicate that excess metals diffuse readily through the VSe2 layer to occupy energetically favorable inter-layer sites. Different ordered arrangements of excess metals are obtained with a maximum occupation close to half a monolayer (here one monolayer refers to the amount of metal atoms in a TMD layer). The ordering of the inserted atoms is probed by scanning tunneling microscopy. Magnetic properties are identified by x-ray magnetic circular dichroism studies and show strong magnetic moments on dilute inserted Cr or Mn atoms. However, as ordered superstructures are formed the measured average magnetic moment per atom decreases, possibly suggesting antiferromagnetic order in the insertion layer.

12:00pm **2D-ThM-13 Atomically Resolved Imaging of CVD-Grown Thin α-Mo_2C Crystals***,* ***Saima Sumaiya****,* Columbia University*; I. Demiroglu,* Eskisehir Technical University, Turkey*; O. Caylan, G. Buke,* TOBB University of Economics and Technology, Turkey*; C. Sevik,* Eskisehir Technical University, Turkey*; M. Baykara,* University of California Merced

Transition metal carbides (TMCs) have been used in bulk form in a variety of applications for decades due to their attractive mechanical and chemical properties. With the advent of nanotechnology, there is renewed interest in synthesizing these materials in thin form, with precise control of thickness for potential applications in fields such as energy storage and electromagnetic shielding. Consequently, it is of utmost importance to investigate the quality of these materials in terms of the presence of defects and their influence on properties, down to the atomic scale. Here, we present an atomic-resolution investigation of defects on thin crystals of molybdenum carbide (α-Mo_2C) grown via chemical vapor deposition (CVD), by way of conductive atomic force microscopy (C-AFM) measurements under ambient conditions. In particular, we observe a periodic modulation in the surface conductivity landscape with a periodicity that is ~5 times higher than the periodicity of the atomic lattice of the (100) surface. It is additionally observed that this electronic super-structure is rotationally misaligned with the underlying atomic lattice. Atomic-resolution imaging additionally reveals the presence of defects on the crystals, with a defect density that is similar to that reported for natural two-dimensional transitional metal dichalcogenides. We characterize defects based on the type (enhancement / attenuation) and spatial extent (compact / extended) of the effect they have on the conductivity landscape of the crystal surfaces. While some have localized influence on conductivity over several unit cells, other defects extend over ten nanometers and more. In addition to surface defects, we are also able to quantify the influence of defects that are present sub-surface. *Ab initio* calculations performed by way of density functional theory (DFT) are employed to gather clues about the identity of the defects. The findings presented here provide insights for defect engineering aimed at achieving tailored electronic properties of TMCs in thin form.

Magnetic Interfaces and Nanostructures Division
Room B110-112 - Session MI+2D+TF-ThM

2D Magnetism and Superconductivity

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

8:00am **MI+2D+TF-ThM-1 Heterostructures for Tunneling and Point-Contact Spectroscopy of Two-Dimensional Superconductors***,* ***Benjamin Hunt****, Q. Cao,* Carnegie Mellon University*; E. Telford, C. Dean,* Columbia University **INVITED**

Tunneling spectroscopy is an indispensable experimental tool of modern condensed matter physics. Vertical planar tunneling, which uses a fixed-width tunnel barrier, offers advantages over other spectroscopic tools such as scanning tunneling microscopy (STM). One such advantage is the ability to tunnel in reorientable and very large (≥40 T) magnetic fields at dilution refrigerator temperatures (≤30 mK), a capability that has application in, for example, determining the order parameter symmetry of novel two-dimensional (2D) superconductors. We demonstrate a novel vertical planar tunneling architecture for van der Waals heterostructures based on via contacts, namely, metallic contacts embedded into through-holes in hexagonal boron nitride (hBN). This via-based architecture overcomes limitations of other planar tunneling designs and produces high-quality, ultra-clean tunneling structures from a variety of 2D materials. The physical area of our via-based tunnel contacts is limited only by nanofabrication techniques, and we demonstrate a crossover from diffusive to point contacts in the small-contact-area limit by studying the spectrum of a 2D superconductor, $NbSe_2$. We show that our tunneling technique may enable highly-sought measurements of newly-discovered 2D superconductors such as monolayer 1T'-WTe_2, rhombohedral trilayer graphene, twisted trilayer graphene, and twisted bilayer BSCCO.

8:40am **MI+2D+TF-ThM-3 Ghost States and Topography Inversion in 2D Materials***,* ***Mina Yoon****,* Oak Ridge National Laboratory, USA **INVITED**

In this talk, I will discuss the challenges associated with characterizing the surface structures of single-atom thick materials, such as graphene and boron nitride, on metallic substrates or the surface of bulk systems, including quantum topological Kagome systems, using scanning tunneling microscopy (STM). The understanding of fundamental properties of two-dimensional (2D) materials and surface properties depends critically on the presence of "ghost" states, which arise due to different decay lengths in the wave function of the underlying layers and surfaces.

The existence of these ghost states, in conjunction with long-lived substrate states or underlying layers, plays a crucial role in interpreting and understanding the surface properties of 2D materials. These ghost states can originate from various sources, such as the bulk or the substrate, and can even arise from the boundary on the opposite side. The appearance of ghost states due to different decay lengths leads to unexpected results in surface structure measurements, including the intriguing phenomenon of topography inversion. Topography inversion refers to the counterintuitive result where the observed topography in STM images is opposite to the expected atomic geometry, as discussed in our recent study [1,2]. This inversion occurs as a consequence of the pervasive substrate states overshadowing the intrinsic states of the 2D materials. As a result, the measurement of the intrinsic properties of 2D materials becomes complicated, with the ghost and substrate states dominating the observed topography. To address these challenges, we employ a combination of first-principles density functional theory calculations and analytical modeling. Through our investigations, we demonstrate the critical role played by these ubiquitous substrate and ghost states in the observed topography inversion in STM images. By unraveling the influence of these states on STM measurements, we provide crucial insights for the accurate interpretation of STM topographies of atomically thin materials.

Our findings not only shed light on the phenomenon of topography inversion, but also contribute to the further development of 2D materials in (opto)electronic and quantum applications. Understanding and characterizing the ghost and substrate states is essential to unlock the full potential of 2D materials and enable their use in various technological advancements.

[1] “Spatially resolved on-dimensional boundary states in graphene-hexagonal boron nitride planar heterostructures”, J. Park et al., Nat.Com. 5, 5403 (2014).

[2] “Topography inversion in scanning tunneling microscopy of single-atom-thick materials from penetrating substrate states”, C. Park and M. Yoon, Sci. Reports 12, 7321 (2022).

11:00am **MI+2D+TF-ThM-10 Spatially-Resolved Photoemission Studies of Magnetic Weyl Semimetals***, S. Sreedhar,* University of California, Davis*; M. Staab, R. Prater,* University of California at Davis*; A. Rossi,* Italian Institute of Technology, Italy*; V. Ivanov,* Lawrence Berkeley Lab*; Z. Shen,* University of California at Davis*; G. Conti,* Lawrence Berkeley Lab*; V. Taufour, S. Savrasov,* University of California at Davis*; S. Nemsak,* Lawrence Berkeley Lab*; **Inna Vishik**,* University of California-Davis **INVITED**

$Co_3Sn_2S_2$ is a magnetic Weyl semimetal below its Curie temperature (T_c) of 177K. I will discuss spatial and temperature-dependent angle-resolved photoemission spectroscopy (ARPES) and x-ray photoelectron spectroscopy (XPS) studies in this system.Across T_c, we observe signatures of a topological phase transition, but also observe changes in bulk bands which are inconsistent with a simple lifting of exchange interactions, suggesting enhanced electronic correlations in the regime without long-range magnetic order.I will also discuss spatial-dependent ARPES and XPS data which quantify the characteristic differences between Sn- and S-terminated surfaces, with relevance for interpreting surface-dominated phenomena.

11:40am **MI+2D+TF-ThM-12 High-Temperature Superconductor FeSe Films Enabled Through Temperature and Flux Ratio Control***, **Maria Hilse**, H. Yi, C. Chang, N. Samarth,* The Pennsylvania State University*; R. Engel-Herbert,* Paul-Drude-Institut für Festkörperelektronik, Germany

FeSe, a bulk superconductor with a T_C of 9 K has attracted a high level of attention since a skyrocketing boost in TC was reported for a single unit cell (UC) layer of FeSe grown on SrTiO3(001) by molecular beam epitaxy (MBE) to as high as 100 K. FeSe-SrTiO3 heterostructures have since been fabricated by many groups but the record TC proved difficult to reproduce and thus the mechanism behind it remains concealed. After extensive work in the past, the field appears to agree on certain key “ingredients” in the heterostructure sample preparation that are believed essential for the boost in TC. Those are; 1. an ultra-clean substrate surface of a double TiO_{22} termination realized by a chemical and thermal *ex-situ* and/or thermal *in-situ* substrate preparation; 2. ultra-thin – one UC thickness – limit of FeSe; 3. a high number of Se vacancies in the FeSe film ensured through post-growth annealing steps in ultra-high vacuum (UHV) for several hours; 4. followed by a capping layer growth protecting FeSe against oxidation during *ex-situ* characterization.

We present our findings on FeSe thin film growth by MBE and present a roadmap for high-T_C – 222 % higher than the reported bulk value in *ex-situ* transport measurements – circumventing above mentioned steps 1, 2, and 3 by simple *in-situ* Se/Fe flux ratio and temperature control during FeSe growth. FeSe films of 20-UC-thickness grown at varying temperatures and Se/Fe flux ratios and the structural and morphological properties of the obtained uncapped FeSe films were analyzed. The morphology of the films showed a sensitive dependence on the growth temperature and flux ratio spanning from perfectly smooth and continuous films with atomic terraces at 450 °C growth temperature and a low flux ratio of 2.5 to exclusively disconnected island growth of large height but smooth top surfaces at lower temperatures and/or higher flux ratios. Surprisingly, the tetragonal P4/nmm crystal structure of beta-FeSe was maintained for all investigated films and the *in-situ* observed diffraction pattern in reflection high energy diffraction also maintained the streaky pattern characteristic for smooth FeSe films even for the samples with the most pronounced island growth resulting in a root mean square atomic force microscopy roughness of more than 18 nm. Smaller flux ratios than 2.5 resulted in mixed – beta-FeSe/elemental Fe – phase samples. FeSe films grown under optimized conditions at 450 °C and a flux ratio of 2.5 (but without any post-growth UHV anneal) and capped with the commonly used FeTe (300 °C) and elemental Te (room temperature) layers yielded superconducting onset temperatures of about 30 K and a TC of 20 K.

