2D Materials
Room A216 - Session 2D+EM+MI+NS-MoM

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties I
Moderator: Sanghoon Bae, Massachusetts Institute of Technology

8:20am 2D+EM+MI+NS-MoM1 Extreme Fatigue Life of Graphene, *Teng Cui, S. Mukherjee, P.M. Sudeep, G. Colas, J. Tam,* University of Toronto, Canada*; P.M. Ajayan,* Rice University*; C.V. Singh, Y. Sun, T. Filleter,* University of Toronto, Canada

Materials can fail when subjected to cyclic loading at stress levels much lower than the ultimate tensile strength or yielding limit, which is known as mechanical fatigue. Understanding the fatigue behavior is critical for any emerging material in order to evaluate its long-term dynamic reliability. Two-dimensional (2D) materials have been widely applied to mechanical and electronic applications, where they are commonly subjected to cyclic stress. However, the fatigue life and underlying damage mechanisms of these atomically thin, nearly defect-free, materials are unknown. Here we show the first fatigue study of freestanding 2D materials, in particular graphene and graphene oxide (GO). Monolayer and few layer graphene and GO were found to all exhibit ultrahigh fatigue life of more than one billion cycles at large stress level in the GPa range. Such a remarkable fatigue life is higher than that of any material reported to date at similar stress levels. Graphene exhibits global and catastrophic fatigue failure preceded by bond reconfiguration near the defective site due to inhomogeneous charge distribution and higher potential energy. Graphene can fracture under cyclic loading but without progressive damage, which is distinct from the fatigue failure mechanism of any other materials. The presence of functional groups on GO imparts a local and progressive fatigue damage mechanism, which fits the macroscopic fatigue convention. The extraordinary fatigue life was found to diminish significantly when the material is scaled up in thickness (10s of layers). This work not only provides new fundamental insights into the widely observed fatigue enhancement behavior of graphene-embedded nanocomposites, but also serves as a starting point for the mechanical dynamic reliability evaluation of other 2D materials.

8:40am 2D+EM+MI+NS-MoM2 Epitaxial Growth and Thermal Degradation of Monolayer MoS_2 on $SrTiO_3$ Single Crystal Substrates, *Peiyu Chen, W. Xu, Y. Gao, P. Holdway, J.H. Warner, M.R. Castell,* University of Oxford, UK

Monolayer MoS_2 crystals grown on amorphous substrates such as SiO_2 are randomly oriented. However, when MoS_2 is grown on crystalline substrates, the crystal shapes and orientations are also influenced by their epitaxial interaction with the substrate. In the first part of this talk, we present the results from chemical vapor deposition growth of MoS_2 on three different terminations of single crystal strontium titanate ($SrTiO_3$) substrates: (111), (110), and (001). On all three terminations of $SrTiO_3$, the monolayer MoS_2 crystals try to align their <2 -1 -1 0>-type directions (i.e., the sulfur-terminated edge directions) with the <1 -1 0>-type directions on $SrTiO_3$. This arrangement allows near-perfect coincidence epitaxy between seven MoS_2 unit cells and four $SrTiO_3$ unit cells. On $SrTiO_3$(110), this even distorts the crystal shapes and introduces an additional strain detectable by photoluminescence (PL). Our observations can be explained if the interfacial van der Waals (vdW) bonding between MoS_2 monolayers and $SrTiO_3$ is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this study is that the vdW interaction between MoS_2 and $SrTiO_3$ substrates determines the supported crystal shapes and orientations by epitaxial relations.

Monolayer MoS_2 is also a wide-bandgap semiconductor suitable for use in high-temperature electronics. It is therefore important to understand its thermal stability. In the second part, we uncover the thermal degradation behavior of monolayer MoS_2 supported on $SrTiO_3$ in ultrahigh vacuum (UHV) because of sulfur loss. MoS_2 was found to degrade on the (111), (110), and (001) terminations of $SrTiO_3$ substrates in a similar way. The sulfur loss begins at 700 °C, at which point triangular etch trenches appear along the sulfur-terminated edge directions of the MoS_2 crystals (in scanning tunneling microscopy). The sulfur vacancies can be filled byannealing the crystals in a hot sulfur atmosphere, and the optical properties (by Raman spectroscopy and PL) of monolayer MoS_2 can nearly be fully recovered. At higher UHV annealing temperatures, the remaining Mo is oxidized by the $SrTiO_3$ substrates into MoO_2 and MoO_3. The initial sulfur loss and the formation of MoO_x are confirmed by X-ray photoelectron spectroscopy. The sulfur annealing no longer takes effect when all the Mo has been oxidized, which happens at a temperature between 800 °C and 900 °C in UHV. The MoS_2 crystal shapes are stable upon annealing until the residual MoO_3 particles evaporate at above 1000 °C. This infers that any triangular crystals that look intact under low-magnification optical microscopy and SEM may not mean pristine MoS_2.

9:00am 2D+EM+MI+NS-MoM3 3D Printed and Injection Molded Polymer Matrix Composites with 2D Layered Materials, *Sangram Mazumder,* University of North Texas*; J.A. Catalan,* University of Texas at El Paso*; N. Hnatchuk, I. Chen,* University of North Texas*; P. Perez,* University of Texas at El Paso*; W. Brostow, A.B. Kaul,* University of North Texas

The two-dimensional layered materials (2DLMs), MoS_2 and WS_2, as well as three-dimensional (3D) graphite were infused in thermoplastic polymer matrices, specifically acrylonitrile butadiene styrene (ABS) and polyethylene terephthalate glycol (PETG). Two techniques were explored for the production of these composites into dog-bone structures for mechanical testing, which included 3D printing and injection molding. The ductility of the composites was generally seen to decrease with the addition of the fillers compared to the otherwise ductile polymer matrix counterparts. Also, changes in Young's modulus, yield and tensile strengths, as well as percent strain at fracture, were analyzed as a function of filler loadings. The effect of processing technique on microstructures was also investigated by scanning electron microscopy of the fracture surfaces which revealed the presence of microstructural defects in the form of voids in the injection molded samples, which act as stress concentrators in the composite samples. Additionally, dynamic friction data of the composites was measured in an attempt to exploit the traditional, inherent solid phase lubricating properties of the 2DLMs. Graphite was indeed seen to lower dynamic friction in case of 3D printed PETG and injection molded ABS. Also, MoS_2 and WS_2 were found to reduce friction in 3D printed PETG and ABS. Graphite being an intrinsically good conductor, while the other 2DLMs explored, specifically MoS_2 and WS_2 given their semiconducting nature, can also be used as avenues for introducing electrical conductivity within these otherwise insulating parent polymer matrices. Thermal conductivity was also found to increase in both ABS and PETG composites containing graphite, MoS_2 and WS_2, irrespective of their processing routes. The use of 2DLM-based polymer composites remains an area that is bound to open up avenues for a wide range of applications in the future related to wearable electronics and sensors with low-cost additive manufacturing approaches.

9:20am 2D+EM+MI+NS-MoM4 Semiconducting WS_2 and h-BN Inks for Printing Optically-active Nanodevices, *Jay A. Desai,* University of Texas at El Paso*; S. Mazumder, A.B. Kaul,* University of North Texas

We present our work on dispersions of WS_2 and h-BN using cyclohexanone and terpineol (C/T) as the solvent to subsequently print prototype nanodevices. Current-voltage measurements, Raman spectroscopy, and photoluminescence spectroscopy were used to characterize the properties of these inks produced by various sonication techniques such as horn tip sonication, magnetic stirring and shear mixing. Both photodetector and capactive heterostructure devices were formed with these materials. From this analysis, the photoresponsivity and detectivity of the graphene-WS_2-graphene heterostructure devices were calculated to be ~ 0.86 A/W and ~ 10^{13} J, respectively. Capacitance-voltage (C-V) and C-frequency (f) measurements were also conducted, where the V was swept from – 6 V to + 6 V, while the change in C was measured from f ~ 20 kHz up to 3 MHz to gain insights into the nature of the graphene-WS_2 interface. An all-inkjet-printed graphene-h-BN-graphene capacitors were fabricated and leakage current density, $J_{Leakage}$, of up to ~ 0.072 µA/mm² and *capacitance density* of up to ~ 2.4 µF/cm² is reported. Finally, the influence of temperature, frequency, and LED illumination on the performance of the graphene-h-BN-based capacitor is explored with the help of *capacitance density*-voltage measurements at different parameters to promote the all-inkjet-printed capacitor for photosensitive detector applications.

10:40am 2D+EM+MI+NS-MoM8 Engineering Interfaces in the Atomically-Thin Limit, *Deep Jariwala,* University of Pennsylvania **INVITED**

The isolation of a growing number of two-dimensional (2D) materials has inspired worldwide efforts to integrate distinct 2D materials into van der Waals (vdW) heterostructures. While a tremendous amount of research activity has occurred in assembling disparate 2D materials into "all-2D" van der Waals heterostructures, this concept is not limited to 2D materials alone. Given that any passivated, dangling bond-free surface will interact with another via vdW forces, the vdW heterostructure concept can be extended to include the integration of 2D materials with non-2D materials that adhere primarily through noncovalent interactions. I will present our work on emerging mixed-dimensional (2D + nD, where n is 0, 1 or 3)

heterostructure devices. Two distinct examples of gate-tunable p-n heterojunctions with anti-ambipolar field efect will be presented. The anti-ambipolar field effect observed in the above systems is also shown generalized to other semiconducting heterojunction systems and extended over large areas with practical applications in wireless communication circuits. Recent work on high performance 2D/3D triodes will also be presented.

The second part of talk will focus on engineering interfaces on photovoltaic devices from 2D semiconductors such as transition metal dichalcogenides (TMDCs).High efficiency inorganic photovoltaic materials (e.g., Si, GaAs and GaInP) can achieve maximum above-bandgap absorption as well as carrier-selective charge collection at the cell operating point. Experimental demonstration of light confinement in ultrathin (< 15 nm) Van der Waals semiconductors (MoS_2, WS_2 and WSe_2) leading to nearly perfect absorption will be demonstrated concurrently with record high quantum efficiencies. Ongoing work on addressing the key remaining challenges for application of 2D materials and their heterostructures in high efficiency photovoltaics which entails engineering of interfaces and open-circuit voltage will be presented in addition to on going work on probing of buried metal/semiconductor interfaces with sub 50 nm resolutions as well as near field luminescence spectroscopy. I will conclude by giving a broad perspective of future work on 2D materials from fundamental science to applications.

11:20am 2D+EM+MI+NS-MoM10 Ultrasoft Slip-mediated Bending in Few-layer Graphene, *Jaehyung Yu*, E. Han, E. Annevelink, J. Son, E. Ertekin, P.Y. Huang, A.M. van der Zande, University of Illinois at Urbana-Champaign
A challenge and opportunity in nanotechnology is to understand and take advantage of the breakdown in continuum mechanics scaling laws as systems and devices approach atomic length scales. Such challenges are particularly evident in two-dimensional (2D) materials, which represent the ultimate limit of mechanical atomic membranes as well as molecular electronics. For example, after more than a decade of study, there is no consensus on the bending modulus of few layer graphene, with measured and predicted values ranging over two orders of magnitude, and with different scaling laws. However, comparing these studies is challenging because they probe very different and often fixed curvatures or magnitudes of deformation. To unravel the discrepancy, a systematic measurement of bending stiffness versus deformation is needed. The results have practical implications on predicting and designing the stiffness of many 2D mechanical systems like origami/kirigami nanomachines, stretchable electronics from 2D heterostructures, and resonant nanoelectromechanical systems.

In this study, we combine atomistic simulation and atomic scale imaging to theoretically and experimentally examine the bending behavior of few-layer graphene. First, we experimentally probe the nanoscale bending by laminating few-layer graphene over atomically sharp steps in boron nitride and imaging the cross-sectional profile using aberration-corrected STEM. Second, we use DFT simulations to examine the bending of few-layer graphene under compression. By measuring the nanoscale curvatures, we extract the simulated and experimental bending modulus while varying both the number of layers and the degree of nanoscale curvature.

We find remarkable agreement between the theory and experiment and observe an unexpected curvature dependent bending stiffness of few-layer graphene that deviates from continuum scale bending mechanisms. We find that the bending stiffness of few layer graphene versus curvature corresponds with a gradual change in scaling power with thickness from cubic to linear. We find that the transition in scaling behavior originates from a transition from shear, slip and the onset in superlubricity between the graphene layers at the van der Waals interface, verified by a simple Frenkel-Kontorova model. Our results provide a unified model for the bending of 2D materials and show that their multilayers can be orders of magnitude softer than previously thought, among the most flexible electronic materials currently known.

Actinides and Rare Earths Focus Topic
Room A215 - Session AC+LS+MI-MoM

Magnetism, Complexity, Superconductivity, and Electron Correlations in the Actinides and Rare Earths

Moderators: Krzysztof Gofryk, Idaho National Laboratory, Ladislav Havela, Charles University, Prague, Czech Republic

8:20am AC+LS+MI-MoM1 Possible Structural Quantum Phase Transition in UCr2Si2 Accessed Through Cr → Ru Chemical Substitution, *Ryan Baumbach*, Florida State Universityy   **INVITED**
Materials with intertwined magnetic, electronic, and structural degrees of freedom often can be tuned (e.g., using pressure or chemical substitution) to induce novel behavior, including unconventional superconductivity. Examples include the cuprates, iron based superconductors, and lanthanide/actinide-based compounds, and despite the their diversity of structure, chemistry and interaction mechanisms, their individual phase diagrams often conform to a semi-universal format that features a quantum phase transition. As a result, there have been prolonged efforts to develop new families of materials based on this paradigm. Even so, there still are few examples of f-electron intermetallics that combine both magnetic and structural quantum phase transitions. In this talk, we will present results from recent efforts to tune the ordered states of UCr_2Si_2, which is a Kondo lattice metal with antiferromagnetic ordering near $T_N \approx 24$ K and a structural phase transition near $T_S \approx 200$ K. In particular, we will focus on the influence of Cr to Ru chemical substitution, where we find that both T_N and T_S are rapidly suppressed towards separate quantum phase transitions. The impact of the quantum phase transitions on the structural, magnetic, and electronic properties will be examined in detail.

9:00am AC+LS+MI-MoM3 Dynamic Spin Transport in Antiferromagnetic Insulators: Angular Dependent Spin Pumping in Y₃Fe₅O₁₂/NiO/Pt Trilayers, *Fengyuan Yang*, The Ohio State University   **INVITED**
In recent years, pure spin transport driven by ferromagnetic resonance (FMR) spin pumping or a thermal gradient has attracted intense interest and become one of the most active frontiers in condensed matter and materials physics. Extensive research efforts have demonstrated pure spin currents in a broad range of materials, which enrich our understanding of dynamically-driven spin transport and open new paradigms for energy-efficient, spin-based technologies. Antiferromagnetic (AF) insulators possess various desired attributes, such as low loss and high speed up to THz frequencies, for future spintronic applications.

To probe the dynamic spin transport phenomena and the underlying mechanisms in AF insulators, we use high-quality $Y_3Fe_5O_{12}$ (YIG) epitaxial thin films excited by FMR as a source to inject spins into AF insulator NiO layers and detect the transmitted spin current using inverse spin Hall effect (ISHE) signals in YIG/NiO/Pt trilayers [1, 2]. We observed robust spin currents from YIG to Pt across AF insulators, which initially enhances the ISHE signals and can transmit spin currents up to 100 nm thickness, demonstrating highly efficient spin transport through an AF insulator carried by magnetic excitations. Recently, we studied the angular dependence of spin pumping in a series of YIG/NiO/Pt trilayers as the orientation of the applied magnetic field is rotated out of plane [3]. A simple sinusoidal angular dependence of V_{ISHE} has been viewed as a signature of spin pumping. Surprisingly, we observe an extensive plateau in the V_{ISHE} vs. ϑ_H plots with a pronounced peak feature at an out-of-plane angle of 45° to 60° when the measurement temperature is close to the Néel temperature (T_N) of NiO. This phenomenon can be understood as arising from the competition between the exchange coupling at the YIG/NiO interface, the easy-plane and in-plane easy-axis anisotropies of NiO, and the effect of the applied magnetic field. While insulating antiferromagnetic films can efficiently transmit spin currents and show promise for integration in spintronic devices, the underlying physics of spin ordering and dynamics is richer than currently understood.

References:

1. H. L. Wang, *et al.PRB* **91**, 220410(R) (2015).

2. H. L. Wang, *et al.PRL***113**, 097202 (2014).

3. Y. Cheng, *et al.PRB* 99, 060405(R) (2019)

9:40am AC+LS+MI-MoM5 Pressure Studies of Strongly Correlated Phases in Rare Earth Compounds, *Rena Zieve*, University of California, Davis   **INVITED**
Various strongly correlated materials have complex low-temperature phase diagrams, exhibiting magnetism and superconductivity as well as spin glass,

non-Fermi liquid, and other behaviors. Since each material has its own quirks, determining the underlying universal influences has been challenging. Pressure is a key tool in these efforts, since pressure can tune the interactions within a material without changing its chemical composition or impurities. I will discuss how hydrostatic or uniaxial pressure can probe strongly correlated materials by changing valence, breaking crystal symmetry, or altering the dimensionality of the electron system. I will draw examples from various rare earth compounds. Finally, I will mention recent pressure application techniques that expand the range of possible characterization measurements.

10:40am **AC+LS+MI-MoM8 Fermi Surface Reconstructions and Transport Properties in Heavy-fermion Materials**, *Gertrud Zwicknagl,* Institut f. Mathemat. Physics, TU Braunschweig, Germany

The search for new types of exotic topological orders has recently rekindled the interest in Fermi surface reconstructions. Of particular interest are Electronic Topological (Lifshitz) transitions where the number of FS sheets changes abruptly under the influence of external parameters like chemical doping, pressure, or magnetic field. Lifshitz transitions (LTs) are generally associated with the presence of critical points in the electronic band structure, i. e., maxima, minima, or saddle points whose presence follows directly from lattice periodicity. As their separation from the Fermi energy is of the order of the bandwidth the critical points usually do not affect the low temperature behavior. In heavy-fermion materials, however, magnetic fields can drive LTs which are reflected in pronounced anomalies in thermodynamic and transport properties. Here we demonstrate that the magnetic field-dependent anomalies in the Seebeck coefficient provide detailed information not only on the critical points, i. e., their character and position relative to the Fermi energy but also on the quasi-particle dispersion in the vicinity of the critical points, i. e., the effective mass tensor. For lanthanide-based HFS, the theoretical analysis is based on Renormalized Band (RB) structure calculations assuming that the heavy quasiparticles result from a Kondo effect. For U-based HFS, on the other hand, we adopt the "dual nature" model which allows for a microscopic description of the heavy bands. The calculated Lifshitz transitions reproduce the observed positions of anomalies in the Seebeck coecients surprisingly well.

11:00am **AC+LS+MI-MoM9 Direct Measurement the $5 f_{5/2}$ and $5 f_{7/2}$ Unoccupied Density of States of UO_2**, *James G. Tobin,* University of Wisconsin-Oshkosh*; S. Nowak,* SLAC National Accelerator Laboratory*; C.H. Booth,* Lawrence Berkeley National Laboratory*; E.D. Bauer,* Los Alamos National Laboratory*; S.W. Yu,* Lawrence Livermore National Laboratory*; R. Alonso-Mori, T. Kroll, D. Nordlund, T.C. Weng, D. Sokaras,* SLAC National Accelerator Laboratory

In a world of ever increasing population and diminishing resources, the need for abundant and inexpensive energy remains critical. [1] Despite the problems associated with radioactive contamination/disposal and nuclear proliferation, electricity generated by nuclear power remains immensely important, [2] providing for 20% of the electrical grid of the USA and 50% or more for several European nations. [3-6] Uranium Dioxide (UO2) is by far the widely used nuclear fuel for the generation of electricity. [7] Thus, a fundamental understanding of the electronic structure of UO2 is crucial, if only to provide the best theoretical models for its disposal and storage. [7, 8]

Using High Energy Resolution Fluorescence Detection (HERFD) in a Resonant Inelastic Scattering (RIXS) experiment and electric dipole selection rules, the U 5f5/2 and U 5f7/2 Unoccupied Densities of States (UDOS) were determined. Significant changes were observed in going from UF4 (localized, 2 5f electrons) to UCd11 (localized, 3 5f electrons), consistent with the predictions of the Intermediate Coupling Model. The results for UO2 were experimentally confirmed by direct comparison with the Bremsstrahlung Isochromat Spectroscopy for Uranium Dioxide.