12:00pm **MI+2D+TF-ThM-13 Unraveling Picosecond Dynamic Material Processes on the Mesoscale by X-Ray Microscopy***, **Thomas Feggeler**,* University of California, Berkeley*; J. Lill, D. Guenzing, R. Meckenstock, D. Spoddig, B. Zingsem,* University of Duisburg-Essen, Germany*; M. Efremova,* Eindhoven University of Technology, Netherlands*; S. Pile, T. Schaffers,* Johannes Kepler University, Austria*; S. Wintz,* Max Planck Institute for Intelligent Systems, Germany*; M. Weigand,* Helmholtz Center Berlin, Germany*; A. Ney,* Johannes Kepler University, Austria*; M. Farle, H. Wende, K. Ollefs,* University of Duisburg-Essen, Germany*; D. Shapiro,* Lawrence Berkeley National Laboratory*; R. Falcone,* University of California, Berkeley*; H. Ohldag,* Lawrence Berkeley National Laboratory

Dynamic processes govern a multitude of phenomena in physical, chemical and material sciences. Time- and spatially resolved element-specific monitoring of such processes is crucial in the understanding of phenomena like magnetization dynamics, battery charging and discharging, and phase transitions of several kinds. Time-Resolved Scanning Transmission X-ray Microscopy (TR-STXM) [1] is a versatile tool fulfilling these demands on the mesoscopic scale, offering element-specific observations with sub 50 nm spatial resolution and picosecond time sampling. By introducing a phased-locked-loop excitation synchronization scheme, TR-STXM also allows to sample dynamics originating from continuous wave excitations. This presentation introduces the TR-STXM technique and its principle of operation, and the setup developed at the Advanced Light Source at Lawrence Berkeley National Laboratory. The presentation is complemented by examples of dynamic magnetic measurements, which allow for local monitoring of magnetization dynamics in fields such as spintronics, magnonics, biomedical and energy related applications. Here we demonstrate TR-STXM results on Py/Co microstructures [2], Py stripe ensembles [3] and magnetite nanoparticle chains inside magnetotactic bacteria *Magnetospirillum Magnetotacticum* [4,5], showcasing localized uniform and non-uniform resonant magnetic responses, supplemented by micromagnetic simulations in good agreement.

This work is funded by German Research Foundation projects OL513/1-1, 321560838, 405553726 TRR 270, and the Austrian Science Fund project: I 3050-N36. Lawrence Berkeley National Laboratory is acknowledged for funding through LDRD Award: Development of a Continuous Photon Counting Scheme for Time Resolved Studies. T.F. and R.F. acknowledge support from STROBE: A National Science Foundation S&T Center, under Grant No. DMR-1548924. This research used resources of the Advanced Light Source, a U.S. DOE Office of Science User Facility under contract no. DE-AC02- 05CH11231. The use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. We thank HZB for the allocation of synchrotron radiation beamtime.

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2D Materials Technical Group
Room C123 - Session 2D1-ThA

2D-Materials: Topological and Quantum Properties

Moderators: Harriet Åhlgren, University of Vienna, **Miaofang Chi**, Oak Ridge Natinal Laboratory

2:20pm **2D1-ThA-1 2D Transition Metal Chalcogenide Semimetals*, David Cobden,*** University of Washington **INVITED**

Graphite (graphene) is a 2D semimetal that after nearly two decades still continues to surprise. Only one other 2D semimetal, WTe_2, has been studied in detail down to the monolayer limit, where it too exhibits diverse properties including topological edge conduction, superconductivity, ferrolectricity, and probable excitonic order. The indications are therefore that 2D semimetals in general form an extraordinarily rich class of materials that deserves more exploration. We will talk about our ongoing work to understand the properties of monolayer WTe_2 better, to investigate the hybrid semimetal system of graphene/WTe_2, and to isolate and study other semimetallic 2D transition-metal chalcogenides.

3:00pm **2D1-ThA-3 Artificial Graphene Nanoribbons with Tailored Topological States*, Nathan Guisinger,*** *P. Darancet,* Argonne National Laboratory, USA

Low-dimensional materials functioning at the nanoscale are a critical component for a variety of current and future technologies. From the optimization of light harvesting solar technologies to novel electronic and magnetic device architectures, key physical phenomena are occurring at the nanometer and atomic length-scales and predominately at interfaces. In this presentation, I will discuss low-dimensional material research occurring in the Quantum and Energy Materials (QEM) group at the Center for Nanoscale Materials. Specifically, the synthesis of artificial graphene nanoribbons by positioning carbon monoxide molecules on a copper surface to confine its surface state electrons into artificial atoms positioned to emulate the low-energy electronic structure of graphene derivatives. We demonstrate that the dimensionality of artificial graphene can be reduced to one dimension with proper "edge" passivation, with the emergence of an effectively-gapped one-dimensional nanoribbon structure. Remarkably, these one-dimensional structures show evidence of topological effects analogous to graphene nanoribbons. Guided by first-principles calculations, we spatially explore robust, zero-dimensional topological states by altering the topological invariants of quasi-one-dimensional artificial graphene nanostructures. The robustness and flexibility of our platform allows us to toggle the topological invariants between trivial and non-trivial on the same nanostructure. Our atomic synthesis gives access to nanoribbon geometries beyond the current reach of synthetic chemistry, and thus provides an ideal platform for the design and study of novel topological and quantum states of matter.

3:20pm **2D1-ThA-4 Critical Materials: Fine Tuning Electronic and Structural Properties of Rare-Earth Based 2-D Structures at the Atomic Limits*, Kyaw Zin Latt,*** Nanoscience and Technology Division, Argonne National Laboratory*; T. Ajayi,* Nanoscience and Technology Division, Argonne National Laboratory ; Nanoscale and Quantum Phenomena Institute, and Department of Physics & Astronomy, Ohio University*; X. Cheng,* Department of Chemistry and Biochemistry, Ohio University*; N. Dandu,* Materials Science Division, Argonne National Laboratory*; A. Ngo,* Materials Science Division, Argonne National Laboratory; Chemical Engineering Department, University of Illinois*; E. Masson,* Department of Chemistry and Biochemistry, Ohio University*; S. Hla,* Nanoscience and Technology Division, Argonne National Laboratory; Nanoscale and Quantum Phenomena Institute, and Department of Physics & Astronomy, Ohio University

Rare-earth metals have many important applications including quantum information, energy up-conversion, emission, and catalysis. In the rare-earth based molecules, the interaction between the metal atom and local electronic states plays a vital role in determining its properties. This can be exploited by engineering molecular ligands to tailor for desired applications. These molecular ligands not only protect the rare-earth metal atoms from the surrounding environment but also influence electronic and magnetic properties [1,2]. Thus, they can be used to tailor the properties of rare-earth ions. Based on the design of the ligands, it can form different types of self-assembled structures which further opens the opportunity to fine tune the properties. In our research, we have designed a variety of rare-earth (Eu,Tb,La) based molecular systems which are deposited onto noble metal surface such as Au(111) under ultrahigh vacuum(UHV) environment to form self-assembled 2D layers. Using a low temperature scanning tunneling microscope, atomic level characterizations of electronic and structural properties of rare-earth complexes absorbed on metal surfaces are performed. Furthermore, tunneling spectroscopic mapping of a self-assembled cluster reveals the spatial variation of electronic orbitals. The experimental results are supported by density functional theory calculations.

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3:40pm **2D1-ThA-5 Quantum Sensing with Spin Qubits in Hexagonal Boron Nitride*, Tongcang Li,*** Purdue University **INVITED**

The recent discovery of spin qubits in hexagonal boron nitride (hBN), a van der Waals (vdW) layered material, has opened up exciting possibilities for quantum sensing. Owing to its layered structure, hBN can be easily exfoliated and integrated with various materials and nanostructures for in-situ quantum sensing. In this talk, I will provide a brief overview of recent advancements in quantum sensing and imaging using spin defects in hBN [Advances in Physics: X, 8, 2206049 (2023)] and discuss our contributions to this emerging field. We have demonstrated high-contrast plasmon-enhanced spin defects in hBN for quantum sensing [Nano Letters 21, 7708 (2021)] and investigated their excited-state spin resonance [Nature Communications, 13, 3233 (2022)]. Additionally, we achieved optical polarization and coherent control of nuclear spins in hBN at room temperature [Nature Materials 21, 1024 (2022)], paving the way for manipulating nuclear spins in vdW materials for quantum information science and technology applications. Finally, we will discuss our work on sensing paramagnetic ions in water using hBN spin defects [arXiv:2303.02326], which demonstrates the potential of ultrathin hBN quantum sensors for chemical and biological applications.

2D Materials Technical Group
Room B110-112 - Session 2D2-ThA

2D-Materials: Surface and Interface Effects

Moderators: Huamin Li, University at Buffalo-SUNY, **Cristina Satriano**, University of Catania

2:20pm **2D2-ThA-1 Two-dimensional van der Waals Materials and Their Mixed Low-Dimensional Hybrids for Electrochemical Energy Applications*, Fei Yao,*** University at Buffalo-SUNY

Compared with their 3D counterparts, two-dimensional (2D) van der Waals (vdW) materials exhibit quantum confinement where charge carriers are spatially confined at the physical boundaries. Particularly, when mixing 2D materials with other low-dimensional (LD) materials, they exhibit enormous potential in electrochemical energy applications due to the unique properties arising from reduced dimensionality and, more importantly, material integration synergy. In this work, 2D transition metal dichalcogenides and their mixed low-dimensional hybrids (MLDHs) are introduced with an emphasis on innovations covering 2D-based hybrid structure construction and electrochemical applications. Fundamental insight into the synergistic effect of the MLDHs integration for advancing the development of Li-ion batteries and electrocatalytic hydrogen evolution reaction will also be discussed. Leveraging the unique microreactor platform based on the 2D vdW platform, a mechanistic understanding of charge transport dynamics at the electrified interface will be highlighted. The knowledge gained on how mixed-dimensional physics and chemistry will shed light on the design principle of the electrode materials and deepen the understanding of the process-structural-property-performance (PSPP) relationship of the vdW-based hybrid structures.

2:40pm **2D2-ThA-2 Influences of Fe Vacancy and Te Vacancy on Magnetic Domains on Fe_3Gete_2 Surfaces*, TeYu Chien,*** University of Wyoming*; D. Baral,* University of Arkansas*; Z. Fu, J. Tian,* University of Wyoming*; H. Chen,* Colorado State University

Fe_3GeTe_2 (FGT) is a van der Waals (vdW) ferromagnetic metallic material with Curie temperature around 230 K. Despite the central symmetric crystal structure, magnetic skyrmions and various magnetic domain textures have been reported in FGT. The magnetic domain textures can be widely tuned with thickness, temperature and magnetic field. Several ideas regarding the origin of the wild magnetic domain textures have been proposed, including oxidized layer induced DMI, Fe defect vacancy etc. Here, by utilizing spin polarized scanning tunneling microscopy (SPSTM), we revealed that, compared to Fe vacancies, the Te vacancies have stronger effects on altering the magnetic domains in the otherwise ferromagnetic system. A theoretical model will also be discussed to explain the difference between the Te vacancies and the Fe vacancies on the magnetic domain wall pinning.

3:00pm **2D2-ThA-3 Emergent Moiré Phonons Due to Zone Folding in WSe$_2$-WS$_2$ Van Der Waals Heterostructures***, **Hsun Jen Chuang**, B. Jonker,* Naval Research Laboratory

Bilayers of 2D materials offer opportunities for creating devices with tunable electronic, optical, and mechanical properties. In van der Waals heterostructures (vdWHs) where the constituent monolayers have different lattice constants, a moiré superlattice forms with a length scale larger than the lattice constant of either constituent material regardless of twist angle. Here, we report the appearance of moiré Raman modes from nearly aligned WSe$_2$-WS$_2$ vdWHs in the range of 240 cm^{-1} -260 cm^{-1}, which are absent in both monolayers and homobilayers of WSe$_2$ and WS$_2$ and in largely misaligned WSe$_2$-WS$_2$ vdWHs. Using first-principles calculations and geometric arguments we show that these moiré Raman modes are a consequence of the large moiré length scale which results in zone-folded phonon modes that are Raman active. These modes are sensitive to changes in twist angle, but notably, they occur at identical frequencies for a given small twist angle away from either the 0-degree or 60-degree aligned heterostructure.Our measurements also show a strong Raman intensity modulation in the frequency range of interest, with near 0 and near 60-degree vdWHs exhibiting a markedly different dependence on excitation energy. In near 0-degree aligned WSe$_2$-WS$_2$ vdWHs, a nearly complete suppression of both the moiré modes and the WSe$_2$ A_{1g} Raman mode (~250 cm^{-1}) is observed when exciting with 532 nm CW laser at room temperature. Temperature-dependent reflectance contrast measurements demonstrate the significant Raman intensity modulation arises from resonant Raman effects.