References

1. "Reasons for increase in demand for energy," BBC News, https://www.bbc.com/bitesize/guides/zpmmmp3/revision/1

2. Y. Guerin, G.S. Was, S.J. Zinkle, MRS Bull. 34, 10 (2009).

3. Nuclear Energy Institute, Nuclear shares of electricity generation, http://www.world-nuclear.org/info/nshare.html

4. Eleanor Beardsley, France presses ahead with nuclear power, Nat'l Pub. Radio, http://www.npr.org/templates/story/story.php?storyId=5369610

5. Nuclear energy, Environmental Protection Agency, USA, http://www.epa.gov/cleanenergy/energy-and-you/affect/nuclear.html

6. Energy, electricity, and nuclear power: developments and projections-25 years past and future, International Atomic Energy Agency, Vienna, 2007,www-ub.iaea.org/mtcd/publications/pdf/pub1304

7. F. Gupta, A. Pasturel, G. Brillant, Phys. Rev. B 81, 014110(2010).

8. J.G. Tobin and S.-W. Yu, Phys. Rev. Lett, 107, 167406 (2011).

11:20am **AC+LS+MI-MoM10 Optimizing the Magnetic Performance of Tetragonal $ReFe_{12-x}M_x$ Phases by First Principles Computational Simulations**, *Heike Christine Herper,* O.Y. Vekilova, P. Thunström, O. Eriksson, Uppsala University, Sweden

The increase of environmentally friendly energy production is coupled to an increasing demand for new magnetic materials. Especially, new Rare earth (Re) lean permanent magnets are highly sought after as possible replacement for high-performance magnets based on Nd-Fe-B and Dy to limit costs and supply risk. In this context the tetragonal 1:12 phase (TmMn₁₂) which contains 35% less Re than commercial Nd-Fe-B magnets are rediscovered. To stabilize this phase with light Re and Fe instead of Mn a nonmagnetic phase stabilizing element is needed but this degrades the magnetic performance.

To identify new 1:12 phases being suitable for permanent magnet applications materials design based on computational simulations has become an important tool. Here we focus on $ReFe_{12-x}M_x$. with Re = Y, Ce, Nd, Sm and M = Ti and V. We use state of the art density functional theory methods (VASP; full potential LMTO (RSPt)). The phase stability and the magnetic properties were calculated depending on the M concentration. Aiming to reduce the Re amount we monitor the performance depending on the Nd/Y ratio.

The key quantities are the magnetocrystalline anisotropy (MAE) and the magnetization. To capture the correct magnetic behavior, it is crucial to describe the localization of the 4f electron properly for each Re. While for Sm-based systems the spin-polarized core approximation is sufficient to describe the localized 4f electrons, it fails for Nd, e.g. the low temperature MAE of NdFe11Ti would be uniaxial instead of conic. Using a DFT+U approach with U = 5 eV, J = 1.1 eV for NdFe11Ti reproduces the experimentally observed behavior. Ce is special since the uniaxial MAE of CeFe11Ti is obtained independent from the treatment of the 4f electron. However, an analysis of the hybridization function analogue to [1] shows that a spin polarized core approximation is more appropriate for Ce-based 1:12 phases. For a deeper insight additional studies are carried out to examine the crystal field splitting.

With SmFe11V system a new phase was found leading to an increase of the magnetization by 17% compared to the commonly used concentrations of V. In view of the MAE a replacement of Nd by Y turned out to be preferable over a reduction of Ti. MAE values of 1.3 MJ/m³ ((NdY)Fe11Ti) and 1.7 MJ/m³ (SmFe11V) are predicted [2]. The latter could already be verified in recent experiments [2].

[1] H.C.Herper et al., Phys. Rev. Materials**1**, 033802 (2017)

[2] A. M. Schönhöbel et al., JALCOM **786**, 969 (2019)

11:40am **AC+LS+MI-MoM11 Optical Excitation Effect on Magnetodielectric and Photodielectric Properties of Rare Earth doped ZnO:Na Nanoparticles**, *Mohammed Bsatee,* F.P.N. Inbanathan, Ohio University*; R. Martínez,* University of Puerto Rico*; H. Huhtinen,* University of Turku, Finland*; R. Palai,* University of Puerto Rico

There have been ongoing efforts in developing rare earth (RE) ions doped semiconductors responsive to optical and magnetic stimuli for developing multifunctional devices. ZnO is considered as a promising semiconductor with wide range of applications in optoelectronics and spintronics due to its optical properties (*i.e*. direct band gap, high electron mobility, high thermal stability, strong absorption of UV), and at the same time being an attractive host for RE doping resulting in enhanced spin polarization in ZnO:RE matrix [1]. In this project, undoped and RE ions (Er and Yb) doped and co-doped ZnO:Na nanoparticles were studied with an aim to understand recently reported magnetodielectric and photodielectric effects stimulated by magnetic field and UV excitation stimuli [2]. After synthesizing well-defined Er and Yb-co-doped ZnO:Na by sol-gel route, evaluation of structural, optical, magnetic and electrical characteristics of synthesized nanoparticles was performed. Structure, morphology, and composition of the samples were analyzed by XRD and SEM showing high quality hexagonal crystal structure. The absence of secondary phases was confirmed by Raman spectroscopy and XPS analysis of all elements in

ZnO:NaErYb compound. Optical properties were investigated by optical reflectance spectroscopy, photoluminescence (PL), PL excitation, and PL kinetics with photons excitation energy corresponding to above and below bandgap energy. PL spectra were investigated under magnetic field of up to 2 Tesla in 7 K – 400 K temperature range. It was observed that PL spectra exhibit broad green-yellow defects emission band without NBE excitonic peak. PLE spectra revealed that both Er^{3+} and Yb^{3+} ions are optically active and involved in complex energy transfer between ZnO:Na host and 4f-shall levels of RE^{3+} ions dopants. PL spectra show features related to intra-shell 4f-4f transitions of the Er^{3+} ion (at 522 nm) and Yb^{3+} ion (at 980 nm). It was observed that luminescence decay of the ZnO defect band is unexpectedly long (> tens of 10^{-3} second), strongly affected by RE^{3+} ions doping and depends on the magnetic field strength when excited at 3.814 eV. In the presentation we will attempt to correlate reported magnetodielectric and photodielectric properties of the Er,Yb-co-doped ZnO:Na [2] with observed optical characteristics.

References

[1] A.G. El Hachimi, H. Zaari, A. Benyoussef, M. El Yadari, A. El Kenz, J. Rare Earths, 32, p.715 (2014).[2] R. Martinez Valdes, N. Kumar, H. Huhtinen, W. M. Jadwisienczak, R Palai, MRS Adv. (2019), DOI: 10.1557/adv.2019. 66.

Thin Films Division
Room A122-123 - Session TF+EM+MI+MN+OX+PS-MoM

Functional Thin Films: Ferroelectric, Multiferroics, and Magnetic Materials

Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Jessica Kachian, Intel Corporation

8:20am **TF+EM+MI+MN+OX+PS-MoM1 A Room-Temperature Magnetoelectric Multiferroic made by Thin Film Alchemy**, *D.G. Schlom, Megan Holtz,* Cornell University **INVITED**
Materials that couple strong ferroelectric and ferromagnetic order hold tremendous promise for next-generation memory devices. Meticulous engineering has produced novel ferroelectric and multiferroic materials, although known single-phase multiferroics remain limited by antiferromagnetic or weak ferromagnetic alignments, by a lack of coupling between the order parameters, or by having properties that emerge only well below room temperature. Here we construct single-phase multiferroic materials in which ferroelectricity and strong magnetic ordering are coupled near room temperature. Starting with hexagonal $LuFeO_3$—a geometric ferroelectric with planar rumpling—we introduce individual monolayers of ferrimagnetic $LuFe_2O_4$ within the $LuFeO_3$ matrix, that is, $(LuFeO_3)_m/(LuFe_2O_4)_1$ superlattices. The rumpling of the $LuFeO_3$ drives the ferrimagnetic $LuFe_2O_4$ into a ferroelectric state, reducing the $LuFe_2O_4$ spin frustration. This increases the magnetic transition temperature to 281K for m=9. Moreover, the ferroelectric order couples to the ferrimagnetism, enabling direct electric-field control of magnetism at 200 kelvin. Further, charged ferroelectric domain walls align at $LuFe_2O_4$ layers, resulting in charge transfer which increases the magnetic moment. We are currently pursuing higher temperature multiferroics by incorporating cubic spinels with high magnetic ordering temperatures, such as $CoFe_2O_4$, into the $LuFeO_3$ matrix. Our results demonstrate a design methodology for creating higher-temperature magnetoelectric multiferroics through epitaxial engineering.

9:00am **TF+EM+MI+MN+OX+PS-MoM3 Magnetic Losses in FeGa/NiFe/Al$_2$O$_3$ Laminates for Strain-Mediated Multiferroic Micro-Antenna Applications**, *Kevin Fitzell*, A. Acosta, C.R. Rementer, D.J. Schneider, Z. Yao, University of California, Los Angeles; C. Dong, Northeastern University; M.E. Jamer, D. Gopman, J. Borchers, B. Kirby, National Institute of Standards and Technology (NIST); N. Sun, Northeastern University; Y. Wang, G.P. Carman, J.P. Chang, University of California, Los Angeles
The ability to reduce the size of antennae would enable a revolution in wearable and implantable electronic devices. Multiferroic antennae, composed of individual ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude through the efficient coupling of magnetization and electric polarization via strain. This strategy requires a material with strong magnetoelastic coupling and acceptable magnetic losses at high frequency.

Galfenol ($Fe_{84}Ga_{16}$ or FeGa) is a promising candidate material due to its large magnetostriction (200 με), large piezomagnetic coefficient (5 ppm/Oe), and high stiffness (60 GPa), but it is highly lossy in the GHz regime. On the other hand, Permalloy ($Ni_{81}Fe_{19}$ or NiFe) is a soft magnetic material that has very low loss in the GHz regime, with a ferromagnetic resonance (FMR) linewidth of 10 Oe, but almost no magnetostriction. In this work, nanoscale laminates containing alternating layers of FeGa and NiFe were fabricated via DC magnetron sputtering to combine the complementary properties of the two magnetic phases, resulting in a composite material with a small coercive field, narrow FMR linewidth, and high permeability (Rementer et al., 2017). Optical magnetostriction measurements confirmed that these laminates retain the large saturation magnetostriction of FeGa (200 με) while enhancing the piezomagnetic coefficient (7 ppm/Oe), allowing for optimal piezomagnetic actuation at substantially reduced magnetic bias fields. Furthermore, multiferroic composites incorporating these magnetic laminates were studied via polarized neutron reflectometry, demonstrating uniform rotation of the individual layers' magnetization with an applied electric field across distances much larger than the exchange length of either material.

Due to the metallic nature of these FeGa/NiFe multilayer composites, however, resulting devices would be inefficient due to the generation of eddy currents at high frequency. To mitigate these losses, ultrathin layers of Al_2O_3 were incorporated into the multilayer materials to reduce the conductivity and mitigate the generation of eddy currents. The effect of Al_2O_3 thickness, FeGa:NiFe volume ratio, and multilayer architecture on the soft magnetic properties was also studied, resulting in a 50% reduction in the FMR linewidth. Optimized magnetic laminates were shown to exhibit a small coercive field (<20 Oe), narrow ferromagnetic resonance linewidth (<50 Oe), and high relative permeability (>500) while maintaining excellent magnetoelastic coupling, showing great promise for the use of FeGa/NiFe/Al$_2$O$_3$ laminates in strain-mediated micro-scale communications systems.

9:20am **TF+EM+MI+MN+OX+PS-MoM4 Multiferroic Gd-substituted HfO$_2$ Thin Films**, *John Hayden*, F. Scurti, J. Schwartz, J.-P. Maria, Pennsylvania State University
Modern ferroelectric technologies utilize perovskite structured materials, which have limited Si compatibility and modest bandgaps requiring thick films to reduce leakage current, hindering their implementation in realizable thin film devices. HfO_2 has been extensively researched as a gate dielectric thin film with excellent Si processing compatibility and has recently been found to exhibit ferroelectricity induced by a combination of impurity substitution, mechanical confinement by capping, intergranular surface area, and film thickness effects. This work investigates the microstructural characteristics, the ferroelectric response, and the potential for concomitant magnetic properties in sputtered Gd:HfO$_2$ thin films.

Gd-substituted HfO_2 thin films are a promising candidate as a multiferroic material, due to the presence of the magnetically active Gd^{3+} ion. Though substituting with Gd is known to induce ferroelectricity in HfO_2, the magnetic properties of Gd:HfO$_2$ have yet to be studied in depth. In this study, Gd:HfO$_2$ films are fabricated on TaN substrates by radio frequency sputtering of a composite Gd metal and HfO_2 oxide target in a mixed Ar and O_2 atmosphere. Grazing incidence x-ray diffraction is used to evaluate the suppression of the paraelectric monoclinic phase and stabilization of the ferroelectric orthorhombic phase. Electrical polarization measurements are used to study the room temperature spontaneous polarization in TaN/Gd:HfO$_2$/TaN metal-insulator-metal capacitors. Surface morphology of the films is characterized using atomic force microscopy, while magnetic properties are measured by variable temperature magnetometry. Initial magnetometry shows that Gd-substituted HfO_2 exhibits remnant magnetization at room temperature.

The scalability and simplicity of Gd:HfO$_2$, if it exhibits magnetoelectric coupling, make it an attractive model system for future developments in thin film multiferroics, having potential impacts for spintronics and other magnetoelectronic devices.

9:40am **TF+EM+MI+MN+OX+PS-MoM5 Epitaxial Growth of Antiferromagnetic NiO Films by Off-axis Sputtering for Spintronic Devices**, *A. Churikova, G.S.D. Beach,* Massachusetts Institute of Technology; *Larry Scipioni,* A. Shepard, J. Greer, T. Newhouse-Illige, PVD Products, Inc.
High-quality epitaxial growth of antiferromagnetic thin films is essential for future spintronic devices, as it allows small antiferromagnetic domain sizes and efficient electrical manipulation of domain walls via reading and writing currents. Antiferromagnetic materials are candidates for ultrafast operation due to THz antiferromagnetic spin dynamics, high packing densities due to the absence of stray magnetic fields, and stability due to insensitivity to external magnetic fields [1,2]. Meanwhile, the long spin

diffusion lengths [3] and theoretically predicted superfluid transport of spin currents [4] in antiferromagnetic insulators are crucial for low-power device operation. The electrical control of magnetic spin textures has been thus far realized in epitaxially grown NiO on MgO substrates [5] and ferrimagnetic maghemite (γ–Fe2O3) and magnetite (Fe3O4) thin films [6].

We report the preparation of antiferromagnetic NiO thin films with (111) orientation on *c*-plane sapphire (1000) substrates by off-axis RF magnetron sputtering from a NiO target. The off-axis angle was 45°, and the sputtering pressure was 5 mTorr. Samples were grown with thicknesses ranging from 5 – 50 nm, and with growth temperatures from room temperature to 600°C, to determine optimum conditions. Structural characterization by x-ray diffraction demonstrates a high degree of epitaxy across a range of deposition temperatures and thicknesses. The deposition temperature and thickness dependence of epitaxial quality is investigated, with a characterization of the strain state, mosaicity, and crystallographic relationship between substrate and film. Evidence for antiferromagnetic order forming domains in NiO is provided via magnetic characterization of the films. Our results are essential for the optimization of the fabrication of high quality epitaxial antiferromagnetic films for practical spintronics devices.

[1] J. Železný, P. Wadley, K. Olejník, A. Hoffmann, and H. Ohno, Nat. Phys. 14, 220 (2018)

[2] V. Baltz, A. Manchon, M. Tsoi, T. Moriyama, T. Ono, and Y. Tserkovnyak, Rev. Mod. Phys. 90, 015005 (2018).

[3] R. Lebrun, A. Ross, S. A. Bender, A. Qaiumzadeh, L. Baldrati, J. Cramer, A. Brataas, R. A. Duine, and M. Kläui, Nature 561, 222 (2018).

[4] S. Takei, B. I. Halperin, A. Yacoby, and Y. Tserkovnyak, Phys. Rev. B 90, 094408 (2014).

[5] T. Moriyama, K. Oda, T. Ono, Sci. Rep. 8, 14167 (2018).

[6] L. Baldrati, A. Ross, T. Niizeki, C. Schneider, R. Ramos, J. Cramer, O. Gomonay, M. Filianina, T. Savchenko, D. Heinze, A. Kleibert, E. Saitoh, J. Sinova, and M. Kläui, Phys. Rev. B 98, 024422 (2018).

10:00am TF+EM+MI+MN+OX+PS-MoM6 Structural and Magnetic Properties of CoPd Alloys for Non-Volatile Memory Applications, *S. Gupta, J.B. Abugri, B.D. Clark,* University of Alabama*; P. Komninou,* Aristotle University of Thessaloniki*; Sujan Budhathoki, A.J. Hauser, P.B. Visscher,* University of Alabama

A study of perpendicular magnetic anisotropy (PMA) CoPd alloys is presented as a simple means of pinning MgO-based perpendicular magnetic tunnel junctions (pMTJs) for spin transfer torque magnetic tunnel junction (STT-MRAM) applications. A compositional study of the Co_xPd_{100-x} alloys at 50 nm thickness showed that the maximum coercivity and anisotropy was found for $Co_{25}Pd_{75}$. Perpendicular magnetic tunnel junction stacks were deposited using different compositions of CoPd. Current-in-plane tunneling measurements indicated that the TMR values roughly correlated with the coercivity and anisotropy of the single layers. A thickness study indicated that the alloy was fully perpendicular for thicknesses as low as 20 nm. Various seed layers were employed to optimize the coercivity of the $Co_{25}Pd_{75}$ layer. Magnetometry, X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy studies were carried out to relate the magnetic and structural properties of these layers. These studies showed that the highest coercivity $Co_{25}Pd_{75}$ was achieved on a seed layer of Ta/Pd which helped to crystallize the CoPd layer in an fcc (111) orientation.

10:40am TF+EM+MI+MN+OX+PS-MoM8 Size Effects of the Electromechanical Response in Ferroic Thin Films: Phase Transitions to the Rescue, *Nazanin Bassiri-Gharb,* Georgia Institute of Technology **INVITED**

Silicon-integrated ferroelectric thin films have been leveraged over the last two decades for fabrication of high performance piezoelectric microelectromechanical systems (MEMS) devices. Ceramic $Pb(Zr_xTi_{1-x})O_3$(PZT) thin films have been often the material of choice, due to their large electromechanical response, especially at morphotropic phase boundary compositions (MPB at x ~0.52), where co-existence of multiple crystallographic distortions can enhance extrinsic electromechanical contributions. However, ferroelectric thin films suffer from extrinsic size effects that lead to deteriorated piezoelectric properties in thin and ultra-thin films. Here we report on different strategies for processing of thin films with enhanced piezoelectric response with respect to traditionally processed PZT thin films.

Specifically, we will discuss preparation of superlattice-like polycrystalline PZT thin films through chemical solution depositions, polycrystalline relaxor-ferroelectric thin films (PMN-PT), and finally alternative non-ferroelectric compositions, where the electric field-induced phase transitions can result in substantial enhancement in thinner films, even where traditional

11:20am TF+EM+MI+MN+OX+PS-MoM10 Ferroelectrics Meet Ionics in the Land of van der Waals, *S. Neumayer,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; J. Brehm,* Vanderbilt University*; M.A. McGuire,* Oak Ridge National Laboratory*; M.A. Susner,* Air Force Research Laboratory*; E. Eliseev,* National Academy of Sciences of Ukraine*; S. Jesse, S.V. Kalinin,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; A.N. Morozovska,* National Academy of Sciences of Ukraine*; S. Pantelides,* Vanderbilt University*; N. Balke, Petro Maksymovych,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Van der Waals crystals of metal thiophosphates can be thought of as derivatives of transition metal dichalcogenides where 1/3 of metal atoms is replaced with diphosphorous, thereby stabilizing the remaining 2/3 of metal ions in low oxidation states.1 Consequently, thiophosphates enable ultrathin magnetic, ferroelectric and Mott insulating materials, in q2D materials while also providing new opportunities for multifunctional interfaces .

Of particular interest is $CuInP_2S_6$, where ferroelectricity emerges out of ionically conducting state .2,3 In this work, we discuss unusual and perhaps anomalous properties observed in $CuInP_2S_6$ in both states.