3:20pm **2D2-ThA-4 Stabilizing Metastable Constituent Structures via 2D Interlayer Interactions in Heterostructures***, **Fischer Harvel**, D. Johnson,* University of Oregon

The interactions between constituent layers in heterostructures provide an opportunity to stabilize 2D compounds not found in equilibrium phase diagrams. Utilizing 2D layers of 3D structures like rock-salt structured PbSe, commonly found in thermodynamically stable heterostructures known as misfit compounds, phenomena such as charge transfer to and surface stabilization can be used to stabilize new structures. In the iron-selenide system β-FeSe exhibits high-temperature superconductivity (T_c ~ 107 K) when grown in a monolayer on a SrTiO$_3$ substrate. This motivation sparked our interest in investigating possible Fe-Se phases when layers of controlled composition are spatially confined between adjacent layers of PbSe. Using a computational “island” approximation, potential candidate Fe-Se structures were placed between bilayers of PbSe and were relaxed in DFT calculations to assess stability of different structures. Of the trialed candidates, $(PbSe)_{1+\delta}(FeSe_2)$ with Fe in octahedral coordination (1T) maintained its structure when relaxed. Using the predicted densities of the relaxed model, precursors that mimic the nanoarchitecture of the heterostructure were prepared and annealed at low temperatures to prepare the heterostructures $(PbSe)_{1+\delta}(FeSe_2)_n$ where n = 1, 2, and 3. To probe the effect of different adjacent layers on the stability of the 1T FeSe$_2$ layers, we successfully stabilized 1T-FeSe$_2$ in $(PbSe)_{1+\delta}(NbSe_2)(PbSe)_{1+\delta}(FeSe_2)$. These systems provide insights into interfacial interactions between constituent layers in 2D heterostructures that can be used to prepare layers with structures not found in the phase diagrams of the constituent elements.

3:40pm **2D2-ThA-5 Comparative Study of How Growth Parameters Affect the Optoelectronic Properties of MoSe$_2$ and WS$_2$ on Sapphire Substrates Grown by Chemical Vapor Deposition (CVD)***, **Selena Coye**,* Department of Physics, Clark Atlanta University*; K. Johnson,* Morehouse College, Department of Dual Degree Engineering*; I. Matara Kankanamge, M. D. Williams,* Department of Physics, Clark Atlanta University

Two-dimensional molybdenum diselenide (MoSe$_2$) and tungsten disulfide (WS$_2$) exhibit remarkable properties that make them ideal for various applications in nanoelectronics, spintronics, valleytronics, and optoelectronics. The bandgap of these materials increases as their thickness decreases. Specifically, when reduced to a monolayer, the bandgap changes from indirect to direct. The bandgap of MoSe$_2$ is 1.1 eV for the bulk layer and 1.5 eV for the few layers. On the other hand, monolayer WS$_2$ has a direct bandgap of 2.15 eV, whereas bulk WS$_2$ has an indirect bandgap of 1.3 eV. These materials are grown on different substrates however, sapphire is an excellent substrate for growing these materials due to its remarkable mechanical and thermal properties and chemical stability. Consequently, it produces a mechanically robust and thermally stable film, making it indispensable for devices requiring durability and the ability to withstand high temperatures. By growing WS$_2$ on a sapphire substrate, it can achieve epitaxial growth by reducing the lattice mismatch between sapphire and WS$_2$. This leads to a high-quality WS$_2$ film with fewer defects, thus enhancing the material's overall structural quality. Chemical vapor deposition (CVD) is the widely used technique to grow these materials. However, the quality of the layers (including their crystallinity, crystallite size, and coverage area) grown by CVD depends on factors such as growth temperatures, growth time, precursors, flow rate, and substrate nature. Our research will study the effect of carrier gas flow rate and growth time on the bandgap, lattice structure, optical properties, and structural quality of MoSe2/sapphire andWS$_2$/Sapphire layers grown by CVD. We will analyze the properties of these films using Raman/PL, FTIR spectroscopy, and confocal microscopy.

4:00pm **2D2-ThA-6 Imaging Spin Filter for NanoESCA Based on Au/Ir or Oxide Passivated Fe***, M. Escher, N. Weber, T. Kuehn, **Marten Patt**,* FOCUS GmbH, Germany

The energy-filtered photoelectron microscope NanoESCA [1,2] is a powerful tool for various application including work-function mapping, imaging XPS and in the last years more prominently for momentum microscopy on 2D materials (e.g. see [3]).

This analyzer can be used with an efficient spin filter that enables to image a 2D-distribution of the electron spin polarization by scattering the electrons at a polarizing target. We will show results from the first commercial build Au/Ir Imaging Spin Filter. Sherman functions of +68% and -58% were found at a reflectivity of more than 1% (also see literature [4]).

Spin-filtered images of magnetic domains show that along the diameter of the field of view more than 100 separate image points can be resolved. This increases the effective 2D figure-of-merit of this analyzer by nearly four orders of magnitude compared to single-channel spin detectors. We also present proof of principal measurements of an Imaging Spin Filter with oxide passivated Fe as scattering target [5]. Oxide passivated Fe allows for an easy switch of the polarization detection direction, like it is known from FERRUM detectors [6] for ARPES.

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2D Materials Technical Group
Room Oregon Ballroom 203-204 - Session 2D-ThP
2D-Materials: Poster Session

2D-ThP-1 Multi-MOF-Based Chemical Gas Sensors with Enhanced Selectivity and Sensitivity via Quartz Crystal Microbalances*, **Tzer-Rurng Su**, J. Dhas, C. Pan, M. Paul, C. Simon, C. Chang,* Oregon State University

Metal-organic frameworks (MOFs) have emerged as promising materials for gas sensing applications due to their high surface area, chemical stability, and absorbent selectivity. In this work, we study the combination of thin film MOFs, including Zeolitic Imidazolate Framework (ZIF)-4, ZIF-7, ZIF-8, and ZIF-71 on Quartz Crystal Microbalances (QCM) as chemical sensors. ZIF thin films with controllable thickness were deposited using chemical bath deposition. ZIF films' physical and chemical properties were characterized by X-ray diffraction, Scanning Electron Microscopy, Brunauer-Emmett-Teller analysis, Fourier-transform infrared spectroscopy, and X-ray Photon Spectroscopy. The sensing response of MOFs/QCM sensors depends strongly on the pore properties of sensing material and molecular chemical properties[1]. The physical properties of each MOF, including its pore size, pore volume, and surface area, result in different uptake and release dynamic responses to various gas species, such as Ammonia, Carbon Dioxide, Water, and Volatile Organic Compounds. By simultaneously testing these MOFs/QCM sensors, we obtain different sensing responses to mixtures of gases; these data, combined with a data analytics tool, improve the overall selectivity of the sensing arrays.

Our results demonstrate that the MOF/QCM-based chemical sensing arrays can detect and distinguish a mixture of gas species, enabling the identification and quantification of different gas species.

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2D-ThP-2 Graphene/Noble Metal Nanoparticles Nanocomposites at the Biointerface with a Blood Brain Barrier Model to Scrutinize Brain Wound Healing*, A. Foti, L. Calì, A. Agafonova, A. Cosentino, C. Anfuso, G. Lupo, **Cristina Satriano**,* University of Catania, Italy

Graphene-based nanomaterials represent an emerging aspect of regenerative medicine, and graphene oxide (GO) has been especially exploited to overcome the blood–brain barrier (BBB). Noble metal nanoparticles (NPs), including gold (Au), silver (Ag), and palladium (Pd), have the properties of adjustable size, optical properties, flexible surface modification, and biocompatibility, which makes them very attractive for nanomedicine of brain diseases. NPs are able to cross the BBB, therefore can be used as drug delivery carriers or, given their intrinsic anti-inflammatory properties, as theranostic platforms.

In this work, we prepared Au, Ag, and Pd NPs, 20-100 nm in size, and their respective hybrid systems with GO (NP@GO), aiming to investigate wound healing, a complex process involving cell adhesion, migration, and proliferation processes. The wound healing is critically affected by hypoxia, which inhibits endothelial wound repair as a result of decreased migration and proliferation. A derangement of brain wound healing may cause some cases of Alzheimer's disease, leading to an impairment of BBB integrity and function.

The physicochemical characterization was assessed by UV-visible spectroscopy, AFM, DLS and zeta potential, to investigate the plasmonic response thus estimating the NP optical diameter, the morphology, the hydrodynamic size and the surface charge, respectively.

In order to mimic *in vitro* the condition of hypoxia related to pathological situations, we used human brain microvascular endothelial cells (BMECs), the principal components of the BBB together with pericytes and astrocytes, and human umbilical vein endothelial cells (HUVECs). The cytotoxicity and/or proliferation were inspected via MTT assay, and cell migration by the wound scratch assay, while the cellular uptake and the organelle perturbation were scrutinized by confocal microscopy. Moreover, the levels of inflammatory cytokines such as IL-1β, IL-6, IL-8, TNF-α, and HIF1-α and VEGFA were detected at protein and mRNA levels, evaluating the reduction/increase of inflammatory cytokines/anti-inflammatory IL-10.

2D-ThP-4 Performance and Reliability Improvement of IGTO TFTs via Co-Sputtering*, **Seung Jin Kim**, B. Choi,* Sungkyunkwan University, Korea

In this study, highly improved positive bias stress(PBS) and negative bias stress(NBS) stability of IGTO (InGaSnO) thin film transistor is achieved by simultaneous co-sputtering of HfO2and IGTO target. Channel doping via co-sputtering has been extensively studied, and its effect on improving reliability under bias stress has been confirmed through several studies. However, side effects such as decrease in on/off ratio or mobility degradation have also been observed. In this study, we fabricated TFTs with a 2-layer structure, where the bulk channel material was deposited separately after thin co-sputtering deposition of HfO2 and IGTO at the interface the gate oxide and channel material, instead of co-sputtering the entire channel material. The threshold voltage shift under positive bias and negative bias stress at a stress time of 3000s was improved from 11.5V to 5.8V, and 2.9V to 1.2V respectively. In result, this study suggests an ultimate device fabrication method that can improve the reliability issues due to stress, which is an inherent problems in oxide semiconductors.