$CuInP_2S_6$ exhibits giant negative electrostriction (Q_{33} = -3.2 m^4/C^2), which leads to large piezoelectric coefficients despite small polarization values and increase of Tc with applied pressure. It's the only material other than polymer PVDF for which such behavior is experimentally confirmed. Density functional theory reveals that the reason for negative electrostriction is a slight movement of Cu ions into the van der Waals gap due to anharmonicity of the potential well.4 Moreover, under high compressive strain, Cu starts to form interlayer bonds with sulfur across the van der Waals gap, leading to an additional phase of high polarization. Consequently, the potential distribution exhibits 4 instead of the usual two minima - a quadruple well, that is precisely tunable by strain. In the paraelectric state above ~70°C, Cu ion mobility drastically increases. Intriguingly, Cu can be reversibly extracted out of the lattice without visible damage. Finally, the selenide sibling $CuInP_2Se_6$, exhibits a lower transition temperature and propensity toward antiferroelectric ordering under the effect of depolarizing fields. In this material, we have for the first time observed piezoelectric response confined to domain walls (opposite to ferroelectrics), fulfilling the long-standing predictions for polar antiferroelectric domain walls and providing a new model system for emergent properties of topological defects in ferroic order parameter fields.

Research sponsored by Division of Materials Science and Engineering, Basic Energy Sciences, US Department of Energy. Microscopy was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

1Susner et al, Adv. Mater. 29,1602852 (2018)

2Neumayer et al, Phys. Rev. Materials **3**, 024401 (2019)

3Balke et al, ACS Appl. Mater. Interfaces 10, 27188 (2018)

4Brehm et al, in review

11:40am TF+EM+MI+MN+OX+PS-MoM11 Adsorption-controlled Epitaxial Growth of the Hyperferroelectric Candidate LiZnSb on GaSb (111), *D. Du, P. Strohbeen,* University of Wisconsin - Madison*; H. Paik,* Cornell University*; C. Zhang, P. Voyles, Jason Kawasaki,* University of Wisconsin - Madison

A major challenge for ferroelectric devices is the depolarizing field, which competes with and often destroys long-range polar order in the limit of ultrathin films. Recent theoretical predictions suggest a new class of materials, termed hyperferroelectics [1], should be immune to the depolarizing field and enable ferroelectric devices down to the monolayer limit. Here we demonstrate the epitaxial growth of hexagonal LiZnSb, one of the hyperferroelectric candidate materials, on GaSb (111) substrates. Due to the high volatility of all three atomic species, we find that stoichiometric films can be grown in a thermodynamically adsorption-controlled window, using an excess zinc flux. Outstanding challenges

remain in controlling the point defects of LiZnSb and in controlling polytypism. While the films primarily grow in a hexagonal "stuffed wurtzite" phase (space group $P6_3mc$), which is has the desired polar structure, there exists a competing cubic "stuffed zincblende" polymorph that is nonpolar ($F\text{-}43m$). We will discuss our strategy towards controlling defects and polytypism in LiZnSb, which is based in large part on the wurtzite – zincblende polytypism observed in InAs. We will also present preliminary electrical measurements on phase pure ferroelectric capacitor structures.

[1] K. F. Garrity, K. M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. **112**, 127601(2014).

2D Materials

Room A226 - Session 2D+AP+EM+MI+MN+NS+PS+TF-MoA

Nanostructures including Heterostructures and Patterning of 2D Materials

Moderator: Deep Jariwala, University of Pennsylvania

1:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA1 Tailoring and Patterning 2D Material Interfaces Through Chemical Functionalization***, Arend van der Zande,* University of Illinois at Urbana-Champaign **INVITED**
Two-dimensional materials are all surface, so any change in the surface chemistry affects the entire material. This offers a challenge and an opportunity to engineering the material properties and new device behavior. There are many strategies to altering the chemical structure of 2D materials, yet one of the most successful is the chemical functionalization with low energy plasmas such as hydrogen and fluorine. Functionalization enables phase changes within materials to dramatically alter their properties, can be applied post synthesis and device fabrication, and is compatible with lithography for spatial patterning. Most studies of chemical functionalization focus on single functionalization of single 2D materials, yet there are many opportunities when applying the principles of chemical functionalization to spatially engineer the properties though in plane interfaces or out of plane in heterostructures.

First, we will examine selective etching with XeF_2 to pattern heterostructures using graphene etch stops. These techniques are self-limiting, yet scalable, and enable the patterning of 2D heterostructures into 3D multilayer circuitry. Moreover, devices like encapsulated graphene transistors fabricated with these techniques have exceptionally low contact resistances and mobilities which approach theoretical limits.

Second we will present a new strategy for tailoring the stoichiometry of functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate new ternary HFG compounds and reversible switching of material stoichiometry via the sequential exposure of graphene to low energy H plasma and XeF_2 gas. By patterning regions of different functionalization on a single chip, we perform direct comparisons and show spatially controlled tuning of the relative surface properties such as wettability, friction, electronic conductivity and molecular adhesion. Taken together, these studies show that chemical functionalization offers new atomically precise nanofabrication and materials engineering techniques for scalable engineering of circuitry along all three dimensions.

2:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA3 Dual-Route Hydrogenation of the Graphene/Ni Interface***, Rosanna Larciprete,* CNR-Institute for Complex Systems, Roma, Italy*; D. Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy*; M.I. Trioni,* CNR-Institute of Molecular Science and Technologies, Milano, Italy*; P. Lacovig, L. Bignardi, S. Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy*; R. Martinazzo,* Università degli Studi di Milano, Milano, Italy
Although the high surface-to-weight ratio would make graphene (Gr) one of the most promising material for hydrogen accumulation, up to now only moderate gravimetric density values of 1-2% have been obtained at room temperature (RT). The ultimate H coverage is limited by the competition between the adsorption and desorption/abstraction processes and by the elastic energy that accumulates in the C lattice once puckered by the local sp3rehybridization of the C atoms binding hydrogen. Moreover, for epitaxial Gr on metals, the substrate-induced Gr corrugation might modulates periodically H adsorption. In this respect, the Gr/Ni(111) interface appears much more favorable than other graphene/metal systems, as the limitations due to the presence of the moirè supercell vanish due to commensurate relation between the Gr and Ni(111) lattices. Moreover, hydrogenation might be favored by the peculiar reactivity of Gr/Ni(111).This issues motivated a re-investigation of the interaction of this particular interface with hydrogen.

In this study [1]we used x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure spectroscopy (NEXAFS) to follow the RT hydrogenation of Gr/Ni(111) and determined the configuration of the hydrogenated interface by scanning tunneling microscopy (STM). We found that hydrogenation proceeds through a dual path that includes hydrogen chemisorption on top of the graphene followed by a slow but continuous intercalation below graphene. At low coverage H atoms predominantly adsorb as monomers and chemisorption saturates when ≈ 25% of the surface is hydrogenated. The formation of C−H bonds determines new components in the C 1s core level spectrum that are attributed by DFT calculations to C atoms directly bonded to H and to their first neighbors. In parallel with chemisorption, with a much lower rate, H atoms intercalate below Gr and bind to Ni surface sites. Thermal programmed desorption measurements showed that chemisorbed hydrogen is released around 600 K, whereas the intercalated phase desorbs abruptly slightly below 400 K. Then the Gr cover, besides offering a storage volume for the intercalated H, stabilizes it above room temperature rising by a few tens of kelvins the H2 release temperature with respect to the bare Ni(111) surface.

The effectiveness of these results can be expanded by using Ni substrates with large specific surface, as nanoparticles or nanostructured foils, which, when covered with Gr, might become media where hydrogen can be loaded and stored above room temperature.

[1] D. Lizzit et al. ACS Nano 13 (2019) 1828

2:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA4 Assembly of Arrays of Predefined Monolayer Features into vdW Heterostructure by a Continuous Exfoliate-align-Release Process***, Vu Nguyen, H. Taylor,* University of California at Berkeley
One of the major challenges of van der Waals (vdW) integration of 2D materials is the high-yield and -throughput assembly of pre-defined sequence of monolayers into heterostructure arrays. Although a variety of techniques have been developed to exfoliate the 2D materials from the source and deterministically place them onto a target substrate, they typically can transfer only either a wafer-scale blanket or a small flake at a time with uncontrolled size and shape. Here we present a method to exfoliate arrays of lithographically defined monolayer MoS_2 and WS_2 features from multilayer sources and directly transfer them in a deterministic manner onto target substrates. The continuous exfoliate-align-release process, without the need of an intermediate carrier substrate, was enabled by a new transfer medium fabricated by spin-coating a low-crosslinked and transparent adhesive on a transparent, electrostatically active backing material with low surface energy. MoS_2/WS_2 vdW heterostructure arrays produced by this method were characterized, showing coupled photoluminescence between the monolayers. Light-emitting devices using WS_2 monolayer were also demonstrated, proving the functionality of the fabricated materials. This method promises to produce large-area monolayer and multiplex heterostructure arrays with capability to integrate with existing semiconductor manufacturing equipment.

3:00pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA5 van der Waals Heterojunction Photothermoelectric Effect in MoS_2/Graphene Monolayers***, Yunqiu Kelly Luo,* The Ohio State University*; T. Zhou,* University at Buffalo, State University of New York*; M. Newburger,* The Ohio State Univesity*; R. Bailey-Crandell, I. Lyalin,* The Ohio State University*; M. Neupane,* U.S. Army Research Laboratory*; A. Matos-Abiague,* Wayne State University*; I. Zutic,* University at Buffalo, State University of New York*; R. Kawakami,* The Ohio State University
Two-dimensional (2D) van der Waals (vdW) heterostructures provide a vast playground for exploring new phenomena due to its unique ability to tailor and combine dissimilar materials with atomic precision. In particular, the combination of graphene and transition metal dichalcogenides (TMDC) garners immense interest due to their novel optoelectronic, valleytronic and spintronic properties. Here, we report the observation of a highly tunable vdW heterojunction photothermoelectric effect (HPTE) in dual-gated MoS_2/graphene heterostructures, identified by a signature six-fold photocurrent pattern as a function of heterojunction bias and carrier density. In stark contrast to photovoltaic and photothermionic effects, we discover a new mechanism arising from photoexcitation of hot electrons in graphene and subsequent thermoelectric transport across the vdW junction. While analogous to lateral photothermoelectric effects at quasi-1D junctions in single layers, the vertical geometry of HPTE offers area scaling of 2D active regions and establishes, for the first time, the photothermoelectric response in vdW heterostructures. Operating at both low (18 K) and room temperatures, the discovery of HPTE creates new

possibilities for electrically-tunable broadband photodetectors and atomically-thin spin caloritronic devices.

3:20pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA6 Formation of Edge-bonded MoS₂-graphene Nanoribbons by On-surface Synthesis, *Mark Haastrup, M. Mammen, J. Rodríguez-Fernández, J.V. Lauritsen,* Aarhus University, Denmark

2D materials exhibiting unique material properties have the potential for a huge impact on our future. Graphene, as the first discovered truly 2D material, has been extensively studied. However, the lack of an intrinsic band gap makes it inadequate for electronic and optical devices. MoS_2 from the family of transition metal dichalcogenides has been intensively investigated for its possibility to be used in future applications. The vision is to integrate various 2D materials to realise an actual device. However, the actual assembly of these materials with high controllability remains a challenge. Vertical heterostructures, supported by Van der Waals interactions, have already been realised by manually stacking 2D materials on top of each other[1]. An ultimate thin device can be realised by creating lateral heterostructures with atomically sharp interfaces where each material is directly bonded to another. Currently, methods for in-plane bonding of MoS_2 to other materials (e.g. graphene) are limited due to poor structural match. One possible solution is to develop selective bottom-up methods for synthesis of molecular nanostructures by self-assembly.

This study aim to investigate the fundamental nature of bonding of graphene nanoribbons (GNRs) to the edges of MoS_2 nanoparticles by scanning tunnelling microscopy (STM). The aim is to synthesise GNRs from precursor molecules through a thermally activated Ullmann reaction already used elsewhere[2,3]. After initial growth of MoS_2, it is necessary to anneal in a hydrogen atmosphere to activate the edges to facilitate the attachment of an intermediate structure of poly(para-phenylene) (PPP) wires. STM reveals the PPP wires have an affinity for the corners of the MoS_2 nanoparticles with a distance, obtained from line scans across the adsorption site, consistent with a covalent C-S bond.

[1]: Pant et al., Nanoscale, 2016, 8, 7, 3870-3887

[2]: Cai et al., Nature, 2010, 466, 7305, 470–473

[3]: Basagni et al., J. Am. Chem. Soc., 2015, 137, 5, 1802-1808

4:00pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA8 The Effects of Metal-modification and Two Dimensional (2D) Lamellar Structure on Catalytic Performance of MFI Zeolite for Ethylene Conversion into Liquid Aromatics, *Laleh Emdadi, L. Mahoney, D. Tran, I. Lee,* US Army Research Laboratory

The effects of two dimensional (2D) meso-/microporous structure and metal modification with gallium or zinc on catalytic performances of lamellar MFI zeolites in ethylene conversion reaction to liquid aromatics were investigated. Dual template technique was used to synthesize the 2D zeolite and metal modification of the zeolite was carried out by wet impregnation method. The results of multiple analysis techniques such as TEM, XRD, Ar adsorption-desorption, UV-Visible spectroscopy, and H_2-TPR showed that the zeolite structure is a pivotal factor for controlling the type of metal dopant species forming on zeolite, their size, and their distribution. Adding metal dopants to 2D zeolite structures improved the yield of liquid aromatics and selectivity for mono-benzene alkylated aromatics compared to their microporous commercial MFI analogies while decreased the coke formation rate. Zinc loaded lamellar MFI had the most efficient catalytic performance among all studied catalysts with lowest amount of total coke and highest fraction of light coke including mono-benzene alkylated aromatics determined by combination of different techniques such as FTIR, UV-Vis, MS-temperature programmed oxidation (TPO), FTIR-TPO, and GC-MS. This can be explained by higher accessibility of reactants to active sites and facilitated transport of products and coke precursors from lamellar structure of this zeolite and the lower Brønsted/Lewis acid site ratio of this catalyst provided by metal modification which is more suitable for ethylene aromatization and suppresses the formation of heavy coke species. The catalytic performance of zeolite catalyst can be tuned by modulating both the textural and acidity properties of the zeolite structure. The metal modified 2D lamellar MFI zeolites as bifunctional catalysts open an avenue for converting large reactant molecules to desired products by designing a catalyst with an optimal structure, acidity, and dispersion of metal dopants.

4:20pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA9 Structural Stability of Graphene Nanoflakes:From the View Point of Aromaticity, *M. Ushirozako, H. Matsuyama, A. Akaishi,* **Jun Nakamura,** The University of Electro-Communications (UEC-Tokyo), Japan

Recently, nano-scale graphene nanoflakes (GNFs) have attracted great attention as one of the promising materials for electronics and spintronics. Kim *et al.* have successfully fabricated GNFs with various sizes up to 35 nm and have reported that the photoluminescence property of GNFs depends on the size and the edge shape [1]. From the view point of the structural stability of GNFs, we have not yet acquired the systematic comprehension with regard to effects of shapes and sizes of GNFs on the stability. In the present study, we have examined how the stability of GNFs is dominated by the edge shape and the size of GNFs, using first-principles calculations within the density functional theory.

In order to evaluate the stability of GNFs, we calculated the edge formation energy. First, we consider GNFs with the six-fold symmetry (D_{6h}) and classify them into zigzag GNFs (ZZGNFs) and armchair GNFs (ACGNFs). ACGNFs have two subtypes, AC(1) and AC(2), depending on whether carbon atoms are just at the corner of the outermost envelope hexagon of GNFs. We define the edge purity as the ratio of the number of carbon atoms at the edge unambiguously regarded as the armchair to the total number of edge atoms. The purity of AC(1) is higher than that of AC(2). The chemical formulae associated with ZZ, AC(1), and AC(2) are $C_{6n^2}H_{6n}$, $C_{18n^2-18n+6}H_{12n-6}$, $C_{18n^2-30n+12}H_{12n-12}$, respectively. In addition, we also evaluate the structural stabilities of triangular and rhombus GNFs.

We calculated the edge formation energy of the GNFs having up to 1200 carbon atoms as a function of the number of edge carbon atoms [3]. The formation energy of ZZGNFs is higher than that of ACGNFs irrespective of the size of GNFs. This instability of ZZGNFs is attributed to the presence of the so-called edge state. Indeed, it has also been shown that the formation energy of the zigzag graphene nanoribbon is higher than that of the armchair one [4]. It is noted that AC(2) is slightly more stable than AC(1), whereas the purity of AC(2) is lower than that of AC(1). Such peculiar stabilization can be reasonably explained in terms of the aromaticity of GNFs. The Nucleus Independent Chemical Shifts (NICS) values, which is averaged for the six-membered rings in GNFs, for AC(2) are lower than those for AC(1). This means AC(2) is more aromatic than AC(1). We will discuss the quantitative relationship between the stability and the aromaticity of GNFS.

[1] S. Kim et al., ACS Nano, **6**, 9, 8203 (2012)

[2] W. Hu *et al*., J. Chem. Phys. **141**, 214704 (2014)

[3] A. Akaishi, M. Ushirozako, H.Matsuyama, andJ.Nakamura, Jpn.J.Appl.Phys. **57**, 0102BA(2018)

[4] S. Okada. Phys. Rev. B, **77**, 041408 (2008)

4:40pm 2D+AP+EM+MI+MN+NS+PS+TF-MoA10 Wafer-scale 2D-3D Mixed Heterostructures Enabled by Remote Epitaxy through Graphene, *Jeehwan Kim,* Massachusetts Institute of Technology **INVITED**

The current electronics industry has been completely dominated by Si-based devices due to its exceptionally low materials cost. However, demand for non-Si electronics is becoming substantially high because current/next generation electronics requires novel functionalities that can never be achieved by Si-based materials. Unfortunately, the extremely high cost of non-Si semiconductor materials prohibits the progress in this field. Recently our team has invented a new crystalline growth concept, termed as "remote epitaxy", which can copy/paste crystalline information of the wafer remotely through graphene, thus generating single-crystalline films on graphene [1,2]. These single-crystalline films are easily released from the slippery graphene surface and the graphene-coated substrates can be infinitely reused to generate single-crystalline films. Thus, the remote epitaxy technique can cost-efficiently produce freestanding single-crystalline films including III-V, III-N, and complex oxides. This allows unprecedented functionality of flexible device functionality required for current ubiquitous electronics. I will also present detailed mechanism behind remote atomic interaction through graphene [2]. In addition, we have recently demonstrated a manufacturing method to manipulate wafer-scale 2D materials with atomic precision to form monolayer-by-monolayer stacks of wafer-scale 2D material heterostructures [3]. In this talk, I will discuss the implication of this new technology for revolutionary design of next generation electronic/photonic devices with combination of 3D/2D mixed heterostructures.

[1] Y. Kim, et al, and J. Kim, "Remote epitaxy through graphene enables two-dimensional material based layer transfer" *Nature*, Vol. 544, 340 (2017)

[2] W. Kong, et al, and J. Kim, "Polarity govern atomic interaction through two-dimensional materials", *Nature Materials*, Vol. 17, 999 (2018)

[3] J. Shim, S. Bae, et al, and J. Kim, "Controlled crack propagation for atomic precision handling of wafer-scale two-dimensional materials" *Science*, 362, 665 (2018)

2D Materials
Room A216 - Session 2D+AP+EM+MI+NS+PS+TF-MoA

2D Materials Growth and Fabrication
Moderator: Sarah Haigh, University of Manchester, UK

2:00pm **2D+AP+EM+MI+NS+PS+TF-MoA2 Synthesis of High Quality Monolayer Transition Metal Dichalcogenides using Direct Liquid Injection**, *Kathleen M. McCreary, E.D. Cobas, A.T. Hanbicki, M.R. Rosenberger, H.-J. Chuang, B.T. Jonker,* U.S. Naval Research Laboratory
In recent years, interest in monolayer transition metal dichalcogenides (TMDs) has rapidly increased, spurred by the possibility for integration into a variety of technologies such as photodetection, flexible electronics, and chemical sensing. While fundamental investigations can be performed on exfoliated flakes or chemical vapor deposition synthesized isolated islands, the limited size resulting from these techniques poses a significant barrier forimplementation of TMDs in technological applications. To overcome these obstacles, new synthesis avenues should be explored. Here, we outline a novel technique that utilizes a commercially available Anneal Sys growth chamber equipped with direct liquid injection (DLI) heads for all precursors. The use of liquid, rather than solid precursors, provides fine control of both metal and chalcogen precursors leading to the synthesis of monolayer MoS_2 across cm^2 areas. Photoluminescence, Raman, XPS, and conductive AFM are used to evaluate DLI grown MoS_2, and indicate high quality material having low defect density, with metrics comparable to or better than exfoliated and chemical vapor deposition grown MoS_2.

2:20pm **2D+AP+EM+MI+NS+PS+TF-MoA3 Understanding and Controlling the Growth of 2D Materials with Non-Equilibrium Methods and in situ Diagnostics**, *David Geohegan, Y-C. Lin, Y. Yu,* Oak Ridge National Laboratory*; C. Liu, G. Duscher,* University of Tennessee Knoxville*; A. Strasser,* University of Texas at Dallas*; A.A. Puretzky,* Oak Ridge National Laboratory*; K. Wang,* Intel Corporation, USA*; M. Yoon, C.M. Rouleau,* Oak Ridge National Laboratory*; S. Canulescu,* DTU Nanolab, Technical University of Denmark*; P.D. Rack,* University of Tennessee Knoxville*; L. Liang, W. Zhang, H. Cai, Y. Gu, G. Eres, K. Xiao,* Oak Ridge National Laboratory **INVITED**
Atomically-thin two-dimensional (2D) materials, including layered 2D transition metal dichalcogenide (TMD) semiconductors and their heterostructures, exhibit remarkable quantum properties that are envisioned for energy-efficient photovoltaics, flexible optoelectronics, catalysis, and quantum information science. However, significant synthesis and processing challenges currently limit the technologic development of these "all-surface" materials, including wafer-scale, bottom-up synthesis of uniform layers of crystalline 2D materials that are comparable in quality to exfoliated flakes of bulk materials. As-synthesized crystals of 2D TMDs display remarkable heterogeneity on both the atomistic level (e.g., vacancies, dopants, and edge terminations) and on the mesoscopic length scale (e.g., misoriented grains, layer orientations, and interactions with substrates and adsorbates) that can strongly influence the structure and electronic properties in 2D materials. This heterogeneity offers a serious challenge for synthesis and processing, yet offers a tremendous opportunity to tailor functionality.

Here we describe several approaches that are being developed for in situ diagnostic analysis and control of synthesis and heterogeneity. In addition to conventional vapor transport techniques, progress in laser-based approaches for 2D synthesis and modification, such as pulsed laser deposition (PLD) and pulsed laser conversion of precursors, are presented that permit control of the growth environment using time-resolved in situ diagnostics. The non-equilibrium advantages of PLD to form alloys and vertical heterojunctions are demonstrated using the tunable kinetic energy and digital nature of the process. Correlated atomic-resolution electron microscopy and atomistic theory are used to understand the size and stoichiometry of the "building blocks" deposited for synthesis and the forces that guide assembly. 2D crystals are grown directly on TEM grids within custom chambers and transmission electron microscopes where the ability to 'see' every atom in these atomically-thin crystals permits a unique opportunity to understand the forces governing their synthesis and functionality. In situ optical spectroscopy techniques are described to characterize the material's evolving structure and properties, offering the opportunity to 'close the loop' between synthesis and optoelectronic functionality of 2D materials and heterostructures.

3:00pm **2D+AP+EM+MI+NS+PS+TF-MoA5 Area-Selective Atomic Layer Deposition of 2D WS₂ Nanolayers**, *Shashank Balasubramanyam* [1] *,* Eindhoven University of Technology, The Netherlands, Noord Brabant*; M.J.M. Merkx,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; A.J.M. Mackus,* Eindhoven University of Technology, The Netherlands, Nederland*; A.A. Bol,* Eindhoven University of Technology, The Netherlands, Netherlands
With continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS_2 are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising candidate for bottom-up processing to address the complexities of nanopatterning. Till date, AS-ALD of metals[1] and dielectrics[2] have been successfully demonstrated. However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS_2 nanolayers by using a three-step (ABC-type) plasma-enhanced ALD process.

AS-ALD of WS_2 was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H_2S plasma (C) pulses. This process resulted in immediate growth on SiO_2 while a significant nucleation delay was observed on Al_2O_3, as determined from *in-situ* spectroscopic ellipsometry (SE) and *ex-situ* X-ray photoelectron spectroscopy (XPS) measurements. The surface chemistry of this selective process was analysed by *in-situ* Fourier transform infrared spectroscopy (FTIR). The analyses revealed that the inhibitor adsorbed on the Al_2O_3 surface, blocking precursor adsorption, while little or no inhibitor adsorption was detected on the SiO_2 surface where WS_2 was readily deposited. Furthermore, the area-selective growth was demonstrated on SiO_2 samples with patterned Al_2O_3 on top. On SiO_2, WS_2 could be deposited with angstrom-level thickness control.

To improve the crystallinity, the AS-ALD WS_2 films were annealed at temperatures within the thermal budget of industrial semiconductor processing (≤ 450°C). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS_2. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO_2-Al_2O_3 interface which confirmed that annealing had no impact on selectivity.

To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

[1] R. Chen and S.F. Bent, *Adv. Mater.* (2006).

[2] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels and A.J.M. Mackus, *ACS Nano* (2017).

3:20pm **2D+AP+EM+MI+NS+PS+TF-MoA6 Growth Behavior of Hexagonal Boron Nitride on Cu-Ni Binary Alloys**, *Karthik Sridhara,* Texas A&M University*; J.A. Wollmershauser,* U.S. Naval Research Laboratory*; L.O. Nyakiti,* Texas A&M University*; B.N. Feigelson,* U.S. Naval Research Laboratory
Controlled growth of large area n-layered chemical vapor deposited (CVD) hexagonal boron nitride (h-BN) is of great interest as a tunnel dielectric, and substrate for graphene and transition metal dichalcogenides (TMDs). The CVD growth of h-BN has been demonstrated on various transition metal catalytic substrates such as Cu, Ni, Pt and Fe. Of these metal substrates, Cu and Ni are frequently used due to their relative abundance and low cost. However, h-BN growth on Cu leads to monolayer films, and growth on Ni yields thicker, substrate grain-dependent films. Therefore, a

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

cost-effective transition metal substrate is needed that will facilitate controlled n-layered h-BN growth.

In this work, we prepare isomorphous Cu-Ni binary alloys from 10-90 wt.% Ni by creating Ni-rich (Ni-Cu) and Cu-rich (Cu-Ni) alloys using electroplating of Cu on Ni foils and Ni on Cu foils, respectively. The electroplated foils are then annealed at ~1030° C for >5 hours to create Ni-Cu and Cu-Ni alloys. The alloys are subsequently polished mechanically to create a planarized surface suitable for h-BN growth. The surface morphology before and after polishing is assessed using a scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) characterization of the alloys confirms a designed stoichiometry at every weight percent. h-BN is grown on the alloys using atmospheric pressure chemical vapor deposition (APCVD) at 1030° C, with ammonia borane as the precursor, and H_2/N_2 as the carrier gas flowing at ~200 sccm. Cu and Ni foils are used as control samples for this study. Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) is used to confirm and characterize h-BN growth directly on Cu, Ni and alloy substrates. SEM is performed to evaluate the h-BN film and crystal morphology. The results indicate that the h-BN growth behavior on Ni-Cu is different than on Cu-Ni alloys. A trend of decreasing h-BN amount with reducing Ni concentration is observed on Ni-Cu alloys while no such trend is observed on Cu-Ni alloys. Additionally, there are large (~20 μm) multilayer and monolayer single crystals of h-BN on Ni-Cu alloys, and predominantly monolayer crystals and films of h-BN on Cu-Ni alloys. The difference in growth behavior is studied using x-ray photoelectron spectroscopy (XPS) and electron backscattering diffraction (EBSD), which reveal that the alloy surface composition determines the h-BN growth. This work demonstrates how Cu-Ni alloy substrate of different compositions, along with CVD growth conditions, can be used to control h-BN growth.

4:20pm 2D+AP+EM+MI+NS+PS+TF-MoA9 Controlled Growth of Transition Metal Dichalcogenide Monolayers for Applications in Nanoelectronic and Nanophotonic Devices, *A. George, C. Neumann, D. Kaiser, R. Mupparapu,* Friedrich Schiller University Jena, Germany*; U. Hübner,* Leibniz Institute of Photonic Technology, Jena, Germany*; Z. Tang, A. Winter, I. Staude,* **Andrey Turchanin,** Friedrich Schiller University Jena, Germany

Controlling the flow rate of precursors is highly essential for the growth of high quality monolayer crystals of transition metal dichalcogenides (TMDs) by chemical vapor deposition. Thus, introduction of an excess quantity of precursors affects the reproducibility of the growth process and results in the multilayer growth. Here, we demonstrate the use of Knudsen-type effusion cells for controlled delivery of sulfur precursor for the large area, high density, size-controlled and highly reproducible growth of monolayer TMD crystals [1]. The size of the grown crystals can be tuned between 10 - 200 μm. We grow MoS_2, WS_2, $MoSe_2$ and WSe_2 monolayer crystals as well as $MoSe_2$-WSe_2 lateral heterostructures and characterize them by optical microscopy, atomic force microscopy, Raman spectroscopy, photoluminescence spectroscopy and electrical transport measurements. It has been found that they possess a high crystalline, optical and electrical quality based on their single crystalline nature. We demonstrate their implementation in novel field-effect and nanophotonic devices and discusse an influence of the point defect density on their functional characteristics [2-3]. Moreover, we present a novel synthetic route for the integration of TMDs into lateral heterostructures with other 2D materials [4].

[1] A. George et al., *J. Phys.: Mater.* 2 (2019) 016001.

[2] T. Bucher et al., *ACS Photonics* 6 (2019) 1002.

[3] R. Meyer et al., *ACS Photonics* 6 (2019) DOI: 10.1021/acsphotonics.8b01716

[4] A. Winter et al., *Carbon* 128 (2018)106.

4:40pm 2D+AP+EM+MI+NS+PS+TF-MoA10 Atomic Layer Deposition of BN as a Novel Capping Barrier for B_2O_3, **Aparna Pilli,** *J. Jones, J.A. Kelber,* University of North Texas*; A. LaVoie, F. Pasquale,* Lam Research Corporation

The deposition of boron oxide (B_2O_3) films on Si and SiO_2 substrates by atomic layer deposition (ALD) is of growing interest in microelectronics for shallow doping of high aspect ratio transistor structures. B_2O_3, however, forms volatile boric acid (H_3BO_3) upon ambient exposure, requiring a passivation barrier, for which BN was investigated as a possible candidate. Here, we demonstrate, deposition of BN by sequential BCl /NH reactions at 600 K on two different oxidized boron substrates: (a) B O deposited using BCl /H O ALD on Si at 300 K ("B O /Si"); and (b) a boron-silicon oxide formed by sequential BCl /O reactions at 650 K on SiO followed by annealing to 1000 K ("B-Si-oxide"). X-ray photoelectron spectroscopy (XPS) data

demonstrate layer-by-layer growth of BN on B_2O_3/Si with an average growth rate of ~1.4 Å/cycle, accompanied by some B_2O_3 removal during the first BN cycle. In contrast, continuous BN growth was observed on B-Si-oxide without any reaction with the substrate. XPS data also indicate that the oxide/nitride heterostructures are stable upon annealing in ultrahigh vacuum to >1000 K. XPS data, after the exposure of these heterostructures to ambient, indicate a small amount of BN oxidation at the surface NH species, with no observable hydroxylation of the underlying oxide films. These results demonstrate that BN films, as thin as 13 Å, are potential candidates for passivating boron oxide films prepared for shallow doping applications.

5:00pm 2D+AP+EM+MI+NS+PS+TF-MoA11 Atomic Layer Deposition of SiO_2 on Group VIII Metals: Towards Formation of a 2D Dielectric, *T. Suh, R. Yalisove,* **James Engstrom,** Cornell University

The atomic layer deposition (ALD) of many metals, particularly Group VIII (now known as Groups 8, 9 and 10), on SiO_2 has been an active area of research in many fields, which include microelectronics and heterogeneous catalysis. There have been many fewer studies of the inverse—the deposition of SiO_2 on many of these same metals. One possible reason to explore the ALD growth of SiO_2 on transition metals is that it might provide a route to an atomically thick SiO_2 dielectric, *silicatene*. Silicatene is a 2D material that consists of a bilayer of Si_2O_3 linked to each other by bridging oxygen atoms (giving SiO_2), where there are no dangling bonds or covalent bonds to the underlying substrate on which it is grown. For example, an established route to form silicatene involves deposition of elemental Si in UHV and subsequent high-temperature annealing on various single-crystalline metal surfaces including, but not limited to, Ru(0001), Pt(111), and Pd(100). Such a process, unfortunately, is likely not compatible with high-volume manufacturing. With this motivation we embarked on a study of the plasma-assisted ALD of SiO_2 on e-beam deposited polycrystalline thin films of Ru, Pt and Pd using a commercial ALD reactor. We analyzed both the thin films and the starting substrates using a combination of techniques including contact angle, spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy. Thin films of SiO_2 were deposited using tris(dimethylamido)silane and an oxygen plasma at a substrate temperature of 200 °C, and we examined growth for 5, 10, 20, 50 and 100 cycles. Contact angle measurements showed immediate evidence for SiO_2 deposition on all metal surfaces, and the contact angle decreased and remained constant and < 10° from 5 to 100 cycles of ALD. From SE we found little evidence of an incubation period, and growth was linear for the range of sample examined and the thickness deposited per cycle was remarkably constant at a value of 0.76-0.78 Å-cycle^{-1}. Analysis of these films using angle-resolved XPS was consistent with the formation of a thin film of SiO_2 with uniform thickness. Having characterized the thin film thickness-ALD cycle relationship we subjected SiO_2 thin films with thickness of ~ 7-15 Å to post-deposition high-temperature anneals in oxygen furnace. Initial attempts to form silicatene with an anneal at 800 °C, produced a structure suggesting possible interfacial reaction between the SiO_2 and Ru, perhaps involving silicide formation. We will end our presentation with a discussion of recent work involving a more extensive examination of the post-deposition annealing step, and deposition on patterned wafers.

2D Materials

Room A216 - Session 2D+AS+MI+NS-TuM

2D Materials Characterization including Microscopy and Spectroscopy

Moderator: David Geohegan, Oak Ridge National Laboratory

8:00am **2D+AS+MI+NS-TuM1 Near-field Infrared Spectroscopy of Single Layer MnPS₃**, *Sabine Neal,* University of Tennessee Knoxville*; H-S. Kim,* Rutgers University*; K.A. Smith, A.V. Haglund, D.G. Mandrus,* University of Tennessee Knoxville*; H.A. Bechtel,* Advanced Light Source, Lawrence Berkeley National Laboratory*; G.L. Carr,* National Synchrtoron Light Source II, Brookhaven National Lab*; K. Haule, D. Vanderbilt,* Rutgers University*; J.L. Musfeldt,* University of Tennessee Knoxville

In order to explore the properties of a complex van der Waals material under confinement, we measured the near-field infrared response of the magnetic chalcogenide $MnPS_3$ in bulk, few-, and single-layer form and compared the results with traditional far field vibrational spectroscopy and complementary lattice dynamics calculations. Trends in the activated B_u mode near 450 cm^{-1} are particularly striking, with the disappearance of this structure in the thinnest sheets. Combined with the amplified response of the A_g mode and analysis of the $A_u + B_u$ features, we find that the symmetry is unexpectedly *increased* in single-sheet $MnPS_3$. The monoclinicity of this system is therefore a consequence of the long-range stacking pattern rather than local structure.

8:20am **2D+AS+MI+NS-TuM2 Multi-parameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime***, Alessandra Bellissimo,* ETH Zürich, Switzerland*; G.M. Pierantozzi,* CNR - Istituto Officine Materiali, Italy*; A. Ruocco, G. Stefani,* Università degli Studi Roma Tre, Italy*; O. Ridzel, V. Astašauskas, W.S.M. Werner,* Technische Universität Wien, Austria*; M. Taborelli,* CERN, Switzerland*; G. Bertolini, U. Ramsperger,* ETH Zürich, Switzerland*; O. Gürlü,* ETH Zürich, Switzerland, Turkey*; D. Pescia,* ETH Zürich, Switzerland

The mechanisms responsible for electron-induced Secondary Electron Emission (SEE) generation of these ubiquitous Secondary Electrons (SEs) in a solid surface is not yet fully understood. In particular, the question *how many* "true secondary" electrons are generated and emitted from the target per incident primary electron awaits resolution and is of great fundamental as well as technological importance. The present work reports on a study of these and related questions by means of a variety of spectroscopic tools of increasing finesse. The interaction of Low-Energy Electrons with surfaces exhibiting different long-range order, was investigated by combining measurements of the Total Electron Yield in absolute units, single-electron as well as (e,2e)-coincidence spectroscopy. This investigation has led to the disentanglement of the elementary processes that need to be considered and comprehended for the understanding of the SE-generation probability, fully taking into account both energy and momentum conservation in the collision and the band structure of the solid. Single ionising scattering events, assisted by collective excitations, i.e. *plasmons*, constitute one of the fundamental ingredients leading to SEE. In the Low-Energy-regime the electron yield of a material is constituted by the interplay of reflectivity and SEE, both strongly dictated by the target band structure. The gathered information is further used in an attempt to interpret the signal generation mechanisms relevant in Scanning Field-Emission Microscopy (SFEM) [1].

Reference:

[1] A. Bellissimo, PhD Thesis, *"Multiparameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime"*, URL:

https://www.researchgate.net/publication/332684398_Multiparameter_Analysis_of_Genesis_and_Evolution_of_Secondary_Electrons_produced_in_the_Low_Energy_regime

8:40am **2D+AS+MI+NS-TuM3 Probing Point Defects, Folds and Interfaces in 2D Material Heterostructures using Scanning Transmission Electron Microscopy***, Sarah Haigh,* University of Manchester, UK **INVITED**

Scanning Transmission Electron Microscopy (STEM) is one of the few techniques able to probe the structure and chemistry of 2D materials when these are stacked to form vertical heterostructures. By combining STEM with electron energy loss spectroscopy and energy dispersive X-ray spectroscopy it is possible to characterise individual point defects,[1] to measure interlayer distances for dissimilar materials [2] and to investigate the microstructure of mechanically deformed structures at the atomic scale [3]. We have extensively employed plan view and cross sectional STEM imaging to investigate complex 2D heterostructures. For example, we have

shown that protruding defects prevent the realisation of pristine interfaces between transition metal selenides (MoSe2, WSe2, NbSe2) and boron nitride, unless exfoliation is performed in an inert environment.[2]

We have analysed microstructures produced when 2D van der Waals materials (graphite, boron nitride, MoSe2) are subjected to mechanical deformation and find that the types of defect can be predicted from just the bend angle and thickness of the materials.[3] In particular we find that above a critical thickness the materials exhibit numerous twin boundaries and for large bend angles these can contain nanoscale regions of local delamination. Such features are proposed to be important in determining how easily the material can be thinned by mechanical or liquid exfoliation.[3]

2D material heterostructures are also enabling new STEM imaging capabilities. We show they can be used as a platform to study real time reactions in liquid environments with unprecedented spatial resolution and spectroscopic capabilities [4]. We further demonstrate that graphene encapsulation allows imaging of point defect dynamics, structural degradation and mechanically induced stacking faults in 2D monochalcogenides, GaSe and InSe [1].

References

[1] D G Hopkinson et al, ACS Nano, (2019) 10.1021/acsnano.8b08253

[2] A P Rooney et al. Nano Letters, (2017) 17, 5222.

[3] A P Rooney et al. Nature Communications (2018) 9, 3597

[4] D J Kelly et al Nano Letters, (2018) 18, 2, 1168

9:20am **2D+AS+MI+NS-TuM5 Low-Energy Electron Induced Disordering and Decomposition of Self-assembled Monolayers on Au(111)***, Jodi Grzeskowiak*[1]*,* University at Albany - SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

To study the interaction of low energy electrons with thin organic films, measurements have been performed on electron induced disordering and decomposition of 1-decanethiol molecules grown via vapor phase deposition on Au(111). Surface analysis techniques were used to characterize the monolayers before and after electron exposure. LEED was used to determine the structure of the SAM and the rate of disordering and decomposition. It was observed that the diffraction pattern of the lying down phase of the SAM, held near 100 K, almost completely disappears within about three minutes of exposure. However, when the temperature of the irradiated sample was raised to 300 K and then cooled back down to around 100 K, most of the intensity of the diffraction pattern returns, indicating that electron exposure is primarily inducing disorder. TPD was used to evaluate the thermal stability of the SAMs and the resulting desorption products after electron exposure. For the standing up phase SAM, two desorption features for the hydrocarbon fragments of the SAM are observed, one around 130 °C and a second near 220 °C. For the lying down phase, only the higher temperature desorption feature is observed, which indicates that the SAM is converting from the standing up phase to the lying down phase during the heating process. For both phases, desorption peaks for S and H_2S at around 250 °C were observed, suggesting that there is a high probability for the alkane chain of the decanethiol molecule to detach from the sulfur head group. After electron exposure of the standing up phase, a large reduction in the intensity of the two desorption peaks for the masses monitored for the hydrocarbon fragments was observed. However, the intensities of the peaks associated with S and H_2S were similar to those for the samples that were not irradiated with electrons. For the lying down phase, the intensities and positions of all of the desorption peaks were similar to the unexposed SAMs, which indicates that the cross-section for electron beam damage for the lying down phase is much lower than that for the standing up phase. Ex-situ XPS was used to monitor the decomposition of the SAMs. After irradiation with 80 eV electrons, an uptake of oxygen was observed in the XPS measurements for both samples. This oxygen uptake gives evidence that oxygen in the air is reacting with carbon and sulfur atoms whose bonds were broken during electron exposure.