2D-ThP-5 NanoFrazor Technology: Enabling Unique Nanowire and 2D Material Device Fabrication*, **Nicholas Hendricks**, A. Ubezio, M. Käppeli, J. Vergés, J. Chaaban, E. Çağin,* Heidelberg Instruments Nano, Switzerland

Thermal scanning probe lithography (t-SPL), enabled by the NanoFrazor technology, is a nanolithography technique particularly suitable for patterning, contacting, and modifying 2D materials and nanowires [1-5]. t-SPL generates patterns by scanning a heated ultrasharp tip over a sample surface to induce local changes. By using thermal energy as a stimulus, it is possible to perform various modifications to the sample via removal, conversion, or addition of/to the sample surface. Along with an ultrasharp tip, the t-SPL cantilever contains several other important functions such as an integrated thermal height sensor and an integrated heating element both of which are advantageous for generating devices from nanowires and 2D materials.

Nanowires and 2D materials have been the focus of intense academic and industrial research as these materials provide great promise as next generation electronic devices. However, when patterning electrical contacts to nanowires and 2D materials with conventional fabrication techniques (photolithography, electron beam lithography), the fabrication process becomes challenging and time consuming due to overlay requirements. These techniques can also lead to less than desired device performance due to damage from charged particles or ultraviolet irradiation, as well as contamination from residual resist. The issue of time intensive processing comes from the random positioning of nanowires and 2D material flakes on substrates which makes overlay challenging. This point of overlay is addressed with t-SPL by having an integrated thermal height sensor that allows for a non-invasive, in-situ measurement technique to detect buried nanowires or 2D materials prior to patterning. Such capabilities allow for real-time imaging and markerless overlay with high precision [6].

Within this presentation, the background and workings of t-SPL will be briefly introduced, nanostructuring on nanowires and 2D materials will be discussed along with electrical and optical device performance for nanowire and 2D material-based devices fabricated using t-SPL.

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2D-ThP-6 Synthesis of 2D-WS$_2$ on c-sapphire using H$_2$S gas-source CVD*, **Kun-An Chiu**, W. Chen, H. Chen, Y. Lin, C. Chen, H. Chen, F. Chen,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Two-dimensional materials are considered one of the key materials for next-generation semiconductor devices and industrial applications. In recent years, semiconductor devices based on two-dimensional electronic channel materials have shown their feasibility in transistor applications, in order to continue Moore's law [1]. WS$_2$ is one of the representative materials in two-dimensional transistors. WS$_2$ exhibits excellent properties, such as high carrier mobility, large on/off ratio, high optical excitation intensity, low response time, and good compatibility with other two-dimensional materials such as graphene [2, 3]. The development of growth processes for rapid and large-scale production of 2D transition metal dichalcogenides (TMDs) are receiving increasing attention in the fields of nanophotonics, flexible electronics, and sensors. Chemical vapor deposition

(CVD) is the most promising method for obtaining high-quality large-area 2D-TMDs. However, current equipment and technology make it difficult to effectively produce large-area, high-quality two-dimensional materials. Most two-dimensional material processes use powder as a precursor. The vapor pressure of metal and sulfur powders is not easily and stably controlled. Although some studies use a mixed H_2S gas (Ar + H_2S), it is difficult to effectively control the H_2S concentration during the process due to the difference in gas density.

In this study, WS_2 was synthesized on a (0001) sapphire substrate using WO_3 powder and pure H_2S gas as precursors in a hot-wall CVD furnace. The experiment was carried out at a process temperature of 950°C, a pressure of 10-50 torr, and a H_2S/Ar flow ratio of 0.5-5%. The synthesized WS_2 flakes were characterized by using optical microscopy, Raman spectroscopy, in-plane X-ray diffraction, and transmission electron microscopy. The in-plane GIXRD results showed that the WS_2 flakes were heteroepitaxially grown on the (0001) sapphire substrate with two sets of orientation relationships: $(100)_{WS2}$ // $(110)_{Al2O3}$, $(110)_{WS2}$ // $(100)_{Al2O3}$, and $(110)_{WS2}$ // $(110)_{Al2O3}$, $(100)_{WS2}$ // $(100)_{Al2O3}$. This indicates that the WS_2 flakes have a consistent orientation. Furthermore, the TEM observation revealed that the WS_2 film thickness was ~ 7 Å, suggesting that the process can synthesize the WS_2 monolayer.

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2D-ThP-8 Polarization Sensitive Frequency Selective Metasurface for the Infrared Spectral Range*, **Micheal McLamb**, P. Stinson, N. Shuchi, D. Louisos, T. Hofmann,* University of North Carolina at Charlotte

Metasurfaces, in the form of perfect reflectors, have received attention for their sensing and filtering capabilities. Plasmonic metasurfaces allow for frequency filtering by controlling the input polarization. We demonstrate a frequency filtering metasurface composed of an array of subwavelength metallic pluses fabricated using two-photon polymerization.

2D-ThP-9 *In-situ* X-ray Absorption Spectroscopy Study of Monodispersed Cobalt Phthalocyanine on Carbon Nanotubes as Electrocatalyst for Carbon Dioxide Reduction to Methanol*, **Mason Lyons**,* Oregon State University*; C. Rooney, H. Wang,* Yale University*; Z. Feng,* Oregon State University

Carbon dioxide (CO_2) is accumulating in the atmosphere, causing entrapment of thermal energy and more chaotic weather. To sustainably decumulate the atmospheric CO_2 and sequester future emissions, it must be utilized in a circular economy. Upcycling of CO_2 to value added products such as hydrocarbons and alcohols requires the use of catalysts, among which molecular catalysts are the most promising due to their product selectivity and high utilization of metals. Unlike many other catalysts which primarily produce the undesired carbon monoxide (CO) intermediate, cobalt phthalocyanine (CoPc) non-covalently anchored on carbon nanotubes (CNTs) exhibits preferential formation of methanol (MeOH) from CO_2 due to a modified Co electronic structure. To investigate the electronic and geometric arrangements of CoPc-CNTs during CO_2 reduction, *in-situ* X-ray absorption spectroscopy (XAS) was employed. The pre-edge peaks at 7710 eV related to orbital mixing increased while the 7715 eV peak related to bonding centro-symmetry decreased, when scanning from open circuit voltage to -1.1 V vs Reference Hydrogen Electrode (RHE) indicating a higher density of states in Co $3d_{z^2}$ and axial coordination from CNT as well as C adsorbate, respectively. An absorption edge shift associated with Co reduction to Co(I) was also observed and persisted at MeOH producing conditions, previously only reported for CO producing systems. Fitting of the extended X-ray absorption fine structure (EXAFS) spectra confirmed the CoPc coordination and bond lengths with theoretical calculations as well as the presence of a carbon adsorbate at potentials more negative than -0.5 V vs RHE, enabling further CO reduction to MeOH. The rich information from *in-situ* XAS elucidated the structure-property relationship of this catalyst to explain the superior performance of CoPc dispersed on CNTs for CO_2 upgrade.

2D-ThP-10 A Method for creating Single Atom Catalysts through Vapor-phase Synthesis of Covalent Organic Frameworks*, **Siamak Nejati**,* University of Nebraska–Lincoln*; S. Gnani Peer Mohamed,* University of Nebraska - Lincoln

The process of synthesizing thin films of covalent organic frameworks (COFs) in situ, without the use of solvents, is an attractive route for the creation of single-atom catalysts (SACs) based on metal-N4 motifs. This one-step synthesis and integration approach makes it suitable for incorporating the materials into the architecture of electrode devices. Compared to traditional SACs preparation methods, this approach allows for an increase in the number of active sites and improved synthetic precision, resulting in highly desirable electrocatalytic performance. In this study, we employed porphyrins as precursors and demonstrated the feasibility of using vapor phase deposition to create COFs with metal-porphyrins. In recent decades, the improved electrocatalytic properties of porphyrin-based COFs with two or three dimensions have garnered significant attention. However, their covalent networks and organic nature make solution-based COF synthesis challenging for creating thin films, which limits their widespread use in various applications. We demonstrate a solvent-free vapor phase synthesis of crystalline and porous porphyrin-based COFs (POR-COFs) using 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP) and its transition metal complex (MTAPP, M = Cu^{2+}, Co^{2+}) through pulse-assisted oxidative chemical vapor deposition (oCVD). Pyridine, a co-crystallizing agent, is used to enhance the crystallinity and structure of the MPOR-COF. We observed varying electrocatalytic activity towards different reactions depending on the occupancy of the porphin center. The synthesized MPOR-COFs exhibit excellent electrochemical performance for nitrate electroreduction to ammonia (Faradaic efficiency of ~86% at 1.7 V vs Ag/AgCl), oxygen reduction and evolution reaction in aprotic media, and as a cathode material for Li-Oxygen battery. This synthetic approach offers a sustainable and scalable method for thin film COF production and opens up new opportunities for their application in energy storage and conversion systems. The measured electrocatalytic activities proved that our approach to synthesizing catalysts from COFs is a viable path to realize the next generation of SACs catalysts.

2D-ThP-11 Real-Time Machine Learning Enhanced Defect Engineering in Ceria Nanostructures*, U. Kumar,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; C. Feit, N. Berriel,* University of Central Florida*; K. Basu,* University of Texas at Dallas*; P. Banerjee, S. Seal,* University of Central Florida*; **Yifei Fu**,* University of Central Florida, Orlando

Ceria nanostructures have been employed in diverse applications due to their distinctive defect structure, which grants them regenerative oxidative properties. The redox activity of ceria depends on its surface defect structure and is generally determined by its Ce^{3+}/Ce^{4+} oxidation state ratio, often measured by ex-situ X-ray photoelectron microscopy (XPS). Numerous studies have demonstrated that defect engineering strategies, such as size and morphology manipulation or introduction of doping, are effective in altering ceria nanostructures for various applications. However, despite the success achieved by these methods, it is still challenging to have precise and reversible control over ceria defect structures. To address this challenge, we propose the use of Machine Learning (ML) techniques to enhance defect engineering in ceria nanofilms.

Deposition conditions, such as temperature, pressure, and the number of cycles, play an important role in the ALD process. Our previous work[1] has demonstrated that well-optimized ALD processes can be achieved with the help of in-situ spectroscopic ellipsometry (SE). Therefore, the desired thickness of ceria thin film can be rapidly developed without the ex-situ characterization usually required by conventional approaches. In the current work, data collected through in-situ SE and ex-situ XPS has been correlated using ML algorithms. Two approaches have been studied to exert better control over the defective structure of ceria thin film. The first method involves an indirect approach of thickness prediction using an ML algorithm, followed by Ce^{3+}/Ce^{4+} estimation using an experimental calibration curve. The second method, with a more direct approach, involves Ce^{3+}/Ce^{4+} prediction using real-time ellipsometry data (amplitude ratio ψ and phase difference Δ) using Gradient Boost and Random Forest Regressor. Overall, in the present work, an ML algorithm trained by in-situ ES data was shown to be an effective approach to control the thickness and defect level of Ceria ALD films.