9:40am **2D+AS+MI+NS-TuM6 Continuous Silicene, Silicene Ribbons and Surface Reconstructions on h-MoSi₂***, Anna Costine, C. Volders,* University of Virginia*; M. Fu,* Oak Ridge National Laboratory*; P. Reinke,* University of Virginia

Silicene has emerged as a 2D material of interest because of its spin -orbit coupling, tunable electronic structure, and Dirac type behavior. Synthesis of silicene with preserved Dirac-type electronic structure has proven

---

[1] **ASSD Student Award Finalist**

challenging, but is critical to realizing theoretically predicted quantum states and devices. To date, Ag(111) remains the most popular substrate for silicene synthesis, but is discussed controversially due to its similarity with surface alloys. Silicene has also been synthesized on other substrates including Ir, IrSi₃, and ZrB₂. Silicene synthesis on a semiconducting substrate with a low buckling conformation to conserve the Dirac-type behavior would be ideal. The synthesis of silicene on new substrates that allow for direct device integration is an important next step.

We developed an alternate approach to silicene synthesis that allows for silicene synthesis on semiconducting silicides. The (0001) surface of h-MoSi2 has hexagonal symmetry and a lattice constant close to that of silicene. Our recent measurements support the assumption that silicene is electronically decoupled from the substrate. The h-MoSi2 crystallites, which are terminated by the (0001) plane are grown by depositing Mo onto a Si (001) or Si(111) surface. Upon annealing to ~800℃ the Si atoms decouple from the underlying surface and form a weakly buckled silicene layer with the √3 x√3 surface as seen by STM.

Our recent work expands this study and uses STM/S at 77 K to achieve a comprehensive description of silicene-on-silicide. The amount of Mo deposited (0.3 nm - 18 nm) and annealing temperature (700- 1000℃) were varied. All surface structures discussed here are on h-MoSi2 crystallites in the (0001) plane,. Three distinct surface structures coexist - silicene ribbons , a 4x4 reconstruction, and a complex reconstruction which is very sensitive to variations in the bias voltage. The electronic structure of silicene-ribbons shows a V-shaped density of states close to EF, indicative of Dirac-like behavior, while the other reconstructions are semiconducting. The surface and electronic structures observed on h-MoSi₂ crystallites as a function of the synthesis conditions will be discussed. The preference for silicene-ribbons in the low T STM/STS measurements is currently attributed to a faster post-deposition cooling rate, but the exact mechanism is still open to debate. We will present a detailed discussion of the electronic structure of silicene and silicene ribbons, and suggest mechanisms for the transition from the (0001) surface to silicene. Our goal is to develop synthesis approaches suitable for device integration of both silicene conformations.

11:00am **2D+AS+MI+NS-TuM10 Epitaxial Growth and Characterization of Single-Orientation Single-Layer Transition Metal Dichalcogenides on Au(111)**, *L. Bignardi,* University of Trieste, Italy; ***Daniel Lizzit,*** Elettra - Sincrotrone Trieste, Trieste, Italy; *B. Harsh, E. Travaglia,* Department of Physics, University of Trieste, Italy; *C.E. Sanders,* iNANO, Aarhus University, Denmark, UK; *M. Dendzik,* Aarhus University, Denmark, Germany; *P. Lacovig,* Elettra-Sincrotrone Trieste, Italy; *M. Michiardi,* iNANO, Aarhus University, Denmark, Canada; *M. Bianchi,* Aarhus University, Denmark; *R. Larciprete,* CNR-Institute for Complex Systems, Roma, Italy; *J.I. Flege, J. Falta,* University of Bremen, Germany; *P.K. Das,* Abdus Salam International Centre for Theoretical Physics, Trieste, Italy; *J. Fujii, I. Vobornik,* IOM-CNR, Laboratorio TASC, Trieste, Italy; *M. Ewert, L. Buß,* University of Bremen, Germany; *A. Baraldi,* University of Trieste, Italy; *P. Hofmann,* Aarhus University, Denmark; *S. Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy

It has been widely demonstrated that Transition Metal Dichalcogenides (TMDs), and in particular MoS₂ and WS₂ could be good candidates for future electronic devices because of their intrinsic electronic properties and their potential for ultimate device scaling. In the single layer (SL) form, the inversion symmetry breaking and the strong spin-orbit coupling of the heavy transition metals (Mo or W) open new possibilities for data storage and computing thanks to the spin and valley degrees of freedom. However, in order to investigate the fundamental physics behind these materials and to produce high quality electronic devices, SL TMDs with enough large area and high quality are demanded. In particular, single domain oriented layers, that are SLs without mirror domains, allow to strongly suppress defects due to the absence of grain boundaries which are known to degrade the overall performances.

We here present a successful synthesis method based on physical vapor deposition that consists in dosing W or Mo in H₂S atmosphere onto Au(111), and provide an in-depth characterization of the synthesized SL TMDs through different surface science techniques. Synchrotron radiation based photoelectron spectroscopy in the fast modality (fast-XPS) was used to carefully tune the growth parameters whereas high resolution (HR-XPS) was used for the characterization. In particular fast-XPS allowed to optimize the growth parameters which turned out to be different for MoS₂ [1] with respect to WS₂[2]. Then, photoelectron diffraction (XPD) was employed to find the structural parameters of the SLs and to unambiguously determine their single orientation character and the relative alignment with respect to the underlying substrate. Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED) and Microscopy (LEEM) added further insight into the lateral extension of the SLs and the structural order at the atomic level.

[1] H. Bana, E. Travaglia, L. Bignardi, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, D. Lizzit, F. Presel, D. D. Angelis, N. Apostol, P. K. Das, J. Fujii, I. Vobornik, R. Larciprete, A. Baraldi, P. Hofmann and S. Lizzit, 2D Materials, 2018, 5, 035012.

[2] L. Bignardi, D. Lizzit, H. Bana, E. Travaglia, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, M. Ewert, L. Buss, J. Falta, J. I. Flege, A. Baraldi, R. Larciprete, P. Hofmann, and S. Lizzit, Physical Review Materials 3, 014003 (2019).

11:20am **2D+AS+MI+NS-TuM11 Surface Reactivity of MoS₂ by ambient pressure X-ray Photoelectron Spectroscopy**, *Rafik Addou, D. Dardzinsky, G.S. Herman,* Oregon State University

Molybdenum disulfide (MoS₂) has potential applications as a low-cost catalyst for the hydrogen evolution reaction (HER). Defect sites in MoS₂ have been demonstrated to have high catalytic activities, where edge sites and sulfur vacancies are the major active sites for HER. Intentionally inducing defects offers a simple way to enhance the reactivity of MoS₂ and other 2D materials. In this study, we have characterized the surface reactivity and the catalytic activities of bulk MoS₂ samples using ambient pressure X-ray photoelectron spectroscopy (APXPS). The pristine surface was exposed to 1 mbar of H₂O vapor for temperatures ranging from 300 to 573 K. APXPS Mo 3*d*, S 2*p*, and O 1*s* core levels do not show any significant changes under these reaction conditions due to the inert nature of the MoS₂ surface. To activate the MoS₂ basal plane to improve surface reactivity, we have formed well-controlled densities of defects using Ar⁺ sputtering. The defective surfaces were exposed to 1 mbar of H₂O vapor for temperatures ranging from 300 to 600 K. Changes in the APXPS Mo 3*d*, S 2*p*, and O 1*s* core levels indicate that the surface is much more reactive to H₂O, with the formation of Mo-O bonds. These results are consistent with the reduction in the H₂O gas phase which was measured by operando mass spectrometry. We have found that the reactivity strongly depends on the temperature and the size and density of defects. Following this first report of APXPS on MoS₂ acquired at more realistic pressure, we will also report the HER activity and X-ray absorption spectroscopy (XAS) on the pristine surface and compare it with defective surfaces. Our findings demonstrate that the reactivity and the catalytic activity of MoS₂ are significantly improved through the formation of defects.

11:40am **2D+AS+MI+NS-TuM12 Surface Characterization of 2D Materials and their 3D Analogues using XPS**, *Jonathan Counsell, S.J. Coultas, C.J. Blomfield, N. Gerrard,* Kratos Analytical Limited, UK; *C. Moffitt,* Kratos Analytical Limited; *A.J. Roberts,* Kratos Analytical Limited, UK

Since the synthesis of Graphene in 2004 there has been significant interest in novel 2D materials. Indeed this area has produced an abundance of high impact publications and so far >$10bn has been committed globally to both fundamental research and commercialisation. This interest has been due to the unique properties exhibited such as mechanical strength and charge/heat transfer. The potential commercial possibilities are diverse with applications as varied as heat management and dissipation to increasing computer processing power. To fully understand the nature and potential of these materials a comprehensive surface characterisation is necessary.

Herein we illustrate how by applying conventional surface analysis techniques with novel methodologies it is possible to create a more complete picture of the chemical and physical nature of deposited 2D materials. Both organic and inorganic 2D materials will be explored to demonstrate the methods and capabilities. Dichalcogenide materials (sulphides and selenides) containing different metal centres were analysed with XPS, and angular resolved methods, to calculate layer thicknesses, stoichiometry and chemical states. The lateral distribution of CVD ultra-thin films was studied using both macro and micro area XPS imaging modes to distinguish uniformity and evenness. The application of UPS will explore the bonding structure, sensitivity of the materials and as a potential tool for identifying damage/defects in the surface lattice. The merits and pitfalls of ion etching will be discussed and a complete method and protocol will be proposed for limiting spectral artefacts and therefore misleading results. The effects of deposition and analysis on the 2D materials' structure and composition will be highlighted as will the characterisation of unwanted reduction/oxidation, contamination and structural defects. Utilising the complete surface analysis tool box allows the analyst to gain further insight and to fully understand the complex nature of these novel materials.

12:00pm **2D+AS+MI+NS-TuM13 Characterization of Catalytic Active Sites on the Surface of MoS2 2-D Materials**, *Miguel Jose Yacaman,* University of Texas at San Antonio*; T. Zepeda, S. Fuentes Moyado,* CNyN UNAM Ensenada, Mexico

Materials such as the MoS2 have been used in catalysis at industrial level for many decades mostly on the hydrodesulfurization of naftas.

However more stringent regulations about the sulfur amount in diesel has printed the need to improve the catalysts .In order to achieve that it is important to understand the nature of the active sites and ways to improve the activity.In this presentation we discuss the use of in-situ techniques to study the surfaces of MoS2 materials made of few layers and discuss the role of the sites on the crystal edges.We also demonstrate that during the reaction the MoS2 material becomes crumpled and changes from semiconductor to metallic.

2D Materials
Room A226 - Session 2D+EM+MI+MN+NS+QS-TuM

Novel Quantum Phenomena

Moderator: Arend van der Zande, University of Illinois at Urbana-Champaign

8:00am **2D+EM+MI+MN+NS+QS-TuM1 Charge Density-Wave States in Single-Layer Transition-Metal Dichalcogenides**, *Phil King,* University of St Andrews, UK **INVITED**

Control over materials thickness down to the single-atom scale has emerged as a powerful tuning parameter for manipulating not only the single-particle band structures of solids, but increasingly also their interacting electronic states and phases. A particularly attractive materials system in which to explore this is the transition-metal dichalcogenides, both because of their naturally-layered van der Waals structures as well as the wide variety of materials properties which they are known to host. Yet, how their interacting electronic states and phases evolve when thinned to the single-layer limit remains a key open question in many such systems. Here, we use angle-resolved photoemission to investigate the electronic structure and charge density wave (CDW) phases of monolayer $TiSe_2$, $TiTe_2$, and VSe_2. Three-dimensionality is a core feature of the electronic structure of all of these parent compounds, but we show how their CDW phases not only persist, but are strengthened, in the monolayer limit. In $TiSe_2$, we observe an orbital-selective CDW, necessarily without a k_z-selectivity in band hybridisation that is of key importance for the bulk instability,[1] while $TiTe_2$ is driven into a charge-ordered phase in the monolayer which is not stable in the bulk at all. In VSe_2, we show how the monolayer hosts a much stronger-coupling CDW instability than the bulk, which in turn drives a metal-insulator transition, removing a competing instability to ferromagnetism.[2] Together, these studies point to the delicate balance that can be realized between competing interacting states and phases in monolayer transition-metal dichalcogenides.

This work was performed in close collaboration with M.D. Watson, A. Rajan, J. Feng, D. Biswas, and colleagues from the Universities of St Andrews, Oxford, Keil, Diamond, Elettra, and SOLEIL.

[1]Watson *et al.*, Phys. Rev. Lett. 122 (2019) 076404.

[2]Feng *et al.,* Nano Lett. 18 (2018) 4493.

9:00am **2D+EM+MI+MN+NS+QS-TuM4 Indirect Transition and Opposite Circular Polarization of Interlayer Exciton in a MoSe2 WSe2 van der Waals Heterostructure**, *Hsun-Jen Chuang,* A.T. Hanbicki, M.R. Rosenberger, C.S. Hellberg, S.V. Sivaram, K.M. McCreary, I.I. Mazin, B.T. Jonker, U.S. Naval Research Laboratory

An emerging class of heterostructures involves monolayer semiconductors such as many of the transition metal dichalcogenides (TMDs) which can be combined to form van der Waals heterostructures (vdWHs). One unique new optical property of heterostructure is an interlayer exciton (ILE), a spatially indirect, electron-hole pair with the electron in one TMD layer and the hole in the other. Here, we fabricated MoSe2/WSe2 hetero-bilayer encapsulated in h-BN with the alignment angle close to 60 degree between MoSe2 and WSe2. Followed by the state-of-the-art preparation techniques (Nano-squeegee) to ensure the optimal contact between the TMDs. The Strong ILE emission is observed with the emission energy around 1.35 eV at room temperature and resolve this emission into two distinct peaks (ILE1 and ILE2) separated by 24 meV at zero field at 5 K. Furthermore, we demonstrate that the two emission peaks have *opposite*circular polarizations with up to +20% for the ILE1 and -40% for ILE2 when excited

by circularly polarized light. A*b initio* calculations provide an explanation of this unique and potentially useful property and indicate that it is a result of the indirect character of *both* electronictransitions. These peaks are *doubleindirect* excitons. *i.e.*indirect in both real and reciprocal space, split by relativistic effects.

This research was performed while H.-J.C. held an American Society for Engineering Education fellowship and M.R.R and S.V.S held a National Research Council fellowship at NRL. This work was supported by core programs at NRL and the NRL Nanoscience Institute. This work was also supported in part by a grant of computer time from the DoD High Performance Computing Modernization Program at the U.S. Army Research Laboratory Supercomputing Resource Center.

9:20am **2D+EM+MI+MN+NS+QS-TuM5 Integrating 2D Magnet 1T-MnSe$_2$ with Topological Insulator Bi$_2$Se$_3$**, *Tiancong Zhu,* The Ohio State University*; D. O'Hara,* University of California, Riverside*; J.J. Repicky, S. Yu, M. Zhu, B.A. Noesges, T. Liu, M. Brenner, L.J. Brillson, J. Hwang, F.Y. Yang, J.A. Gupta, R. Kawakami,* The Ohio State University

Integrating two-dimensional(2D) magnet with topological insulator is an exciting topic. Other than the possible proximity induced magnetic ordering inside topological insulator, the 2D magnet/ topological insulator heterostructure can also lead to more efficient spin orbit torque switching, or the formation of magnetic skyrmions. The recent discovery of room temperature ferromagnetic ordering in 2D material MnSe and VSe further brings more potential in such heterostructure systems. In this talk, we report the synthesis and characterization of 2D magnet 1T-MnSe on topological insulator Bi Se . Monolayer of MnSe is grown on Bi Se with molecular beam epitaxy, and subsequently characterized with various techniques, including X-ray diffractometry (XRD), X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM). STM measurement reveals the co-existence of monolayer a-MnSe(111) and 1T-MnSe$_2$ on Bi_2Se_3 surface. By performing spin-polarized STM measurement with Cr tip, we observed directly the magnetic signal from 1T-MnSe$_2$ on Bi_2Se_3. The growth of 1T-MnSe$_2$ on Bi_2Se_3 further leads to the MBE synthesis of magnetic topological insulator Bi_2MnSe_4, which also shows ferromagnetism down to the monolayer limit. The structural and magnetic characterization of the material will also be discussed in this talk.

9:40am **2D+EM+MI+MN+NS+QS-TuM6 Effect of Exchange-correlation Functional and Structural Constraints on the Transition Temperature of Two- Dimensional Ferroelectrics**, *Shiva P. Poudel, J. Villanova, B. Miller, A. Pandit, S. Barraza-Lopez,* University of Arkansas, Fayetteville

In this presentation, I will discuss two inconsistent models for obtaining the transition temperature (T_c) of two-dimensional (2D) ferroelectrics. It will be shown that the inconsistency arises from the choice of exchange-correlation functional and structural constraints [1-4] by obtaining T_c for a SnSe monolayer with PBE and vdW exchange-correlation functional, and with increased constraints. It has been found that vdW functional gives a larger T_c in comparison with PBE functional. Also, the increasing constraint raises T_c as well. Afterward, a complete analysis of the converged unit cell with seven different exchange-correlation functional will be provided. These results represent the most comprehensive theoretical benchmarks for these intriguing 2D ferroelectric materials.

This work was funded by an Early Career Grant from the DOE (Grant No. DE-SC0016139). Calculations were performed on Cori at the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under Contract No. DE-AC02-05CH11231 and Arkansas High-Performance Computing Center's *trestles*, which is funded through the multiple National Science Foundation grants and the Arkansas Economic Development Commission.

References:

1. M. Mehboudi et al., Nano Lett. **16**, 1704 (2016).

2. M. Mehboudi, et al., Phys. Rev. Lett. **117**, 246802 (2016).

3. S. Barraza-Lopez, et al., PRB **97**, 024110 (2018).

4. R. Fei, et al., Phys. Rev. Lett. **117**, 097601 (2016).

11:00am **2D+EM+MI+MN+NS+QS-TuM10 Sign-change Pairing Symmetry in Single Layer FeSe/SrTiO$_3$ Film**, *Huimin Zhang,* West Virginia University*; Z. Ge, M. Weinert,* University of Wisconsin*; L.L. Li,* West Virginia University

Single layer FeSe film epitaxially grown on SrTiO$_3$(001) substrate has drawn much interest for its novel interfacial effects, which have led to the highest superconducting temperature (T_c) to date amongst all Fe-based superconductors. While several paring states, such as sign-persevering s_{++}-wave, sign-changing nodeless *d*-wave and $s_\pm$-wave have been suggested,

the pairing symmetry remains to be experimentally validated. Here we investigate the intrinsic impurity-induced in-gap bound states and quasiparticle interference (QPI) patterns in single layer $FeSe/SrTiO_3$ by scanning tunneling microscopy/spectroscopy. We observed bound states induced by nonmagnetic impurities, which strongly suggests a sign-changing order parameter. Through detailed analysis of the phase-sensitive QPI patterns, we further confirm that the order parameter indeed changes sign within the electron pockets. This identification of a sign change pairing symmetry in single layer $FeSe/SrTiO_3$ presents a critical step towards the understanding of its high T_c superconductivity.

11:20am **2D+EM+MI+MN+NS+QS-TuM11 High Temperature Superconductivity in Epitaxial Single Layer $FeTe_{1-x}Se_x/STO(001)$**, *Qiang Zou, Z. Ge, C. Yan, H. Zhang, L.L. Li,* West Virginia University

Single crystal FeTe exhibits a distinct long-range bicollinear antiferromagnetic order that can be suppressed by alloying with Se, where superconductivity emerges at a critical Se concentration of 0.3 with a T_c of 10 K. In this work, we show that this phase transition can be further modulated by reducing the thickness of $FeTe_{1-x}Se_x$, downto the single atomic layer limit. High quality single layer $FeTe_{1-x}Se_x$ films are grown on $SrTiO_3(001)$ substrate by molecular beam epitaxy and characterized by scanning tunneling microscopy/spectroscopy and angle-resolved photoemission spectroscopy. We find the electronic properties are strongly dependent on the Se content. For x < 0.1, hole-like bands cross the Fermi level and form a hole-pocket at the Γ point with no states observed around the M point, indicating no superconductivity. With increasing Se content, the top of the valence bands moves away from the Fermi level, accompanied by a decrease in effective mass at the Γ point. For x > 0.1, the hole pocket at Γ point moves below the Fermi level, and an electron-pocket emerges at M point where a superconducting gap opens with a T_c of ~50 K. These findings and their implications for the emergence and stabilization of superconductivity in Fe-based superconductors at reduced dimensions will be presented at the meeting.

11:40am **2D+EM+MI+MN+NS+QS-TuM12 The Observation of Majorana Zero Mode and Conductance Plateau in an Iron-based Superconductor**, *Hong-Jun Gao,* Institute of Physics, Chinese Academy of Sciences, China **INVITED**

Majorana zero-modes (MZMs) are spatially-localized zero-energy fractional quasiparticles with non-Abelian braiding statistics that hold great promise for topological quantum computing. Recently, by using scanning tunneling microscopy/spectroscopy (STM/STS), a new breakthrough of Majorana zero mode (MZM) was achieved in a single material platform of high-T_c iron-based superconductors, $FeTe_{0.55}Se_{0.45}$, which combined advantages of simple material, high- T_c, and large ratio of Δ/E_F [1]. A detail STM/STS study of a $FeTe_{0.55}Se_{0.45}$ single crystal, also revealed the mechanism of two distinct classes of vortices present in this system, which directly tied with the presence or absence of zero-bias peak [2]. To further investigated the MZM, it is still needed to find a "smoking-gun" type of evidence for the existence of MZM, and a quantized conductance plateau is widely believed to be one of them. Here we report an observation of the Majorana conductance plateau in vortices on the iron superconductor $FeTe_{0.55}Se_{0.45}$ surface by using STM/STS [3]. We found that both extrinsic instrumental convoluted broadening and intrinsic quasiparticle poisoning can reduce the conductance plateau value. When extrinsic instrumental broadening is removed by deconvolution, the plateau is found to nearly reach a $2e^2/h$ quantized value. The direct observation of a conductance plateau on a single zero-mode in a vortex strongly supports the existence and protection of MZMs in this iron-based superconductor, which can serve as a single-material platform for Majorana braiding at relatively high temperature.

* In collaboration with, D.F. Wang[1,2], L.Y. Kong[1,2], P. Fan[1,2], H. Chen[1], S.Y. Zhu[1,2], W.Y. Liu[1,2], L. Cao[1,2], Y.J. Sun[1,2], S.X. Du[1,2,3], J. Schneeloch[4], R.D. Zhong[4], G.D. Gu[4], Liang Fu[5], Hong Ding[1,2,3].

[1] Institute of Physics & University of Chinese Academy of Sciences, CAS, Beijing 100190

[2] CAS Center for Excellence in Topological Quantum Computation, UCAS, Beijing 100190

[3] Collaborative Innovation Center of Quantum Matter, Beijing 100190

[4] Brookhaven National Laboratory, Upton, New York 11973, USA

[5] Dept. of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

References:

[1] D. F. Wang et al, *Science.***362**, 333 (2008).

[2] L. Y. Kong et al, arXiv:1901.02293 (submitted to *Nature Physics* on November 19, 2018)

[2] S. Y. Zhu et al, arXiv: 1904.06124 (submitted to *Science* on February 15, 2019)

Thin Films Division
Room A122-123 - Session TF+EM+MI-TuM

Thin Films for Microelectronics, Photonics, and Optoelectronic Applications

Moderators: John F. Conley, Jr., Oregon State University, Halil Akyildiz, Uludag University, Turkey

8:00am **TF+EM+MI-TuM1 Monolithic Integration of III-Vs on Si for Electronic and Photonic Applications**, *P. Staudinger, S. Mauthe, N. Vico Trivino, N. Sousa, C. Convertino, Y. Baumgartner, P. Tiwari, H. Schmid, Kirsten Moselund,* IBM Research Zurich, Switzerland **INVITED**

For more than half a century researcher have been working on monolithic integration of III-V materials on Si in order to achieve seamless integration of III-V with Si CMOS. Progress has been made in recent years for example on nanowires [1], aspect ratio trapping (ART) [2] and other selective growth techniques suitable for III-V device integration. Here, I will discuss our work on Template-Assisted Selective Epitaxy (TASE) [3], as a novel epitaxial technique where III-V nanostructures are grown within an oxide template.

In this method we first use a combination of lithography and etching to define our structures in Si. These might be vertical or lateral nanowires, or more exotic shapes such as hall-bars, rings and disks. The Si features are covered by an oxide, which is opened locally, and the Si is partially etched exposing a Si nucleation seed within a hollow oxide cavity (template). The template is subsequently filled by metal-organic chemical vapor deposition (MOCVD) grown III-V material. The geometries of the III-V features are lithographically defined by the shape of the hollow template and to a large extent independent of growth conditions.

The versatility of this technique will be shown through several experimentally demonstrated devices, such as InGaAs MOSFETs [4], heterojunction tunnel FETs [5] and monolithically integrated room temperature optically pumped GaAs [6] and InP microdisk lasers [7].

The quality of the TASE-grown material is assessed by high-resolution scanning transmission electron microscopy (HR-STEM). Devices are free from propagating defects and dislocations, but stacking faults are present as expected for selective epitaxy. By controlling the twinning, we were successful in demonstrating pure wurtzite InP micro-substrates for the first time. We also compare lasing performance to that of devices based on defect-free bonded material, which currently represents the state-of-the-art in terms of photonic integration.

1. B. Mayer et al., Nano Lett., vol. 16, no. 1, pp. 152–156, 2016.

2. Z. Wang et al., Nat. Photonics, vol. 9, pp. 837–842, 2015.

3. H. Schmid et al. Appl. Phys. Lett. 2015, *106* (23), 233101.

4. L. Czornomaz et al., Symp. VLSI Tech., 2015, pp. T172–T173, 2015.

5. Cutaia, D. et al., Symp. VLSI Tech., pp. 403-407, (2016).

6. S. Wirths et al., ACS Nano 12 (3), pp. 2169, 2018.

7. S. Mauthe et al., submitted to IEEE J. Sel. Top. Quantum Electron. (2019).

8. M. Sousa et al. , 2018 IEEE Nano, DOI: 10.1109/NANO.2018.8626223

9. P. Staudinger et al., Nano Letters, vol. 18 (12), 7856, 2018.

8:40am **TF+EM+MI-TuM3 A Scheme for Better Future Technology by developing AlGaN based Highly Responsive Photosensing Devices**, *Neha Aggarwal, S. Krishna, L. Goswami, G. Gupta,* CSIR-National Physical Laboratory, India

All species on Earth are affected by UV radiation, from environment-to-humans, industrial-to-residential, defense-to-technology; a number of current & futuristic applications of detecting UV radiation exist. For fabricating UV photodetectors (PDs), III-Nitrides are promising candidates due to their superior material properties such as wide-direct bandgap, high thermal conductivity, good radiation hardness, etc. Also, III-nitrides are intrinsically blind to the visible region of EM spectrum; thus, do not require expensive optical filters unlike existing Si-based UV PDs. Among nitrides, AlGaN based heterostructures have gained huge interest in optoelectronic

applications due to their ability to tune the bandgap by modulating Al concentration which allows them to select the cut-off wavelength depending upon the application. Further, to facilitate the integration of AlGaN based devices with existing Si technology, Si substrates were utilized for growing AlGaN heterostructures. However, large lattice mismatch between AlGaN & Si may restrict the growth of defect-free AlGaN, thus a nucleation layer is needed to avoid cracking due to tensile strain. Incorporation of AlN as interlayer reforms the tensile stress in AlGaN layer directly grown on Si into compressive stress which yields the desired crack-free epitaxial structure. In this work, extensive efforts are employed to grow AlN on Si (111) substrate via PAMBE & successfully accomplished best quality AlN with lowest HRXRD FWHM of 15 arcmin having screw dislocation density of 8.5×10^8 cm^{-2}. Then, we have performed hetero-epitaxial growth of Al$_x$Ga$_{1-x}$N on AlN buffered Si (111) for x in 0.30-0.45 range & discusses the compositional fluctuations associated with changes in buffer growth parameters. As the buffer growth conditions changes, Al composition varies from 0.30-0.45 & FWHM is reduced from 55.6 to 36.4 arcmin. To realize a highly responsive UV PD, uniformly oriented AlGaN nano-islands are grown aimed to efficiently absorb photons due to increased surface-to-volume ratio. On this, we also implemented interdigitated (ID) electrode configuration to collect higher photo-generated charge carriers. The fabricated AlGaN UV PDs having cut-off wavelength of 284 nm yielded a significant enhancement in responsivity from 36.4 to 140.5 A/W at 2 V bias upon changing electrodes from non-ID to ID. However, the developed UV detection device exhibit high response towards UV with responsivity value of 182 mA/W under 2.5 V bias which is better than the commercially available UV detectors. Conclusively, the highly responsive AlGaN UV-PD on Si displays potential application in the development of advanced optoelectronic devices.

9:00am TF+EM+MI-TuM4 Correlating the Optical Property Evolution in the Au-Ni Binary Thin Films: From Metastable Solid Solution to Phase Separated Alloy, *Robyn Collette*, Y. Wu, P.D. Rack, University of Tennessee Knoxville

Surface plasmon resonances can be sustained by metallic nanostructures and have been explored for potential optoelectronic device applications. Metallic alloys provide a pathway to tune the plasmonic response of a material. Additionally, alloying may allow for multifunctional materials to be realized. For example, Au-Ni alloys may combine the magnetic properties of ferromagnetic Ni with the plasmonic properties of Au. However, limited studies have been conducted on Au-Ni alloys for use in plasmonic devices. Since the behavior of the alloys depends on the structure, it is first critical to understand the relationship between the structure and the optical properties of the alloy.

In this study, the optical properties of Au$_{1-x}$Ni$_x$ alloy thin films are investigated by employing a combinatorial sputtering approach. The dielectric function is measured using spectroscopic ellipsometry and is correlated to the composition (energy dispersive x-ray spectroscopy), and phases present (x-ray diffraction). As-deposited alloys form a metastable solid solution, however, annealed alloys exhibited phase separation into Au-rich and Ni-rich phases due to the large miscibility gap in the Au-Ni material system. The optical properties are then rationalized by modeling the dielectric function of the solid solution alloys with a Drude-Critical Point analytical model. Lastly, the efficacy of the model is demonstrated which shows that the dielectric function of the phase separated alloys may be approximated using a composition-weighted average of two solid solution dielectric functions.

9:20am TF+EM+MI-TuM5 Integration of Electro-optically Active BaTiO$_3$ and Ba$_x$Sr$_{1-x}$TiO$_3$ with Buffered Si (001) by Chemical Methods, *John G. Ekerdt*, B.I. Edmondson, E. Lin, University of Texas at Austin; *S. Kwon*, University of Texas at Dallas; *A.A. Demkov*, University of Texas at Austin; *M.J. Kim*, University of Texas at Dallas

Recent investigations into thin film BaTiO$_3$ (BTO) show it is a promising candidate for on-chip photonic devices due to its large linear electro-optic (EO) coefficient (r > 100-1000 pm/V) relative to more conventional photonic materials such as LiNbO$_3$ (~30 pm/V) or strained Si (~2 pm/V). However, such high coefficients are achieved only by costly and inherently un-scalable physical vapor deposition techniques. In recent studies, we have investigated chemical routes to the integration of electro-optically active BTO thin films with Si, which offer faster and more scalable methods of deposition. Specifically, atomic layer deposition (ALD) of 40 nm BTO films and chemical solution deposition (CSD) of 85 nm BTO films on SrTiO$_3$ (STO) templates on Si (001) prepared by molecular beam epitaxy (MBE) yield epitaxial BTO films with microstructure and defect nature markedly different from physical deposition techniques. Furthermore, we explored CSD of *c*-axis in-plane Ba$_x$Sr$_{1-x}$TiO$_3$, which is difficult to achieve by physical methods and offers unique insight into the EO behavior of this highly tunable dielectric. X-ray diffraction and scanning transmission electron microscopy confirmed epitaxial, distorted tetragonal structures with a range of structural defects, and electrical and electro-optical measurements showed diminished ferroelectricity and EO response compared to MBE-grown thin films or bulk BTO. ALD-grown films exhibited optical hysteresis with coercivity of ~10 kV/cm, an effective linear EO coefficient of 26 pm/V for 40 nm films, and leakage currents caused by oxygen vacancies. CSD-grown films did not show evidence of ferroelectric hysteresis but maintained EO response with a coefficient of 25 pm/V and had very low leakage current. Past reports of chemical vapor deposited films yielded an EO coefficient of 7 pm/V. These results provide further understanding into the relationship between film structure and linear EO behavior.

9:40am TF+EM+MI-TuM6 Nonlinear Optical Properties of TiO$_2$-based ALD Thin Films, *Theodosia Gougousi*, R. Kuis, I. Basaldua, P. Burkins, J.A. Kropp, A.M. Johnson, University of Maryland, Baltimore County

Nonlinear materials in thin film form are highly desirable for the development of ultrafast all-optical system on-a-chip platforms, optical frequency converters and optical limiting applications. Conventional nonlinear optical (NLO) materials are usually cut from bulk crystals or are liquids that are not suitable for integration with the contemporary semiconductor industry process flow. The third order nonlinear response of ALD TiO$_2$-based films is investigated using thermally managed Z-scan technique. Some of the as-deposited films exhibit very high nonlinear response which is orders of magnitude higher than conventional nonlinear optical materials such as silica fibers and CS$_2$. Thermal treatment of the films at 450°C for 3 hours in an oxygen rich atmosphere affects the films' optical properties and results in the loss of the high nonlinear optical response. TiO$_2$ films deposited by Physical Vapor Deposition (PVD) from a 99.9% TiO$_2$ target at room temperature are used as control samples and their nonlinear optical response is found below the detection limit of the Z-scan setup. This extraordinary nonlinear optical behavior of the TiO$_2$ ALD films is linked to the presence of a very small at. % of TiN bonding in the film. We will present detailed characterization of these films by x-ray photoelectron spectroscopy, x-ray diffraction and UV-Vis absorption. The high level of control of the nonlinear index of refraction, n$_2$, using the deposition process coupled with the ability of ALD to coat nonplanar geometries with atomic level precision and the fact that these processes are CMOS compatible have the potential to provide a breakthrough in optical device design and applications.

11:00am TF+EM+MI-TuM10 Atomic Layer Deposition on Hexagonal Ge and SiGe Nanowires for Surface Passivation, *Willem-Jan Berghuis*, Department of Applied Physics, Eindhoven University of Technology, Postbus 513, 5600 MB Eindhoven, The Netherlands; *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands; *J.E.M. Haverkort, E.P.A.M. Bakkers, A. Dijkstra, E.M.T. Fadaly, M.A. Verheijen*, Eindhoven University of Technology, The Netherlands

Semiconductor nanowires (NWs) are nanoscale rods with a typical length of a few microns. They are made of materials such as Ge, Si, InP, GaAs. Due to their high aspect ratio, nanowires have a very high surface-to-volume-ratio, which leads to a large influence of the surface on their electronic and optical properties. Surface states facilitate recombination of electron-hole pairs, which reduces the photovoltaic conversion efficiency of NW solar cells [1] or which decreases the output of NW based LEDs or lasers. The surface can also induce space charge regions in the nanowires, which greatly affects their conductivity and which can be critical in for example sensing applications [2]. To reach the desired performance of nanowires in their applications, it is important to control the surface effects.

Atomic layer deposition (ALD) is a deposition technique that allows for preparation of ultrathin films with sub-nanometer thickness control and with an excellent conformality on high aspect ratio structures such as nanowire arrays. For these reasons ALD is a suitable technique to cover nanowires with thin films to control the surface properties.

Recently, nanowires have enabled the growth of Ge and SiGe in the hexagonal diamond crystal phase [3]. In contrast to the cubic crystal phase of these materials, the hexagonal crystal phase leads to a direct bandgap. The latter makes this material an interesting candidate to realize solid-state lasers that are compatible with the current silicon-based electronics. One of the important steps to accomplish this is to reduce the surface recombination losses; i.e. to passivate the surface.

The aim of this work is to explore the surface passivation of these hexagonal Ge and SiGe nanowires. We do so by covering the nanowires with ultrathin films of Al_2O_3 prepared by thermal and plasma-assisted ALD (PE-ALD). Secondly, we cover the wires with a stack of PO_x/Al_2O_3. The latter is a relatively new passivation scheme that has proven very successful for the surface passivation of InP nanowires [4] and Si wafers [5]. The change in photoluminescence (PL) of the nanowires as a function of the ALD films has been studied to assess the surface passivation and the influence of various pre- and post-treatments. Conformal coating of hexagonal Ge nanowires has been realized and we have observed an improvement of the photoluminescence for NWs covered with PE-ALD Al_2O_3 and PO_x/Al_2O_3.

11:20am TF+EM+MI-TuM11 Oxidation Studies of Silicon Germanium (SiGe) using In-Situ Steam Generated (ISSG) and Plasma Enhanced Atomic Layer Deposited (PEALD) Oxides, *Yi Song, S. Siddiqui, C. Durfee, A. Pana, J. Li, M. Belyansky, S. Naczas, E.P. Stuckert, L. Jiang, J. Demarest, V. Basker, D. Guo, H. Bu,* IBM Research Division, Albany, NY

SiGe is a versatile material for the semiconductor industry for sub-7 nm node technology development; it can be used as a high mobility channel material in FinFET, and as multiple sacrificial layers to form channel regions in gate all around (GAA) nanosheet device architecture. Understanding SiGe film oxidation is important for matching oxidation rates between SiGe layers with different Ge% in nanosheet applications [1]. In this paper, a study of ISSG (800 °C) and PEALD (room temperature to 300 °C) oxidation processes is performed on blanket $Si_{1-x}Ge_x$ films ranging from x = 0.25 to 0.80. We establish the boundaries of three distinct regions of oxidation behavior for the ISSG process (Region I: $0 < x < 0.5$, Region II: $0.5 < x < 0.67$, and Region III: $x > 0.67$). Historically, low Ge oxidation has been extensively studied [2-4]. Here, we show for Region I, the ISSG oxidation rate is very small (1.7 nm of oxide growth in 5 sec). The oxidation rate rapidly increases in Region II as x increases, where it reaches a maximum (13.8 nm in 5 sec) at the Region II/Region III boundary, then abruptly drops in Region III as x increases due to complete sublimation of Ge (see Figure 1). The abrupt increase in the ISSG oxidation rate between Regions I and II makes it difficult to match oxide thicknesses for the wide range of Ge% utilized by nanosheet device architecture. Therefore, we studied a lower temperature oxidation process (PEALD) which has a lower oxidation rate. We found that PEALD oxidation rates are unchanged across the Region I/II boundary, even for higher temperatures up to 300 °C as shown in Figure 2. This enables oxide thickness matching for a wide range of Ge%. These results are applicable to the development of various nanotechnologies such as nanosheet and high mobility channel FinFET devices.

11:40am TF+EM+MI-TuM12 Precision Defect Engineering of Metal/Insulator/Metal (MIM) Diodes using Localized ALD Transition Metal Impurities in Al_2O_3 Tunnel Barriers, *Konner Holden[1], Y. Qi, J.F. Conley, Jr.,* Oregon State University

Thin film MIM tunnel diodes are receiving increased interest for high-speed applications such as THz detection and rectenna based energy harvesting. Traditionally, current density vs. field (J-$\mathcal{E}$) asymmetry (f_{asym} = J^-/J^+) with MIM diodes has been achieved through metal work function differences ($\Delta\Phi_M$). Recently, nanolaminate insulator tunnel barrier MIIM diodes enabled by ALD showed improved f_{asym}, non-linearity, and responsivity at low voltage by step tunneling through the wider bandgap (E_G) insulator to the conduction band of the narrow E_G insulator.[1] *Intrinsic defects* present in narrow E_G insulators were later demonstrated to further improve low $\mathcal{E}$ asymmetry via defect enhanced direct tunneling, when paired with an insulator dominated by tunneling.[2,3] In this work, we investigate the impact of localized *extrinsic defects* by using ALD to intentionally introduce Ni at precise intervals in an Al_2O_3 tunnel barrier.