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2D-ThP-12 Investigating the Fate of Nanoplastics in Aquatic Environments*, **Tycho Roorda**, I. Groot,* Leiden University, The Netherlands

Plastic particles in the ocean have become a contaminant of emerging concern due to their damage to humans and marine life[1,2]. Of all plastic production, which is increasing still, it has been shown that more than 99% of plastic waste which ends up in the oceans can not be accounted for[2,3].The belief is that part of all this missing plastic degrades to a micro-and nano-sized scale which had not yet been detected[4,5]. Nanoplastics have also been shown to promote the spreading of toxins, such as heavy metals, which would otherwise sink to the ocean floor at their source[6,7]. In order to understand the fate of nanoplastics in aquatic environments, we must have a better understanding of the degradation mechanisms at an atomic and chemical level. In this project, we have successfully deposited nanoplastics onto a substrate in UHV by physical vapor deposition for degradation studies and to investigate their binding mechanism to other toxins in the ocean. The deposition of nanoplastics is confirmed by mass spectrometry, Auger electron spectroscopy and X-ray photoelectron spectroscopy. The degradation mechanisms which will be studied are oxygenation, hydrogenation, UV exposure and thermal annealing which will be investigated in ultra-high vacuum with atomic force microscopy and combined scanning tunneling microscopy. This combination allows for the identification of individual particles by conductivity making it possible to study the binding mechanism between nanoplastics and certain toxins. In this project, we aim to investigate the binding mechanism between nanoplastic particles and heavy metals as well as the nanoplastics' degradation by operando dosing of gases and heating to real world conditions.

2D-ThP-13 Plasma-Induced Energy Band Evolution for Two-Dimensional Heterogeneous Junctions*, A. Ahmed, A. Cabanillas, A. Chakravarty, F. Yao,* ***Huamin Li,*** University at Buffalo

With the rise of two-dimensional (2D) materials and nanoelectronics, compatible processes based on existing Si technologies are highly demanded to enable new and superior device functions. In this work, we exploit the CMOS-compatible O_2 plasma treatment as an effective anionic substitution doping approach for 2D WSe_2, and demonstrate a heterogeneous WSe_2/MoS_2 junction as an anti-ambipolar field-effect transistor (FET) with outstanding performance. Specifically, novel plasma-induced oxidization and doping were performed to achieve a controllable enhancement of hole transport in WSe_2 through moderate or even degenerate doping. By incorporating with 2D MoS_2 dominated by electron transport as well as the applied in-plane and out-of-plane electric fields, an evolution of the energy band structure of the 2D heterogeneous junction can be obtained, and the corresponding charge transport, dominated by the Fowler-Nordheim (FN) tunneling, is comprehensively elucidated. As an anti-ambipolar FET, our prototype device exhibits outstanding and balanced performance including a superior peak-valley ratio (PVR, 2.4×10^5) and a high current density (55 nA/µm). This work demonstrates the great potential of 2D materials and their doping engineering to feasibly integrate with the existing CMOS technology and eventually improve the efficiency of future nanoelectronics.

2D-ThP-14 *in-situ* Electronic structure monitoring of 2D TMDC-field effect transistor by operando-XPS*,* ***Seungwook Choi,*** Korea Research Instutue of Standards and Science (KRISS), Republic of Korea*; G. Oh, T. Kim,* Jeonbuk National University, Republic of Korea*; A. Kim,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea

Two-dimensional transition metal dichalcogenide material-based field effect transistor (2D TMDC-FET) could be one of next-generation transistors because they have novel material properties including high on-off ratio above 10^6, subthreshold swing of 140 mV/dec, Hall mobility around 10 cm^2/Vs, and tunable bandgap depending on the number of layers. "*Operando*", which means under working conditions, analysis method has been proposed to investigate the correlation between devices and materials and observe intermediate state of material while the device is working. To examine chemical and electrical properties at the channel interface of thin film FET under working condition, *operando* X-ray photoelectron spectroscopy (XPS) should be studied due to its surface-sensitive performance.

In this study, we will introduce a lab-source *operando* XPS system specially for commercial XPS system including a transistor probe stage and a special sample holder. Here, we present the change of electronic structure of TMDC-FET depending on a gate voltage using our lab-source *operando*-XPS system. The results reveal that the quantitative band bending of the FET channel can be observed during operating FET (switching on/off). Furthermore, the quality of active channel/insulator interface can be monitored during FET operation. We provide the strategy to minimize beam-damage attributed by the use of micro-focused x-ray beam during *operando* analysis. Furthermore, this *operando*-XPS analysis results enable to provide the optimized material and device structure of 2D TMDC-FET.

2D-ThP-15 Atomic Layer Deposition of Al_2O_3 on Monolayer MoS_2 with Mild NF_3 Remote Plasma Treatment*,* ***Kwangwuk Park,*** *J. Kang, H. Lee, M. Leem, G. Yeom, H. Kim,* Sungkyunkwan University (SKKU), Republic of Korea

Keywords: Plasma treatment, atomic layer deposition, two-dimensional crystals, molybdenum disulfide, surface functionalization.

Abstract. Considering the expected superior immunity to short-channel effects while maintaining high electron mobility even at a few monolayer thicknesses [1, 2], molybdenum disulfide (MoS_2), with a two-dimensional structure, is emerging as a promising alternative to ultrathin Si channels in future sub-nanometer transistors. Nevertheless, from a device integration standpoint, there remains a critical challenge: forming continuous dielectric films with a thickness of less than a few nanometers on MoS_2 via atomic layer deposition (ALD) due to the limited number of active sites on the MoS_2 surface [3]. Although various approaches have been explored to activate the MoS_2 surface for facile chemical interaction with ALD precursors [4], several challenges remain unresolved. These include achieving thickness scalability of MoS_2 down to a monolayer, ensuring thickness scalability of the gate dielectric, and adapting the process to three-dimensional device structures.

In this presentation, we introduce the use of NF_3 remote plasma treatment on the MoS_2 surface prior to ALD of an Al_2O_3 film at 200 °C. Without treatment, direct thermal ALD of Al_2O_3 on MoS_2 results in island-like growth characterized by numerous incomplete boundaries. In contrast, MoS_2 treated with NF_3 remote plasma facilitates the deposition of continuous and pinhole-free Al_2O_3 films, even at a thickness of 2 nm. We confirmed the minimal physical damage of the pretreatment to the monolayer MoS_2 through Raman and photoluminescence spectroscopy. Finally, we will discuss the electrical characteristics of MoS_2 field-effect transistors incorporating NF_3 remote plasma pretreatment.

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2D-ThP-16 AgNFs Supported on Graphene Based Materials as Multi-Wavelength SERS Active Platforms*, A. Brancato, M. Condorelli, S. Sciacca, C. Bonaccorso, M. Barcellona, M. Fragalà, C. Satriano, G. Compagnini,* ***Luisa D'Urso,*** University of Catania, Italy

Surface Enhanced Raman Spectroscopy (SERS) has been successfully employed in several fields of interest such as plasmonic sensing and biosensing, in-situ photocatalysis studies, single molecule detection, and many others real-world applications. Usually, the greatest contribution to the Raman enhancement is explained by an electromagnetic mechanism. To further potentiate the SERS effect, several research studies reported the employ of peculiar plasmonic nanostructures that allow the creation of hot-spots on characterized by strong electromagnetic fields. Moreover, the possibility to amplify Raman signals is strongly linked to the excitation wavelength of the employed laser interacting with the SER active substrate. In order to explore novel functional nanomaterials with a high enhancement in a wide range of excitation wavelengths, in this work we propose Silver Nanoflowers (AgNFs), anchorated to reduced thiolated graphene oxide (r-GOSH) nanosheets. The success of the coupling preparation procedure was verified by comparing the Raman and IR spectra of the materials, before and after coupling metal nanostructures with the 2D layers, and by UV-vis spectroscopy analyses. Furthermore, a morphological characterization of the new materials was carried out using scanning electron and atomic force microscopies. Thanks to the NFs morphology and to the extended surface of 2D materials is possible create numberless hot spot regions between silver petals and in the nanogaps area of the 2D material, exhibiting significant plasmonic effects as well as unique optical feature in the overall visible range. The SERS properties of the 2D hybrid material were studied using a standard molecule 4-mercaptobenzoic acid (4-MBA) as probe analyte at the nanomolar concentration. As the AgNFs extinction spectra cover the entire visible range, we were able to study the enhancement in a laser wavelength range between 532 and 785 nm, finding very high enhancement factors. This suggests that AgNF could be an excellent SERS substrate on the entire visible and near infrared spectral region and demonstrates that such nanomaterial can be easily used to study analytes at low concentrations with any exciting wavelength, opening the possibility to investigate several biological and medical interest analytes without the interference of not desired optical phenomena such as luminescence.

This work has been partially funded by the European Union (NextGeneration EU), through the MUR- PNRR project SAMOTHRACE (ECS00000022).

2D-ThP-17 Angiogenin-Tailored Graphene Oxide Nanosheets to Target Prostate Cancer*, **Diego La Mendola**, T. Marzo,* University of Pisa, Italy*; O. Hansson,* University of Goteborg, Sweden*; C. Satriano,* University of Catania, Italy

Angiogenin (ANG), an ubiquitous protein with a potent angiogenic power, is able to stimulate new vessel growth and cell self-renewal under both physiological and pathological conditions, including neuroprotection, inflammationand immune response. Anovel platform for modulating angiogenic processes in cancer therapies was developed based on graphene oxide (GO)functionalized with ANG.The new GO@ANG nanocomposite was characterized by means of UV-visible and fluorescence spectroscopies. The GO@ANG nanotoxicity was assessed by *in vitro* cellular experiments on human prostatic cancer cells (PC-3 line). Laser confocal microscopy (LSM) cell imaging evidenced an enhanced internationalization of the 2D nanomaterial functionalized with the protein rather than the bare nanosheets. Furthermore, significant changes in cell cytoskeleton organization compared to the cell treatments with free protein in different environmental conditions were detected.These results pointed to the modulating capability by the hybrid nanocomposite for different cellular biochemical response.

2D-ThP-18 Defect Inventory of CVT Grown TaS_2 Crystals*, **Dejia Kong**, R. Peckham,* University of Virginia*; Z. Mao, S. Lee,* Pennsylvania State University*; K. Burns, I. Harrison, P. Reinke,* University of Virginia

Defects are critical to the use and function of transition metal dichalcogenides (TMD), necessitating the study of the defect inventory from point defects to dislocations. The defect inventory sensitively modulates device performance metrics such as electron and phonon conductivity and exciton lifetimes. TMD layers exfoliated from bulk TMD crystals continue to serve as the main vehicle for experiments, and prototype devices. In this work, we present a scanning tunneling microscopy (STM) study at 293 K of the defect inventory in metallic 2H-TaS_2 which is a candidate for contacts in TMD devices. The 2H-TaS2 bulk crystal was grown by chemical vapor transport (CVT) with an iodine transport agent and high crystalline quality is confirmed with XRD. We capture different groups of defects formed during the CVT process across length scales from point defects to screw dislocation. One of the most prominent surface defects are line vacancies that resemble drainage system patterns in geomorphology maps (Figure 1) and are interpreted as remnants of the flux agent reaction at the growth surface. These line defects are closed and overgrown. The subsurface line defects can be resolved in STM as they imprint electronic and structural inhomogeneities on the subsequent layers. TEM analysis will elucidate the structure and composition across the buried line defects. We will include a discussion of recent electrical measurements.

In addition to mapping the defect inventory, we studied tip-induced nanolithography which affords nanoscale control of vacancy island formation in 2H-TaS_2 and is initiated at point defects. A tip-induced reaction allows selective removal of the top layer (Figure 2) with nanometer precision creating well-defined and faceted “holes”, respectively vacancy islands (v-island). The selective area removal of 2H-TaS_2 initiated by SPM probes has been reported previously, but the mechanism of such degradation is still discussed. We propose that it is related to the presence of traces of water at the tip or surface and present a detailed kinetic analysis of the etching process.[1-3] We studied the v-island growth over extended times and will discuss the feasibility of targeted etching of structures within the 2H-TaS_2 as a highly selective and high-resolution lithography process.

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2D-ThP-19 Advance in Momentum Microscopy with NanoESCA MARIS*, **Marten Patt**, N. Weber, M. Escher, T. Kuehn,* FOCUS GmbH, Germany

Since its introduction in 2005, the energy-filtered photoelectron microscope NanoESCA [1,2] has been used for various application including work-function mapping, imaging XPS and in the last years more prominently for imaging the reciprocal space, i.e., momentum microscopy or orbital tomography (e.g., at the NanoESCA at synchrotron Elettra, Trieste [3]).

The latest revision of the analyzer, called NanoESCA MARIS, has a new microscope lens. It was designed to achieve a better angular / momentum resolution while keeping the same good real space resolution < 35 nm from its predecessor. In momentum space mode, the instrument achieves a resolution of 0.005 $Å^{-1}$. We will show the performance on the Rashba split surface state of a Au (111) single crystal (Fig. 1,b). In addition, new working modes, like off-axis zoom, double dispersive imaging mode and an energy dispersion snapshot mode were introduced with the new analyzer and will be presented. Developments in the Imaging Spin Filter for NanoESCA [4] will be discussed.

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2D-ThP-20 A Novel Method to Measure Cross-plane Resistivity of Ultra-Thin Films*, S. Weng,* University of Southern California*; Y. Wang,* Stanford University*; **Celsey Price**, H. Blackwood, M. Choffel, A. Miller,* University of Oregon*; R. Li, M. Chen,* University of Southern California*; D. Johnson,* University of Oregon*; A. Majumdar,* Stanford University*; S. Cronin,* University of Southern California

Two-dimensional van der Waals heterostructures are of great interest because they are ideal for fundamental studies and diverse device applications. By vertically stacking 2D materials, you introduce the ability to control, manipulate, and generate the transport and confinement of charge carriers, excitons, phonons, and photons. Understanding and characterizing charge carrier transport across van der Waals interfaces is critical to the fundamental understanding and application of 2D van der Waals heterostructures. Measuring the cross-plane properties of a heterostructure is difficult, however, due to the measurements being intrinsically 2-probe, with the measured total cross-plane resistance including the lead and contact-sample interface resistances in addition to the resistance of the sample. Here we present a novel method to determine the bottom and top sample-contact and lead resistances through in-plane measurements, modeling the extent of current crowding in the end voltage as a function of contact width. The cross-plane sample resistance is obtained by subtracting these resistances from the measured total cross-plane resistance. This opens a unique opportunity to investigate the nature of charge transport across van der Waals interfaces. Temperature-dependent data for the PbSe(VSe_2) heterostructure is used to demonstrate this approach. The dominant contributor to in-plane transport is the metallic VSe_2 layers. The cross-plane carrier transport is expected to be dominated by the semiconducting PbSe layers. A several order of magnitude difference between cross-plane and in-plane resistivities over the 5.5 – 300 K temperature range has been measured.

2D-ThP-21 Evaluating the Impact of Defects, Interfaces and Boundaries on Thermal Transport in 2D Materials Using a Novel Opto-Thermal Metrology Technique with Sub-Micron Resolution*, **John Gaskins**, A. Jones, P. Hopkins, B. Foley,* Laser Thermal

Two-dimensional materials offer unprecedented, often record setting thermal properties with seemingly robust potential to structurally and chemically manipulate phonon scattering and thermal transport. These phonon scattering events in 2D systems arise from the plethora of defects and interfaces that arise from both growth and post processing that also are routinely used to manipulate the 2D materials functionalities. The thermal transport properties of 2D materials at and around these defect phonon scattering sites, which often have length scales and spacings on the order of nanometers to 10’s of nanometers, are difficult to isolate and measure individually with thermal measurement techniques. For example, optical based techniques for measuring thermal properties of 2D materials (e.g., Raman, TDTR) are ultimately diffraction limited and thus restricted to areal spatial resolution on the order of single micrometers. Techniques using lasers coupled with AFM-tips (e.g., Nano-FTIR) have shown promise in achieving sub-diffraction limited areal resolution to qualitatively interrogate optically excited surfaces, but lack the opto-thermal transduction power afforded by thermoreflectance-based methods to ensure accurate measurement of local temperature and thermal wave modulation.

Here, we introduce a new platform capable of characterizing the thermal properties of 2D materials with ~10 nm areal spatial resolution. Thermal maps of CVD-grown molybdenum disulfide (MoS2) and exfoliated hexagonal boron nitride (hBN) flakes (both on SiO2/Si supporting substrates) are presented, highlighting both (a) the higher in-plane thermal conductivity of the hBN compared to MoS2, as expected per the literature, but more importantly (b) the direct visualization of how the thermal resistance increases near wrinkle defects, adlayer nucleation sites, and flake boundaries. These local increases in resistance are attributed to the impact of the defect on phonon transport. As a result, this new capability enables the direct visualization and estimation of the length scales over which various defect structures exert influence over phonon transport in these 2D materials.

2D-ThP-22 Site-Specific Synthesis of Molybdenum Dichalcogenide Using Chemical Vapor Deposition Technique*, **Chu Te Chen**, A. Butler, Y. Fu, A. Cabanillas, A. Ahmed, A. Chakravarty, S. Jadeja, H. Hui, L. Samson, H. Zeng, A. Yadav, H. Li,* The State University of New York, Buffalo*; K. Wong,* Applied Materials*; F. Yao,* The State University of New York, Buffalo

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) have been extensively explored for their potential as channel materials in electronic devices. The device performance has been significantly improved over the years due to the advancements in understanding of TMD materials, device design, and fabrication process. Despite the early success in demonstrating proof-of-concept devices, scalable and single-crystal growth of TMD films on suitable substrates remains a formidable roadblock to the development of commercially viable TMD-based nanoelectronics. To mitigate this problem, there is a pressing need for the precise growth of high-quality TMD layers at desired locations in the device architecture with consistent layer characteristics.

In this study, we introduce a novel approach for the direct and site-selective synthesis of MoS_2 flakes, a representative type of TMD materials, on silicon substrates using the chemical vapor deposition (CVD) technique. This achievement is enabled through seed layer patterning using E-beam lithography, facilitating site-specific nucleation and growth. By systematically exploring the CVD synthesis parameter space, critical process parameters that govern the sublimation and diffusion processes of the Mo-containing intermediates have been identified. To validate the success of the selective growth of MoS_2 and unveil the structure-property-performance relationship, a series of microscopic and spectroscopic characterizations coupled with electrical measurements are employed to determine the microstructural and transport properties of the obtained flakes. Our results represent technological innovation for direct, scalable synthesis of TMDs in a location-selective manner which has potential to advance the development of next-generation nanoelectronics based on TMD materials.

2D Materials Technical Group
Room C123 - Session 2D+EM-FrM

2D-Materials: Device Application

Moderators: Maria Hilse, Pennsylvania State University, **Tongcang Li**, Purdue University

8:20am **2D+EM-FrM-1 Stochastic Computing Enabled by 2D Memtransistors***, **Saptarshi Das**,* Pennsylvania State University **INVITED**

In the emerging era of artificial intelligence, deep learning, and Big-data, the energy and hardware investments required for conventional high-precision digital computing are becoming increasingly unsustainable. As a result, there is a growing need for a new paradigm that prioritizes energy and resource efficiency over precision for many computing applications. Stochastic computing (SC) is a promising alternative because it can perform basic arithmetic operations using simple logic gates, unlike digital computers that require many logic gates and a high transistor volume. However, the hardware investment necessary to generate stochastic bits (s-bit), the fundamental computing primitive for SC, has hindered its widespread adoption. While traditional silicon complementary metal oxide semiconductor (CMOS) technology can accelerate SC, it still requires extensive hardware investment. Memristor and spin-based devices offer natural randomness but rely on hybrid designs involving CMOS peripherals, which increase the area and energy burden.

To overcome these limitations, we have developed a standalone SC architecture embedded in memory based on two-dimensional (2D) memtransistors. This monolithic and non-von Neumann SC architecture requires only a tiny amount of energy (< 1 nano Joules) for s-bit generation and to perform arithmetic operations, and occupies a small hardware footprint, highlighting the benefits of SC. Additionally, the researchers demonstrate the acceleration of Bayesian inference using their SC platform.

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9:00am **2D+EM-FrM-3 Electrical Characteristics of Semi-Metallic 2H-$NbSe_2$ for Scalable Interconnects***, **Abir Hasan**, T. Alem, C. Rogers, S. Stevenson, S. McDonnell, N. Shukla,* University of Virginia

Despite Copper being the current material of choice for interconnect technology, it suffers from increased resistivity at scaled dimensions and the necessity for a barrier-liner to prevent diffusion. This has motivated the exploration of alternate materials that can overcome these limitations for scaled CMOS technology nodes. Metallic 2D materials can offer a promising option. In this work, we evaluate the properties of 2D semi-metallic material 2H Niobium diselenide (2H-NbSe2) as a candidate for realizing highly scalable interconnect technology without the need for barrier-liner. We performed detailed electrical characterization evaluating the dimensional scaling, dependence of the resistivity on temperature, device lifetime, effect of encapsulation layer etc. on ribbon devices fabricated with 2H-$NbSe_2$ material. 2H-$NbSe_2$ showed negligible change in resistivity compared to the bulk value when scaled down to thicknesses less than 15 nm. High current density transport measurements are performed on 2H-$NbSe_2$ ribbon devices with varied width (0.1-1um) at elevated temperature (>= 100°C) to assess the reliability and failure characteristics. Lifetime of the $NbSe_2$ ribbons improved when an Al_2O_3 encapsulation layer was used. Our work provides critical insights into the potential of $NbSe_2$ for realizing scalable interconnects.

9:20am **2D+EM-FrM-4 Magneto-Transport Measurement and Maximum Entropy Mobility Spectrum Analysis in Semiconductor Substrates for Graphene Growth***, **Ruhin Chowdhury**,* University of New Mexico*; A. Majee,* Intel Corp.*; E. Renteria, D. Ghosal,* University of New Mexico*; M. Arnold, M. Lagally,* University of Wisconsin - Madison*; F. Cavallo,* University of New Mexico

Our study focuses on the multi-carrier electrical transport characterization of heat-treated bulk Ge near its melting point. Single-crystalline Ge has recently gained relevance as a substrate for the chemical vapor deposition (CVD) of high-quality graphene sheets, nanowires, and nanoscale wigglers.[1,2] Deposition of graphene on (110) Ge substrates allows integration of a 2D sheet with widely used semiconductors without the need for release and transfer processes, which may lead to the degradation of graphene's structural and functional properties. Determining the full potential of graphene/Ge for electronic applications requires understanding charge transport in this material combination. To date, quantitative models of lateral charge transport in graphene/Ge (i.e., transport of mobile carriers in the direction parallel to the graphene/Ge interface) are not available, primarily due to the overwhelming contribution of bulk Ge. In this work, we isolated and identified all mobile carrier types undergoing drift in heat-treated Ge at the typical condition for CVD of monolayer graphene. We believe these results to be the basis for quantifying carrier mobilities, carrier concentrations, and carrier types in graphene/Ge.