ALD of Al_2O_3 on TiN was performed at 200 °C using TMA and H_2O. Five samples were prepared in which a 100 cycle Al_2O_3 ALD sequence was interrupted by two cycles (c) of $Ni(^{tBu2}DAD)_2$ and O_3 after 25, 50, 75, and every 25 c of Al_2O_3. As-deposited MIM devices were tested with bias applied to an Al top electrode (Fig. 1).

DC J-$\mathcal{E}$ sweeps of the 100 c device show Fowler-Nordheim tunneling (FNT) at high $\mathcal{E}$, with f_{asym} > 1 due to $\Delta\Phi_M$ ≈ 0.2 eV (Fig. 1). The addition of Ni cycles in all cases leads to an increase in J at low $\mathcal{E}$ vs. the 100 c Al_2O_3 device, suggesting defect related conduction. At high $\mathcal{E}$, however, J of all Ni devices is lower than the 100 c device, suggesting suppression of FNT. The 25/2/75 and 75/2/25 ($Al_2O_3/Ni/Al_2O_3$) devices show f_{asym} *opposite* of the 100 c device, while the 50/2/50 and 25/(2/25)x3 devices are roughly

symmetric (Fig. 1). The greater reduction in J at large negative $\mathcal{E}$, f_{asym} reversal, and reduced J-$\mathcal{E}$ slope for the 25/2/75 and 75/2/25 devices suggest that FNT is suppressed more for emission from the smaller Φ_M electrode (Al) than for TiN. FNT suppression appears greatest for the 75/2/25 device in which Ni is closest to the Al, pointing to an increase in effective barrier height, likely due to negative charge in the Al_2O_3. Capacitance (C) vs. $\mathcal{E}$ sweeps (Fig. 2) reveal a positive voltage shift in C_{min} for all Ni devices, consistent with negative charge.

The asymmetry reversal demonstrates the possibility of precision defect engineering of MIM tunnel devices using ALD. An in-depth discussion of J-$\mathcal{E}$ and C-$\mathcal{E}$, temperature-IV, frequency-CV, other impurities, and annealing will be presented.

1. Alimardani et al., APL 102 143501 (2013).

2. Alimardani et al., JAP 116, 024508 (2014).

3. Alimardani and Conley, Jr., APL 105, 082902 (2014).

12:00pm TF+EM+MI-TuM13 Improvement in the Electrical Characteristics of a-ZTO based TFTs *via* Microwave Assisted Annealing of Channel Layer, *Sunil Uprety, M.P. Khanal, H. Lee, S. Sarwar,* Auburn University; *A. Subramanian,* Stony Brook University; *E. Hassani, T.S. Oh, X. Zhang,* Auburn University; *C.Y. Nam,* Brookhaven National Laboratory; *M. Park,* Auburn University

In this research, we have investigated the effect of microwave-assisted annealing of amorphous zinc tin oxide (a-ZTO) channel layers on the electrical characteristics of the thin film transistors (TFTs). A multi-stacked a-ZTO layer was deposited on the oxidized Si wafer using sol-gel process. The precursor solution was prepared by dissolving zinc acetate dihydrate and tin chloride dihydrate into methoxyethanol. The solution was spin coated and calcined in a hot plate at 285°C. The as-calcined a-ZTO wafers were microwave annealed. The microwave (MW) annealing was carried on a commercial microwave oven at different power levels with the sample placed in a kiln which acts as a susceptor. The films remained amorphous even after MW annealing, which was evidenced by X-ray diffraction. The devices were fabricated using the microwave-annealed and as-calcined samples. Hall measurement is being carried out to study the concentration and mobility of charge carries. The performance of the TFTs with as-calcined and MW annealed channel layers were compared. Improvement in the electrical characteristics of the TFTs with MW annealed films were noted. It is believed that the microwave irradiation may promote the enhancement of the electrical characteristics of TFTs. Further research is being pursued to elucidate the role of microwave annealing in improvement of the device performance.

---

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

2D Materials

Room A216 - Session 2D+EM+MI+NS-TuA

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties II

Moderator: Roland Wiesendanger, University of Hamburg, Germany

2:40pm **2D+EM+MI+NS-TuA2 Resolving the Structural and Electronic Properties of Graphene/Ge(110)**, *Luca Camilli,* Technical University of Denmark, Denmark; *M. Galbiati,* Technical University of Denmark; *L. Persichetti, M. De Seta,* Università degli Studi Roma Tre, Italy; *F. Fabbri,* Italian Institute of Technology, Italy; *A. Scaparro,* Università degli Studi Roma Tre, Italy; *A. Notargiacomo,* Centro Nazionale di Ricerca, Italy; *V. Miseikis, C. Coletti,* Italian Institute of Technology, Italy; *L. Di Gaspare,* Università degli Studi Roma Tre, Italy

Unraveling the structural and electronic properties of the interface between graphene and conventional semiconductors is critical to enable novel graphene-based applications [1].

In this framework, the graphene/Ge(110) system has since last year received unprecedented attention [2-6]. Notably, graphene can be grown via chemical vapor deposition directly on the surface of germanium, similarly to the case of graphene grown on metals [7]. From a structural point of view, the graphene/Ge system is very dynamic, and the Ge surface has been shown by scanning tunneling microscopy (STM) studies to undergo a number of changes (i.e., reconstructions). However, the conclusions drawn in those studies do not always agree, probably also due to the strong dependence of the STM images on the applied voltage bias that makes comparison between different images rather difficult. In Ref. [6], for instance, the authors report three different surface reconstructions that are driven by thermal annealing, while the authors in Ref. [4] find only the unreconstructed surface and a (6x2) reconstruction, which again can reversibly change to unreconstructed surface after annealing at high temperature in hydrogen.

In this study, we aim at resolving the rich phase diagram of the Ge surface protected by graphene. We carry out annealing of the sample at different temperatures, and use a low-temperature STM to investigate the surface structure with atomic precision. At each stage, images at different applied biases are collected in order to allow a more straightforward comparison of the results.

Moreover, we perform electron energy loss spectroscopy (EELS) and scanning tunneling spectroscopy (STS) at temperature below 10 K to shed light on the electronic properties of the graphene/Ge interface, and to get more insights into their interaction.

Finally, we also show through a combination of STM and Raman spectroscopy that graphene can protect the germanium surface from oxidation even after continuous exposure to ambient conditions for more than 12 months, which is surprisingly a far more efficient protection than that offered by graphene on metals [8, 9].

References

[1] J.-H. Lee et al. Science 344, 286 (2014)

[2] G. Campbell et al. Physical Review Materials 2, 044004 (2018)

[3] J. Tesch et al. Nanoscale 10, 6068 (2018)

[4] D. Zhou et al. Journal of Physical Chemistry C 122, 21874 (2019)

[5] H.W. Kim et al. Journal of Physical Chemistry Letters 9, 7059 (2018)

[6] B. Kiraly et al. Applied Physics Letters 113, 213103 (2018)

[7] X. Li et al. Science 324, 5932 (2009)

[8] F. Zhou et al. ACS Nano 7, 6939 (2013)

[9] X. Zhang et al. Physical Chemistry Chemical Physics 18, 17081 (2016)

3:00pm **2D+EM+MI+NS-TuA3 Array of Strain Induced Quantum Dots in Graphene**, *Md Tareq Mahmud, N. Sandler,* Ohio University

Local Gaussian-shaped deformations induce strain fields that are represented by scalar and vector potentials in a continuum model description of electron dynamics in graphene. The ubiquitous strain changes the charge distribution in a very peculiar way, introducing a sublattice symmetry breaking, as has been reported in the literature. This feature can be exploited to design specific charge profiles by combining several deformations. Naturally, a combination of two or more is expected to introduce interference effects that can enhance charge accumulation in specific regions. We have investigated the effects of two overlapping deformations with different separations on the local density of states (LDOS). We showed that the overlap term can enhance the LDOS leading to stronger charge confinement in certain regions. Motivated by the work of Mason et. al (2018) we have extended these studies to a closed pack structure with a unit cell of 3 distinct deformations. This arrangement can be extended by symmetry to a lattice superstructure, thus creating a periodic array of confined charge regions, i.e, quantum dots. This array can be tailored by appropriately choosing the parameters of the deformations and their distances. The total charge distribution in these systems is similar to those observed in twisted bilayer systems, known as 'Moire patterns'. We discuss optimal tuning of deformations to control the physical properties of these graphene devices.

3:20pm **2D+EM+MI+NS-TuA4 Ultrafast Spin and Charge Dynamics in Monolayer WSe2-Graphene Heterostructure Devices**, *Michael Newburger, Y.K. Luo,* The Ohio State University; *K.M. McCreary,* U.S. Naval Research Laboratory; *I. Martin, E. McCormick,* The Ohio State University; *B.T. Jonker,* U.S. Naval Research Laboratory; *R. Kawakami,* The Ohio State University

Monolayer transition metal dichalcogenides (TMDs) have attracted attention due to their long spin/valley lifetimes and ability to couple the helicity of light to spin/valley polarization. Additionally, a strength of TMDs lies in their ability to complement other materials, such as graphene, by acting as a means of optical spin injection or proximity coupling. Recently, multiple groups have demonstrated proximity mediated charge transfer and optical spin injection in TMD/graphene heterostructures. However, the spin transfer dynamics across a TMD/graphene interface remain largely unexplored.

Here we utilize time-resolved Kerr rotation (TRKR) microscopy to image the spatial dependence of spin/valley dynamics in monolayer WSe_2/graphene heterostructure devices. Spatial maps demonstrate long-lived spin/valley lifetimes on the bare WSe_2 but reveal a quenching of spin-valley signal at the WSe_2/graphene interfaces. Time delay scans show these interface lifetimes to be quenched up to 3 orders of magnitude in comparison to bare WSe_2. Furthermore, photoluminescence mapping exhibits quenching at the interfaces while photoconductivity is enhanced in these regions, demonstrating efficient charge transfer from WSe_2 to graphene. Consequently, we attribute the ultrafast spin/valley quenching to the transfer of spin information by conducted charge carriers.

4:20pm **2D+EM+MI+NS-TuA7 Spatially Selective Enhancement of Photoluminescence in MoS by Exciton-Mediated Adsorption and Defect Passivation**, *Saujan V. Sivaram, A.T. Hanbicki, M.R. Rosenberger, G. Jernigan, H.-J. Chuang, K.M. McCreary, B.T. Jonker,* U.S. Naval Research Laboratory

Monolayers of transition metal dichalcogenides (TMDs) are promising components for flexible optoelectronic devices due to their direct band gap and atomically thin nature. The photoluminescence (PL) from these materials is often strongly suppressed by non-radiative recombination mediated by mid-gap defect states. Here, we demonstrate up to a 200-fold increase in PL intensity from monolayer MoS_2 synthesized by chemical vapor deposition (CVD) by controlled exposure to laser light in ambient. This spatially resolved passivation treatment is air and vacuum stable. Regions unexposed to laser light remain dark in fluorescence despite continuous impingement of ambient gas molecules. A wavelength dependent study confirms that PL brightening is concomitant with exciton generation in the MoS_2; laser light below the optical band gap fails to produce any enhancement in the PL. We highlight the photo-sensitive nature of the process by successfully brightening with a low power broadband white light source (< 10 nW). We decouple changes in absorption from defect passivation by examining the degree of circularly polarized PL. This measurement, which is independent of exciton generation, confirms that laser brightening reduces the rate of non-radiative recombination in the MoS_2. A series of gas exposure studies demonstrate a clear correlation between PL brightening and the presence of water. We propose that H_2O molecules passivate sulfur vacancies in the CVD-grown MoS_2, but require photo-generated excitons to overcome a large adsorption barrier. This work represents an important step in understanding the passivation of CVD-synthesized TMDs and demonstrates the interplay between adsorption and exciton generation.

4:40pm 2D+EM+MI+NS-TuA8 Strained Graphene in the Quantum Hall Regime: Valley Splitting and Extra Conducting Channels, *Daiara Faria,* Ohio University / Universidade do Estado do Rio de Janeiro; *C. León,* Brigham Young University; *L. Lima,* Universidade Rural do Rio de Janeiro, Brazil; *A. Latgé,* Universidade Federal Fluminense, Brazil; *N. Sandler,* Ohio University

The coupling between electronic and mechanical properties in 2D materials has become an important tool to control valleytronics. Graphene experiments have been reported with common deformations such as membrane bending that induces strain in the samples [1]. It has also been shown that strain affects charge distributions and graphene transport properties. Motivated by these responses, we have studied the effect of folds and wrinkles in graphene. New 'edge'-like states along the graphene folded region, that are valley polarized, were found and explored [2]. To take advantage of the existence of these new states, it would be desirable to separate their contribution from the continuum extended states that make graphene a semimetal.

Here we present a theoretical study of folds effects on a graphene membrane in the quantum Hall regime. We show that the addition of an external magnetic field allows the isolation of the valley polarized edge states in energy and in real space. Local density of state calculations in the deformation region predict the valley split peaks, as observed in recent experimental [3]. Using recursive Green's function method, we are able to reveal new extra conducting channels due to the "new edges" at the deformation region. These extra conducting channels could be detected in transport measurements.

A discussion is presented to bring attention on the role of the deformation parameters on the graphene quantum Hall regime and their relations with the magnetic lengths. With this in mind, we perform an analytic study based on the continuum (Dirac) description of electrons in graphene. In this model, the deformation is considered as a perturbation to the Landau Level states. The results show the existence of two different regimes, characterized by the ratio between the magnetic length and the deformation width ($\gamma = l_B/b$). For $\gamma<1$ the magnetic confinement allows the electrons to follow the strain potential profile. In this regime, the spatial separation between the polarized currents is larger. This could encourage the design of devices where contacts can efficiently detect these polarized currents.

[1] Y. Jiang et al., Nano Lett. 17, 2839 (2017).

[2] R. Carrillo-Bastos et al., PRB 94, 125422 (2016).

[3] S. Li, arXiv:1812.04344.

5:00pm 2D+EM+MI+NS-TuA9 Unraveling the Novel Quantum Phenomena in Two-dimensional Materials using Transport and Photoemission Spectroscopy, *Jyoti Katoch,* Carnegie Mellon University **INVITED**
The extreme surface sensitivity of two-dimensional (2D) materials provides an unprecedented opportunity to engineer the physical properties of these materials via changes to their surroundings, including substrate, adsorbates, defects, etc. In addition, 2D materials can be mechanically assembled layer-by-layer to form vertical or lateral heterostructures, making it possible to create new material properties merely by the choice of the constituting 2D layers and the relative twist angle between them. In this talk, I will discuss our recent transport [1] and photoemission [2, 3] results that shed light on the intricate relationship between controlled external perturbations, substrate, and electronic properties of 2D materials. I will show that the decoration of the 2D materials with adatoms, such as sub-lattice selective atomic hydrogenation of graphene and alkali metal doping of single layer WS_2 can be utilized to tailor electronic properties and induce novel quantum phenomena in 2D landscape.

[1] Katoch et. al., Physical Review Letters 121, 136801 (2018).

[2] Katoch et. al., Nature Physics 14, 355-359 (2018).

[3] Søren Ulstrup, et. al., arXiv:1904.06681 (2019).

5:40pm 2D+EM+MI+NS-TuA11 Electronic Properties and Charge Density Wave Transition in Single-layer VSe_2, *Kien Nguyen-Cong, P. Neto, M. Batzill, I.I. Oleynik,* University of South Florida
Single-layer VSe_2 has been recently attracted attention due to experimental observations of ferromagnetism and charge density wave (CDW) transition. There are controversies from both theory and experiment concerning ferromagnetism in both bulk and single layer VSe_2.In addition, CDW transition in VSe_2 is not well understood. In this work, structural, electronic, magnetic and CDW properties of this system are investigated using first-principle calculations. The calculated electronic structure is compared with

recent APPRES measurements and conclusions concerning its magnetic state are made. The calculated phonon spectra are used in investigation of CDW transition mechanism. Crystal structure of the CDW state is determined using the evolutionary crystal structure prediction combined with lattice dynamics.

6:00pm 2D+EM+MI+NS-TuA12 Tunable Band Gap and Thermal Conductivity Measurements of Monolayer $MoSe_2$ by S Incorporation, *Shyama Rath, V. Singh,* University of Delhi, India
Monolayer $MoSe_2$ was grown on insulating SiO2/Si substrates by chemical vapor deposition. Scanning electron microscopy and optical contrast images were used to determine the domain size, morphology, and the number of layers. The crystallinity, and thickness of the synthesized domains were determined by Raman spectroscopy. The band gap was determined from Photoluminescence (PL) spectroscopy. The PL emission was absent for more than 4 layers, and the peak position varied from 1.48 eV for 4 layers to 1.55 eV in the monolayer limit. Sulphur incorporation was done to obtain MoS_xSe_{2-x} so as to obtain a further tunability of the bandgap. The band gap changes from 1.55 eV for monlayer $MoSe_2$ to 1.64 eV for monolayer $MoS_{0.32}Se_{0.68}$. Further, larger area domains were achieved in the alloy as compared to binary. The thermal conductivity of the monolayer $MoSe_2$ and MoS_xSe_{2-x} were determined from temperature-dependant Raman spectroscopy.

Complex Oxides: Fundamental Properties and Applications Focus Topic
Room A220-221 - Session OX+EM+HC+MI+NS+SS+TF-TuA

Complex Oxides: Catalysis, Dielectric Properties and Memory Applications
Moderators: Alexander Demkov, University of Texas at Austin, Jeffry Kelber, University of North Texas

2:20pm OX+EM+HC+MI+NS+SS+TF-TuA1 Novel Multiferroic and Ferroelectric Ferrite Thin Films, *Peter A. Dowben, C. Binek, X. Xu,* University of Nebraska-Lincoln **INVITED**
Ferroelectricity and ferromagnetism are foundational to numerous technologies, yet the combination of ferroelectricity and ferromagnetism, namely multiferroicity, may be even more desirable. Multiferroic materials are believed to be a route to voltage controlled spintronic devices. Yet very few single phase materials are known to be ferroelectric and ferromagnetic at the same time, i.e. multiferroic. Even fewer materials are fewer materials are magneto-electric, that is to say materials with magneto-electric coupling, i.e. voltage control of magnetization, but without separate order parameters for magnetism (or antiferromagnetism) and ferroelectricity. This talk will review the electronic structure of the tri-rutile magneto-electric antiferromagnets, like Fe_2TeO_6, as well as rare earth ferrites like $ReFeO_3$ (Re = rare earth) stabilized in the hexagonal phase. Both types of materials are frequently antiferromagnetic, and, in principle, both can exhibit magneto-electric coupling. The surface termination affects the measured spin polarization of the surface and the interface with other materials. This will have a significant influence on the voltage control of magnetization. We have investigated the structural and electronic properties at the surface of these more unusual multiferroic materials using angle-resolved x-ray photoemission spectroscopy (ARXPS), complemented by x-ray diffraction (XRD), x-ray photoemission electron microscopy (X-PEEM), and X-ray circular dichroism. We find that the low local symmetry, especially at surfaces, will split the electronic states, via spin–orbit coupling. In some cases, the result is a net spin polarization at the surface, under electric field cooling. Because of the strongly preferential surface termination of these types of materials, the boundary polarization is roughness insensitive, in some cases making spintronic device applications plausible.

3:00pm OX+EM+HC+MI+NS+SS+TF-TuA3 Potential Applications and Challenges for Complex Oxides in Advanced Memory and Computing Applications, *Sebastian Engelmann, T. Ando, V. Narayanan,* IBM T.J. Watson Research Center **INVITED**
As the semiconductor industry continues to push for and develop higher performance computing systems, there is also a growing trend of redeveloping or optimizing fundamental computing approaches to be more energy efficient. The development of hardware for novel AI systems is no exception. New integration schemes, novel materials, multi-component materials or even nanoscale materials and the ability to integrate all of

these approaches together becomes the compounded challenge. Deposition and etch technologies that offer differentiating solutions to these issues therefore need to meet somewhat conflicting demands, such as low damage processing as well as high rate processing beside many other issues.

Novel thin films, thin film laminates and alloys promising unprecedented performance are very interesting candidates to enable such computing paradigm shifts. In particular the class of complex oxides is a very interesting area of research as they offer new phenomena such as ferroelectricity, ferromagnetism or high temperature conductivity. While new phenomena are being discovered, unraveling the fundamental physics behind these properties is a critical element for an industrial exploitation of these properties.

In addition, these new and complex materials are growing the need for the ultimate process solution: atomic layer precision processing. Atomic layer etching is a promising path to answer the processing demands of new devices at the Angstrom scale. Self-limiting reactions, discrete reaction and activation steps or extremely low ion energy plasmas are some of the pathways being pursued for precise material removal control and maintaining the original film performance. Depending on the nature of the material, the etch response may be either too much or not enough chemical modifications of the material. Resulting modifications of the films is an important variable to consider in the readiness of material systems. In particular synergy to deposition approaches such as atomic layer deposition has been proposed as a solution, but more work is needed.