We performed magneto-transport measurements of heat-treated Ge between 50 K and 400 K and a magnetic field spanning from -7T to 7T to extract the conductivity tensor of the material. The Ge substrates were nominally intrinsic before annealing. Next, we used maximum entropy mobility spectrum analysis (MEMSA)[3] to identify the carrier types contributing to transport in Ge (110). Our analysis consistently shows the contribution of heavy holes (HH) and light holes (LH) in bulk Ge. The excess holes in bulk Ge are attributed to the formation of acceptor-like vacancies during high-temperature annealing of Ge.[4] The trend of carrier mobility vs. temperature indicates that different scattering mechanisms are dominant for HH and LH in a given temperature range. In addition to the contribution of HH and LH in bulk Ge, we identified two additional carrier types, namely electron and ultra-low mobility holes. We attribute the electrons to donor-type interstitials and the low-mobility holes to accumulated HH near the native oxide/Ge interface.

ACKNOWLEDGMENT. This work was supported by the U.S. AFOSR and Clarkson Aerospace Corporation under award No. FA9550-21-1-0460/UNM 21-1-0460.

[1] B. Kiraly, et al. Nano Lett. 15, 11, 7414–7420 (2015)

[2] R.M. Jacobberger et al. Nat. Commun. 6, 8006 (2015)

[3] Kiatgamolchai, S., et al. Phys Rev E Stat Nonlin Soft Matter Phys 66(3 Pt 2B): 036705 (2002)

[4] S. Mayburg, Phys. Rev. 95, 38 (1954).

9:40am **2D+EM-FrM-5 What Are 2D Materials Good for?***, E. Pop, **Tara Pena**,* Stanford University **INVITED**

This talk will present my (biased!) perspective of what two-dimensional (2D) materials could be good for. For example, they could be good for applications where their ultrathin nature gives them distinct advantages, such as flexible electronics [1] or light-weight solar cells [2]. They may not be good where conventional materials work sufficiently well, like transistors thicker than a few nanometers. I will focus on 2D materials for 3D heterogeneous integration of electronics, which presents major advantages for energy-efficient computing [3]. Here, 2D materials could be monolayer transistors with ultralow leakage [4] (due to larger band gaps than silicon), used to access high-density memory [5]. Recent results from our group [6,7] and others [8] have shown monolayer transistors with good performance, which cannot be achieved with sub-nanometer thin conventional semiconductors, and the 2D performance could be further boosted by strain [9]. I will also describe some unconventional applications, using 2D materials as thermal insulators [10], heat spreaders [11], and thermal transistors [12]. These could enable control of heat in “thermal circuits” analogous with electrical circuits. Combined, these studies reveal fundamental limits and some unusual applications of 2D materials, which take advantage of their unique properties.

Refs: [1]A. Daus et al., Nat. Elec. 4, 495 (2021).**[2]** K. Nassiri Nazif, et al., Nat. Comm. 12, 7034 (2021). **[3]** M. Aly et al., Computer 48, 24 (2015). **[4]**

C. Bailey et al., EMC (2019). **[5]** A. Khan et al. Science 373, 1243 (2021). **[6]** C. English et al., IEDM, Dec 2016. **[7]** C. McClellan et al. ACS Nano 15, 1587 (2021). **[8]** S. Das et al., Nat. Elec. 4, 786 (2021). **[9]** I Datye et al., Nano Lett. 22, 8052 (2022). **[10]** S. Vaziri et al., Science Adv. 5, eaax1325 (2019). **[11]** C. Koroglu & E. Pop, IEEE Elec. Dev. Lett. 44, 496 (2023). **[12]** M. Chen et al., 2D Mater. 8, 035055 (2021).

10:40am **2D+EM-FrM-8 Effect of Temperature on the Surface Morphologies of Sulfurized-Grown WS_2*, Md Samim Reza*,** *M. Singh,* Indian Institute of Technology Delhi, India

Tailored morphologies are essential for realizing the diverse applications of tungsten disulfide. This work reports on a successful growth of WS_2 that involves the sulfurization of a sputter-deposited (Angstrom Engineering Evovac) thin film of tungsten (150-300 Å with a rate of 0.4 Å/s) on a SiO_2 substrate (University Wafers) and the effect of temperature on the surface morphology of as-grown WS_2. The as-deposited tungsten substrate was cut into 2cm x 2cm and placed inside a custom-design horizontal CVD system (Quazar Technologies). A sulfur (99.5% pure precipitated powder, 600-1000 mg, Sigma Aldrich) was placed upstream (20-40 cm) from the tungsten heating zone (700-1000 °C) to grow WS_2 under a carrier gas (Ar) flow of 0-400 sccm. Raman spectroscopy (514 nm laser source with a spot size of ~1 um^2 for 100x objective, 1mW power, Renishaw inVia) revealed the peaks at ~350/cm and ~417/cm, confirmed the growth of WS_2 and the peak intensity ratio of in-plane and out-of-plane (E^{1}_{2g}/A^{1g}) < 1, suggest a multilayer growth [1]. The X-ray diffraction (Rigaku Ultima IV) analysis indicates the growth of hexagonal-phased WS_2 (JCPDS: 08-0237) with a mixed plane to a (002)-dominated at higher temperatures. The field emission scanning electron microscopy (Magna LMU, Tescan) scans revealed the growth morphology from a planar to a nanoflower, forming a thin film of WS_2. Different sulfurization temperatures result in distinct morphologies, with a thin film morphology obtained at 700-750°C, followed by the dominance of nanoflower-like WS_2 structures between 850°C and 950°C as observed by field emission scanning electron microscopy. At temperatures higher than 950°C, WS_2 nanoflowers with vertical alignment are grown on a SiO_2 substrate. Electron dispersive X-ray (EDX, Ametek) spectra show a stoichiometry close to 1:2 for W: S. The atomic force microscope analysis (Dimension Icon, Bruker) revealed that surface roughness (sputter-deposited tungsten roughness of ~80 pm) increased from ~5 to 80 nm with the growth temperature. The experimental results emphasize the importance of temperature in determining the surface morphologies of WS_2. The ability to control the growth temperature offers customization of WS_2 morphologies that could allow the fabrication of WS_2-based devices with the desired properties [2-3].

[1] Berkdemir et al., Scientific Reports, 3, 1755 (2013)

[2] Sebastian et al., Nature Communications 12, 693 (2021)

[3] Li et al., The Journal of Physical Chemistry C, 126(22), 9293-9303.

11:00am **2D+EM-FrM-9 The Study of Internal Ion Transport in Ionic $CuInP_2S_6$*, Yujie Sun,*** *B. Liu,* Tsinghua University, China

Memristor-based neuromorphic computing is promising for artificial intelligence. However, most of the reported memristors have limited linear computing states and consume large operation energy which hinder their applications. Herein, we report a memristor based on ionic two-dimensional $CuInP_2S_6$ (2D CIPS), in which up to 1350 linear conductance states are achieved by controlling the migration of internal Cu ions in CIPS. In addition, the device shows a low operation current of ~100 pA. Cu ions are proven to move along the electric field by *in-situ* scanning electron microscopy and energy dispersive spectroscopy measurements. Furthermore, complex signal transport among multiple neurons in the brain is imitated by 2D CIPS-based memristor arrays. Our results offer a new platform to fabricate high-performance memristors based on ion transport in 2D materials for neuromorphic computing.

Applied Surface Science Division
Room B117-119 - Session AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM

Industrial Applications

Moderators: Marko Sturm, University of Twente, Netherlands, **Alan Spool**, Western Digital Corporation, **Yundong Zhou**, National Physical Laboratory, UK

8:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-1 Correlative Analysis Using Time-of-flight Secondary Ion Mass Spectrometry for Beam Sensitive Samples*, Jean-Paul Barnes,*** *C. Guyot, P. Hirchenhahn, A. De Carvalho, N. Gauthier, T. Maindron, B. Gilquin, D. Ratel, C. Gaude, O. Renault,* Univ. Grenoble Alpes, CEA, Leti, France*; A. Galtayries,* Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, France*; G. Fisher,* Physical Electronics USA*; C. Seydoux, P. Jouneau,* Univ. Grenoble Alpes, CEA, IRIG-MEM, France **INVITED**

Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) is now widely used for materials analysis in domains such as semiconductor and energy applications. These challenging applications also provide access to well-controlled, custom made samples that have allowed the limits of TOF-SIMS analysis to be identified and helped in the development of correlative analysis approaches. Recent examples include combining AFM measurements with TOF-SIMS depth profiling to correct for sputter rate differences [1] or to measure mechanical or electrical properties and performing X-ray tomography prior to FIB-TOF-SIMS analysis to allow morphological and compositional data from the same volume to be visualized [2]. Currently we are working on two aspects. Firstly improving the quantification and chemical sensitivity of the technique by combining TOF-SIMS with photoemission techniques (XPS or XPEEM), and secondly trying to improve the lateral resolution by correlation with SEM and AFM measurements. Recent examples will be shown for the analysis of beam sensitive organic samples such as OLED devices, brain tissue samples after medical device implantation [3] and symbiotic microorganisms [4]. As well as the correlative aspects between techniques, we will show how tandem mass spectrometry can help in analyzing complex organic samples. In all cases the importance of sample preparation is paramount, especially for biological samples. For example, for the correlation between TOF-SIMS and XPS on OLED samples, a wedge crater protocol has been developed to allow analysis on exactly the same area of the sample whilst minimizing beam damage to the sample. Wedge crater preparation and transfer between instruments is performed under a protected environment (vacuum or inert gas) to avoid unwanted surface modifications.

Part of this work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the “Recherches Technologiques de Base” and the “CARNOT” program of the French National Research Agency (ANR).

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[2] A. Priebe *et al. ULTRAMICROSCOPY,* vol. 173, pp. 10-13, FEB 2017.

[3] A. G. De Carvalho *et al. Biointerphases,* vol. 15, 2020.

[4] C. Uwizeye *et al. PNAS.* **Vol 118**, e2025252118, 2021.

9:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-3 Secondary Ion Mass Spectroscopy of Battery Surface and Interface Chemistry – Metrology and Applications*, Yundong Zhou,*** *S. Marchesini, X. Yao, Y. Zhao, I. Gilmore,* National Physical Laboratory, UK

Batteries are very important to achieve carbon net zero. Understanding battery materials change, electrode surfaces, solid electrolyte interphase (SEI) evolution and novel solid-state electrolyte structures is very helpful for developing better batteries. Surface chemical analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are often used but they have their limitations. XPS analysis cannot always resolve overlapping binding energies for some key SEI elements. The SEI often has poor Raman signal intensity. These are all hurdles for battery applications.

Secondary ion mass spectrometry has great potential to study interfacial chemistry in batteries owing to high sensitivity and high-resolution imaging in 2D and 3D.In this study, we use an OrbiSIMS instrument which is equipped with two complementary mass spectrometers (MS). A time-of-flight (ToF) MS has the capability for 2D and 3D imaging using a Bi_3^+ liquid metal ion gun with a spatial resolution of up to 200 nm but with modest mass resolving power. The Orbitrap MS offers high mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). The instrument is equipped with low energy Cs and O_2 sputter beams for high resolution depth profiling of inorganic materials. It also has a Leica docking station enabling samples to be transferred using a vacuum sample transfer chamber from an argon glove box without atmospheric exposure. To improve the quality of measurements on battery materials, we have used ion implanted materials to determine relative sensitivity factors for relevant elements. We have also conducted a systematic study to optimise the OrbiSIMS depth profiling capability. These findings along with recommendations to reduce effects of signal saturation will be discussed and examples of the application to batteries will be provided. We will provide examples of the application of ToF MS and Orbitrap MS. (1,2)

1. X. Yao et al., Energy Environ. Sci., 2023, DOI: 10.1039/D2EE04006A.
2. S. Marchesini et al., ACS Appl. Mater. Interfaces, 14(2022)52779-52793.

9:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-4 Characterizing Ion Distribution at the Solid-Electrolyte Interface in Solid-State Lithium Ion Batteries with ToF-SIMS**, ***Teodora Zagorac,*** University of Illinois - Chicago; *M. Counihan, J. Lee, Y. Zhang,* Argonne National Laboratory, USA; *L. Hanley,* University of Illinois - Chicago; *S. Tepavcevic,* Argonne National Laboratory, USA

Interest in solid state lithium-ion batteries as the next generation of energy storage devices has led to intense study of the chemistry, structure, and manufacturing processes for polymer electrolytes. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt is often used to introduce Li ions into the solid-state electrolyte. Lithium bis(fluorosulfonyl)imide salt (LiFSI) and lithium nitrate ($LiNO_3$) are less expensive salts with the potential to improve performance characteristics over pure LiTFSI in certain electrolyte formulations. The differences in distribution and reactivity of these different salts are still unknown but are critical to battery performance. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging and depth profiling was performed to compare the distributions of Li^+ cations and $TFSI^-$, FSI^-, and NO_3^- anions across the solid-electrolyte interface (SEI) formed between the polymer electrolyte and thin lithium metal electrode. Experiments were performed on ~600 nm salt-rich poly(ethylene oxide) electrolytes with ~10 nm overlayers of vapor-deposited Li metal. Samples were probed with 30 keV Bi_3^+ from a liquid metal ion gun while depth profiling with 10 keV Ar_{1400} gas cluster ion beam to collect both positive and negative ion mass spectra. Ion distributions from the three salts and their 3D images will be presented and discussed in terms of the relative composition of their SEI layers. Chemical differences from ToF-SIMS analysis help explain the differences in electrochemical SEI formation and half cell cycling: LiTFSI and LiFSI are similar, but $LiNO_3$ presents much different electrochemical properties.

9:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-5 A Perspective on X-ray Photoelectron Spectroscopy (XPS) Peak Fitting, and Reporting of XPS Data Acquisition and Peak Fitting Parameters in the Literature**, ***Matthew Linford,*** *G. Major, J. Pinder,* Brigham Young University

We recently reported that a rather large fraction (ca. 40 %) of the XPS peak fitting in the literature is at best suspect. In a recent Perspective article (doi: 10.1116/6.0002437) we argue that the various stake holders of the problem can act together to improve the current situation. This Perspective begins with representative examples of poor XPS peak fitting. The purpose of showing these examples is to demonstrate to the reader that we are not quibbling or arguing over subtle interpretations of the data. Increasingly, we see errors that might be classified as egregious. We argue that science is in a state of 'pre-crisis' more than in a state of 'crisis'. We suggest that if too much incorrect data analysis enters the literature it may cease to be self-correcting. We note the very large number of surface and material characterization techniques available today and how this presents a challenge for scientists. Consequently, it is likely that many manuscripts are incompletely reviewed today. Graduate students and post-docs at research institutions are often given minimal training on acquiring and analyzing XPS data. High fees for instruments can limit access to them and student training. Prisoner's dilemmas may help explain situations in science that lead to suboptimal outcomes for the community. Authors are primarily responsible for the quality of the research in their papers, not reviewers or editors. We question the wisdom of placing the names of reviewers and editors on papers. In some cases, staff scientists are not adequately recognized for their intellectual contributions to projects. Selective reviewing may allow more reviews to be performed without overtaxing the community. Reviewing at some open access journals may be inadequate. Collaboration needs to be encouraged to a greater extent at some institutions.

10:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-6 Unsupervised and Supervised Machine Learning Applied to ToF-SIMS of an Organic Matter-Rich Mudstone with Molecular Biomarker**, *M. Pasterski,* University of Illinois Chicago; *M. Lorenz,* Oak Ridge Natinal Laboratory; *A. Ievlev,* Oak Ridge National Laboratory; *R. Wickramasinghe,* ***Luke Hanley,*** *F. Kenig,* University of Illinois Chicago

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging has been used to detect organic compounds including molecular biosignatures (biomarkers) in geologic samples (R.C. Wickramasinghe, *et al.,* Anal. Chem., 2021, 93, 15949). The spatial distribution of these biomarkers can help determine when and how these organics were incorporated into the host rock. ToF-SIMS imaging can rapidly collect a large amount of data, but molecular and fragment ions of different species are mixed together in complex mass spectra that are difficult to interpret. Here, we apply unsupervised and supervised machine learning (ML) to help interpret the mass spectra obtained by ToF-SIMS of an organic-carbon-rich mudstone from the Middle Jurassic of England (UK). It was previously shown that the presence of sterane molecular biomarkers in this sample can be detected via ToF-SIMS (M.J. Pasterski, *et al.*, Astrobiol., in press). We use unsupervised ML on field emission scanning electron microscopy – electron dispersive spectroscopy (SEM-EDS) measurements to define compositional categories based on differences in elemental abundances. We then test the ability of four ML algorithms - k-nearest neighbors (KNN), recursive partitioning and regressive trees (RPART), eXtreme gradient boost (XGBoost), and random forest (RF) - to classify the ToF-SIMS spectra using the categories assigned via SEM-EDS, using organic and inorganic labels, as well as using presence or absence of detectable steranes. KNN provided the highest predictive accuracy and balanced accuracy. The feature importance, or the specific features of the ToF-SIMS data used by the KNN model to make classifications could not be determined, preventing post-hoc model interpretation. However, the feature importance extracted from the other three models was useful for interpreting spectra. We determined that some of the organic ions used to classify biomarker containing spectra may be fragment ions derived from kerogen.

10:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-8 Probing Thin Film Interfaces at the Nanoscale by Low Energy Ion Scattering**, ***Marko Sturm,*** *A. Chandrasekaran, A. Valpreda, A. Zameshin, R. Van de Kruijs, A. Yakshin, F. Bijkerk, M. Ackermann,* University of Twente, Netherlands **INVITED**

The growth of thin films with nanometer range thickness is of great importance for application topics as nanoelectronics, oxidation protection of thin films and optical coatings for X-ray applications. The performance of these coatings often critically depends on the sharpness of the interfaces between different layers. In this talk I will outline how we use Low-energy ion scattering (LEIS) to study interface formation between layers of different transition metals (TMs) and between TMs and Si.

LEIS with noble gas ions as projectiles yields surface peaks that indicate the composition of the outermost atomic layer of a sample. This makes the technique excellently suited to study whether deposition of a thin films leads to a closed layer. However, deposition of an overlayer on top of an underlayer may result in surface segregation of underlayer atoms (driven by surface energy differences or stress), such that the surface composition is not directly representative for the in-depth concentration profile. We analyzed the evolution of surface coverage versus deposited thickness for a large set of TM/TM film combinations, deposited by magnetron sputtering in a system that allows LEIS analysis without vacuum break after deposition. By applying a model that takes into account surface segregation, the interface profiles were derived from these layer growth profiles, which we call deposition depth profile. In addition, we demonstrated that the sharpness of interfaces in TM/TM film systems can be predicted by a phenomenological model with the crystal structure and surface energy of the materials as input parameter. This model in principle predicts the sharpness of the interface in any TM/TM thin film combination! [1]

Apart from surface peaks, LEIS spectra typically also contain so-called tails, caused by projectiles that, after sub-surface scattering, are reionized when leaving the sample. It was demonstrated before that LEIS tails can be used to determine thickness of various thin film systems, when the stopping power of the projectiles is known. Here, we show that LEIS tails can also be used to determine the sharpness of interfaces of few nm Si-on-W and Si-on-Mo films, by comparing LEIS measurements with Monte Carlo simulations with the TRBS code, which takes into account multiple scattering and stopping in the target. This approach allows interface characterization from a single sample, without the need to make a deposition depth profile.

References:

[1] A. Chandrasekaran, R.W.E. van de Kruijs, J.M. Sturm, A.A. Zameshin and F. Bijkerk, ACS Applied Materials & Interfaces **11**, 46311 (2019)

11:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-10 The Effect of Instrument Settings, Sample Distance, and Tilt on TofsimsSecondary Ion Intensities***, **Alan Spool**, L. Finney,* Western Digital

Experiments were performed to explore the effects of various instrument settings and sample placements on secondary ion intensities to better understand what factors have the greatest effect on repeatability and replicability in TOF-SIMS. A batch of magnetic recording disks used in hard disk drive manufacture, natively flat and homogeneous, were used as test samples for the purpose. As expected, by far the largest variable altering raw intensities was the LMIG tip stability. LMIG tips can have stable emission currents while still producing variable pulsed LMIG beam currents with resultant variable secondary ion counts. This variability sometimes is seen in slow current drift, but is sometimes so rapid that measurements taken directly before each measurement are not close enough in time to properly scale the measurement results. In these cases, normalization is the only solution. Secondary ion intensities were remarkably insensitive to small variations in sample height (position relative to the extractor). Far more interesting were the changes to the secondary ion intensities that resulted from tilting the sample. These effects varied amongst the secondary ions detected such that normalization did not remove them. Secondary ion emission as a function of emission angle has long been understood to be like a cosine function and to vary somewhat from ion to ion. These different angular profiles explain the differences seen in ion detection as a function of tilt. Some of these differences proved to be asymmetrical, varying depending on whether the sample was tilted toward or away from the primary ion source, an indication that in some situations some residual momentum from the initial primary ion impact onto the surface is carried into the secondary ion emission. These results have implications for attempts to do quantitative analysis on any sample that is not completely flat.

11:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-11 Evaluation of Unaltered and Irradiated Nuclear Graphite Surfaces through Integrated Traditional XPS and HAXPES Techniques***, **Jonathan Counsell**, L. Soomary, K. Zahra,* Kratos Analytical Limited, UK*; B. Spencer, A. Theodosiou,* University of Manchester, UK

Graphite-moderated reactors have been operational worldwide for several decades. There exists a substantial body of research in this domain, with particular emphasis on investigating the impact of irradiation damage on the graphite matrix. In order to satisfy the design and regulatory requisites of these advanced reactors, it becomes imperative to gain a deeper comprehension of the retention and transportation mechanisms of fission products within graphite.

This study outlines a technique for the precise assessment of the surface chemistry of highly-oriented pyrolytic graphite (HOPG), serving as a representative model akin to the current graphite grades utilized in the nuclear sector. We delve into the process of surface etching aimed at eliminating surface adsorbates and contaminants. This process involves the utilization of both monatomic and cluster ions, the former inadvertently causing undesirable damage to the graphite structure. Such damage is evidenced by a significant reduction in the sp2 component of C 1s. We introduce the use of UPS analysis as a straightforward means of determining the presence of sp2 characteristics in the uppermost atomic layers.

Moreover, we examine the consequences of high-energy ion implantation (Cs+) and the ensuing damage to the HOPG surface. This examination is carried out using XPS (1486eV) and HAXPES (2984eV), thereby showcasing the capability to characterize the resulting surface damage and the associated alterations within the probed depths.

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