4:20pm **OX+EM+HC+MI+NS+SS+TF-TuA7 Epitaxial Design of Complex Oxides for Catalysis and Electrocatalysis**, *Yingge Du,* Pacific Northwest National Laboratory **INVITED**
Predictive synthesis of highly active and cost-effective catalysts and electrocatalysts for energy conversion and storage is critical for leveraging intermittently available energy sources. Transition metal oxides with perovskite (ABO3) and perovskite-related structures (e.g., Brownmillerite and Ruddlesden-Popper) have been identified as robust catalysts with high oxygen reduction reaction (ORR) and/or oxygen evolution reaction (OER) activities that rival the performance of noble metals and their compounds. The study of perovskites as epitaxial thin films enables measurement of their intrinsic catalytic activity, deconvolved from the effects of surface roughness and polycrystalline defects (e.g., grain boundaries and edges between facets). In addition, epitaxial growth facilitates accurate control over the composition, crystallographic orientation, and strain in thin films.

In this talk, our recent efforts in the design of epitaxial complex oxides for catalysis and electrocatalysis will be highlighted. Using $LaNiO_3$, a bi-functional electrocatalyst, as an example, I will show how isovalent substitution, alliovalent substitution, and interfacial strain can be used to tune the structural, electronic, and optical properties of the resultant films, and how these observed changes correlate with their (electro)catalytic performance. The use of complex oxide thin films as support or anti-corrosion layers during catalytic reactions will also be discussed.

5:20pm **OX+EM+HC+MI+NS+SS+TF-TuA10 Vanadia/Tungsten Oxide on Anatase TiO2(101): a Model Catalyst Study by STM and XPS**, *Tao Xu, J.V. Lauritsen, K.C. Adamsen,* Aarhus University, Denmark*; S. Wendt,* iNANO, Aarhus University, Denmark
Nitrogen oxides (NOX) from flue gas are in concern as major sources of air pollution. Increasingly stricter NOX emission control policies (e.g. Euro VI) demand innovation and better performance of NOX reduction technology. The Selective Catalytic Reduction (SCR) of NOX by vanadia supported on anatase titania, with tungsten oxide (WO3) as promoter, has been widely used for this service and attracted much research attention. However, many aspects of the SCR catalysis process remain poorly understood at the atomic level. Particularly, the synergistic effect of tungsten oxide and vanadia remain elusive in literature, despite intensive RAMAN and infrared spectroscopy studies.

In this work, we use mineral a-TiO2 single crystals exposing the (101) facets as the model surface and deposit V2O5 and WO3 in our ultrahigh vacuum chamber (UHV) chamber by e-beam evaporation in oxygen. Combining Scanning Tunneling Microscope (STM) and X-ray photon-electron Spectroscopy (XPS), we systematically investigated the morphology and oxidation state changes of the model catalyst upon heating and reactant adsorption.

The STM results illustrate the distribution of V2O5 and WO3 on anatase TiO2(101) at the atomic level. It is found that both species are highly dispersed in the sub-monolayer region. For the deposition of surface oxide species, we explored different methods to achieve the highest oxidation state of vanadium (5+) and tungsten (6+). The thermal stability of the as-deposited V2O5 and WO3 are investigated by XPS and STM systematically. We found that when V2O5 and WO3 co-exist on the a- TiO2 surface the stability of V2O5 is improved. This work provides atomic level understanding on the V2O5/WO3/TiO2 SCR catalyst and new insights into the synergistic interactions between vanadia and tungsten oxide on the a-TiO2 surface.

5:40pm **OX+EM+HC+MI+NS+SS+TF-TuA11 Observation of Memory Effect and Fractal Surface in SrRuO₃ Epitaxial Thin Films**, *Ratnakar Palai,* University of Puerto Rico*; H. Huhtinen,* University of Turku, Finland
Integration of multifunctional oxide materials (ferroelectrics and multiferroics) into silicon technology is of great technological and scientific interests. The current interest in functional oxides is largely based on engineered epitaxial thin films because of their superior properties compared to the bulk and polycrystalline thin films and their technological applications in dynamic random access memories, magnetic recording, spintronics, and sensors. Most of these applications require bottom and top electrodes to exploit the electronic properties of the functional materials.

SrRuO3 (SRO) has been found to be very useful for electrodes and junctions in microelectronic devices because of its good electrical and thermal conductivities, better surface stability, and high resistance to chemical corrosion, which could minimize interface electrochemical reactions, charge injection in oxide, and other detrimental processes, thus improving retention, fatigue resistance, and imprint. It also has good work function to produce the required large Schottky barrier on most ferroelectric oxide capacitors.

The bulk SRO exhibits several useful properties, such as extraordinary Hall effect, strong magnetocrystalline anisotropy, itinerant ferromagnetism, and spin-glass behavior. Spin-glass materials are currently frontier field of research and the most complex kind of condensed state of matter encountered so far in solid-state physics. Despite of the enormous importance of spin-glass models in neural networks, our knowledge of the underlying mechanistic processes involved is extremely limited. Although memory effect has been reported in bulk SRO, to our knowledge, the behavior is not well understood and there was no such report in thin films.

In this work, we report on the observation of memory effect and strong magnetic anisotropy in extremely smooth 1–3 Å roughness epitaxial (110) and (010) SrRuO3 thin films. The observation of non-zero imaginary susceptibility and frequency dependent cusp at freezing temperatures confirms the spin-glass behavior, which agrees well with the dc magnetization measurement. The origin of memory effect can be attributed to the magnetic frustration and random interaction, which is affected by dynamics of cooling and will be discussed in details.

6:00pm **OX+EM+HC+MI+NS+SS+TF-TuA12** *In situ* **Auger Electron Spectroscopy of Complex Oxide Thin Film Surfaces Grown by Pulsed Laser Deposition***, Thomas Orvis, M. Surendran, Y. Liu, A. Cunniff, J. Ravichandran,* University of Southern California
Complex oxides can enhance the functionality of electronic and photonic devices by supplementing them with interesting properties such as ferroelectricity, superconductivity, and magnetoresistivity. Furthermore, low dimensionality in these materials can result in additional useful properties, inspiring the continued study of complex oxides in thin film form. However, the deposition of these materials is typically governed by notoriously complex growth mechanisms, revealing the need for *in situ* probes to observe and understand their precise nature. To this end, we report the *in situ* observation of chemical composition of complex oxide thin film surfaces with Auger electron microscopy during growth by pulsed laser deposition. Our implementation of real-time monitoring techniques for complex oxide thin films sheds an important light on the intricacies of the relationships between processing conditions and resulting composition.

2D Materials

Room A216 - Session 2D+AS+MI+NS-WeM

2D Materials Characterization by Scanning Probe Microscopy and Spectroscopy

Moderator: Adina Luican-Mayer, University of Ottawa, Canada

8:20am **2D+AS+MI+NS-WeM2 Silicene like Domains on IrSi$_3$ Crystallites**, **Nuri Oncel**, D. Cakir, F. Fatima, D. Nicholls, University of North Dakota
Recently, silicene, the graphene equivalent of silicon, has attracted a lot of attention due to its compatibility with Si-based electronics. So far, silicene has been epitaxially grown on various crystalline surfaces such as Ag(110), Ag(111), Ir(111), ZrB$_2$(0001) and Au(110) substrates. Here, we present a new method to grow silicene via high temperature surface reconstruction of hexagonal IrSi$_3$ nanocrystals. The h-IrSi$_3$ nanocrystals are formed by annealing thin Ir layers on Si(111) surface. A detailed analysis of the STM images shows the formation of silicene like domains on the surface of some of the IrSi$_3$ crystallites. We studied both morphology and electronic properties of these domains by using both scanning tunneling microscopy/spectroscopy and first-principles calculation methods.

8:40am **2D+AS+MI+NS-WeM3 Interfacial and Topological Superconductivity in 2D Layers Studied by Spin-Resolved Scanning Tunneling Spectroscopy**, **Roland Wiesendanger**, University of Hamburg, Germany **INVITED**
In this presentation, we will first focus on interfacial superconductivity in novel types of heterostructures. In particular, we will present a low-temperature SP-STS study of ultrathin FeTe1-xSex (x = 0, 0.5) films grown on prototypical Bi-based bulk topological insulators. We observe fully developed U-shaped superconducting gaps in FeTe0.5Se0.5 layers of one unit cell (UC) thickness with a transition temperature (Tc) of ~11 K, close to the one of the corresponding bulk system (Tc ~ 14.5 K) [1]. Surprisingly, we also find clear evidence for superconductivity up to Tc ~ 6 K for one UC thick FeTe layers grown on Bi2Te3 substrates [2], in contrast to the non-superconducting FeTe bulk compound which exhibits bicollinear antiferromagnetic (AFM) order in a wide temperature range up to 70 K. Even more surprisingly, detailed investigations of the atomic-scale spin-resolved local density of states by SP-STS reveal that superconductivity in one UC layers of FeTe grown on Bi2Te3 appears to spatially coexist with bi-collinear AFM order. By using 3D-vector-resolved SP-STM techniques [3] we find an unusual reorientation of the diagonal double-stripe spin structure at Fe1+yTe thin film surfaces [4]. Moreover, variable-temperature SP-STM studies [5] reveal an enhanced Néel temperature for AFM spin ordering of the ultrathin FeTe films grown on topological insulators [6]. These findings open novel perspectives for theoretical studies of competing orders in Fe-based superconductors as well as for experimental investigations of exotic phases in heterostructures of topological insulators and superconducting layers.

In a second part, we will address experimental and theoretical studies of monolayer topological superconductivity and chiral Majorana edge modes in model-type 2D magnetic Fe islands on elemental superconducting Re [7]. In particular, we demonstrate that interface engineering by an atomically thin oxide layer is crucial for driving the studied hybrid system into a topologically non-trivial state as confirmed by theoretical calculations of the topological invariant, the Chern number.

This work is supported by the EU via the ERC Advanced Grant No. 786020 "ADMIRE".

[1] A. Kamlapure et al., Phys. Rev. B 95, 104509 (2017).

[2] S. Manna et al., Nature Commun. 8, 14074 (2017).

[3] S. Meckler et al., Rev. Sci. Instrum. 80, 023708 (2009).

[4] T. Hänke et al., Nature Commun. 8, 13939 (2017).

[5] J. Warmuth et al., NPG Quantum Materials 3, 21 (2018).

[6] U. R. Singh et al., Phys. Rev. B 97, 144513 (2018).

[7] A. Palacio-Morales, E. Mascot, S. Cocklin, H. Kim, S. Rachel, D. K. Morr, and R. Wiesendanger, arXiv:1809.04503 (2018).

9:20am **2D+AS+MI+NS-WeM5 Geometric Imaging of Borophene Polymorphs**, **Xiaolong Liu**, Northwestern University; L. Wang, Rice University; S. Li, M. Rahn, Northwestern University; B. Yakobson, Rice University; M.C. Hersam, Northwestern University
Two-dimensional (2D) boron, known as borophene, has recently been experimentally realized[1,2] revealing a number of polymorphic structures. A common characteristic of those borophene polymorphs is the presence of hollow-hexagons (HH) in an otherwise triangular lattice. The vast number of possible HH lattices underlies the polymorphic nature of borophene. Superlattices of HHs could be further realized when borophene phases periodically intermix in the form of line defects[3]. While scanning tunneling microscopy (STM) of borophene with conventional metal probes has revealed key features of borophene, significant ambiguity of the exact atomic lattice structure exists due to the convolution of electronic and structural details. With CO-functionalized atomic force microscopy, we unambiguously resolve the HH lattice and reveal features corresponding to B-B covalent bonds[4] that are supported by numerical simulations. We further show that CO-functionalized STM is an equivalent but more accessible technique for HH imaging, allowing us to assemble a growth phase diagram of borophene involving non-rotated, 30°-rotated and randomly rotated borophene phases on Ag(111), confirming the $v_{1/5}$ and $v_{1/6}$ models as the unifying structures for all observed phases. In particular, a transition from rotationally commensurate to incommensurate phases is observed at high growth temperatures, corroborating the chemically discrete nature of borophene.

*Current affiliation of Xiaolong Liu: Kavli Postdoc Fellow, LASSP, Cornell University

1. A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, N. P. Guisinger, Science **350**, 1513–1516 (2015).

2. B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, K. Wu, Nat. Chem. **8**, 563–568 (2016).

3. X. Liu, Z. Zhang, L. Wang, B. I. Yakobson, and M. C. Hersam, Nat. Mater. **17**, 783–788 (2018).

4. X. Liu, L. Wang, S. Li, M. S. Rahn, B. I. Yakobson, and M. C. Hersam, Nat. Commun. **10**, 1642 (2019).

9:40am **2D+AS+MI+NS-WeM6 Atomic Manipulation of Defects in the Layered Semiconductor 2H-MoTe$_2$**, **Sara Mueller**, S. Deng, The Ohio State University; B. St. Laurent, University of New Hampshire; Y. Wang, W. Windl, The Ohio State University; S. Hollen, University of New Hampshire; J.A. Gupta, The Ohio State University
Here we present a charge control of native defects in the bulk transition metal dichalcogenide, MoTe$_2$ by scanning tunneling microscopy (STM). Bulk MoTe$_2$ was cleaved at room temperature in ultrahigh vacuum and imaged with a cut PtIr tip at 9K. Native defects in the MoTe$_2$ are present throughout the sample and image with complex structure. In topographic imaging, the long-range protrusion of a bright defect indicates the species is charged and we image the defects at different depths below the surface. They present with an ionization feature in tunneling spectroscopic mapping which indicates that the charge state of this defect can be manipulated by the band bending caused by the tip. Voltage pulses from the tip migrate the subsurface defects to the surface layer. The migrated defects present with the same spectroscopic signature as native surface defects. We also present DFT results that we use to clarify the identification of these native defects and energy barriers for migration between layers of 2H-MoTe$_2$.

11:00am **2D+AS+MI+NS-WeM10 Scanning Tunneling Microscopy and Spectroscopy of a Heterotriangulene-based 2D Polymer**, **Zachery Enderson**, H. Murali, R. Dasari, T.C. Parker, S.R. Marder, H. Li, Q. Dai, S. Thomas, J.-L. Brédas, P.N. First, Georgia Institute of Technology
Covalent Organic Frameworks (COFs) and similar materials synthesized from bottom-up procedures grant scientists a means to customize a 2D material's final properties from its initial precursors. The dimethylmethylene-bridged triphenylamine (DTPA) COF is an excellent example of the unique systems one can fabricate with these techniques[1]. The DTPA COF is initially synthesized on Au(111) or Ag(111) which facilitates crystalline growth through Ullman-type coupling. With an even number of electrons per unit cell, theory predicts a semiconducting electronic structure for the COF. Further heating in vacuum selectively cleaves the dimethyl groups but leaves the framework intact. This final COF resembles an ultra-flat covalent network of triangulene molecules with enticing proposed electronic properties, which depend on how the demethylated sites are terminated. In the case of hydrogen termination at these sites, calculations indicate that the "radical" COF on a metallic substrate will be a half-metal (fully spin-polarized density of states at the fermi energy)[2]. Using a low-temperature scanning tunneling microscope, the work outlined in this talk presents new information on the electronic structure of the DTPA COF in both its intact (methylated) and radical (demethylated) forms.

[1] Bieri, Marco, Stephan Blankenburg, Milan Kivala, Carlo A. Pignedoli, Pascal Ruffieux, Klaus Müllen, and Roman Fasel. "Surface-Supported 2D Heterotriangulene Polymers." *Chem. Commun.* 47, no. 37 (2011): 10239–41. https://doi.org/10.1039/C1CC12490K .

[2] Kan, Erjun, Wei Hu, Chuanyun Xiao, Ruifeng Lu, Kaiming Deng, Jinlong Yang, and Haibin Su. "Half-Metallicity in Organic Single Porous Sheets." *Journal of the American Chemical Society* 134, no. 13 (April 4, 2012): 5718–21. https://doi.org/10.1021/ja210822c .

11:20am 2D+AS+MI+NS-WeM11 Scanning Tunneling Microscopy Investigations of Molecules Adsrobed on Semiconducting Graphene Nanoribbons, *Sineth Premarathna, K.Z. Latt, S.-W. Hla,* Ohio University
Unlike graphene, semiconducting graphene nanoribbons poccess a band gap and they have the capability to electronic decouple the molecules from the supporting substrate. Here, we study the structural, electronic and vibrational properties of individual para-sexiphenyl molecules adsorbed on semiconducting graphene nanoribbons. The graphene nanoribbons here are grown on the surface of Au(111) using DBBA molecules as the initial building blocks. Para-sexiphenyl molecules adsorb on the graphene naribbons with their long molecular axis positioning parallel to the long axis of the graphene nanoribbons. As expected, the tunneling spectroscopy data reveal the HOMO-LUMO gap of the molecule on graphene nanoribbons much closer to their gas phase values. Moreover, teh vibration spectroscopy measurements of the molecules further provide a strong vibration mode associate with the C=C ring stretching of the molecules. This work provide single molecule level information on the electronic, vibronic and structural properties of the molecules adsorbed on vertically stacked heterostructures formed by graphene nanoribbons on Au(111) surface.

11:40am 2D+AS+MI+NS-WeM12 Molecular Flexure and Atom Trapping with Sexiphenyl Molecules by Scanning Tunneling Microscope Manipulation, *Y. Zhang, Shaoze Wang, K.-F. Braun, S.-W. Hla,* Ohio University
Molecular flexure, and molecule-metal contact of para-sexiphenyl molecules on a Ag(111) surface are investigated by using low temperature scanning tunneling microscopy, and molecular manipulations. Atom trapping with sexiphenyl molecules is realized by laterally manipulating the molecules onto individual silver atoms and up to three silver atoms have been trapped. We also demonstrate breaking of a silver dimer into individual silver atoms by atom trapping. STM manipulation experiments show that the molecule-metal complexes formed by the atom trapping are mechanically stable. Moreover, lateral manipulation of a single seziphenyl across a Ag(111) atomic step highlights how the molecule moves across step-edges; the molecule can easily conform across the step and it recovers original configuration after the manipulation.

12:00pm 2D+AS+MI+NS-WeM13 Localized Strain Effects in Spin-Polarized Density of States for 2D-MnGaN – a Room Temperature Ferromagnetic Monolayer, *Y. Ma,* Ohio University*; K. Meng,* The Ohio State University*; D. Hunt, MA. Barral, V. Ferrari,* CAC-CNEA, Argentina*; F.Y. Yang,* The Ohio State University*; Arthur Smith,* Ohio University
We recently demonstrated the first observation of a 2D *room-temperature-ferromagnetic monolayer* of MnGaN (2D-MnGaN) using spin-polarized scanning tunneling microscopy and spectroscopy. The sample is grown by molecular beam epitaxy on gallium nitride substrates. We resolved ferromagnetic domains using SP-STM, demonstrated magnetic hysteresis using small *out-of-plane* magnetic fields, observed magnetic rim states, and measured magnetic DOS profiles using tunneling spectroscopy which are in excellent agreement with the predicted spin-polarized & spin-split DOS peaks obtained from first-principles theory. This work was published online in December 2017 in *Nano Letters*.[1]

More recently, we are investigating the dependence of magnetization anisotropy on *in-plane* lattice strain. First of all, we have observed from the spectroscopy measurements that the position of the spin-polarized Mn DOS peak varies from spectrum to spectrum, ranging from -1.69 eV up to -1.22 eV (relative to E_Fermi). In order to investigate if these variations could be related to structural variations, we have also carried out theoretical calculations based on first principles for both isotropic and local anisotropic lattice strains. The isotropic strain case shows that the occupied-states Mn peak can indeed shift by many tenths of an eV if the 2D-MnGaN is strained *in-plane*; for example, E = -1.58 eV for the no-strain case, whereas E = -1.33 eV for tensile strain (+9.1%) and E = -2.22 eV for compressive strain (-6.0%). On the other hand, we find an opposite behavior in the local anisotropic calculation.

Using atomic resolution STM, we have also found that significant strain variations exist within the 2D-MnGaN. As compared to an ideally periodic hexagonal lattice, the 2D-MnGaN lattice displays local spacing variations, and the spacing distribution is highly non-Gaussian and may instead be characterized as *tri-modal* with the central peak matching closely the expected average for 2D-MnGaN of 5.52 Å, but with left and right peaks centered around 5.00 Å and 5.92 Å. Therefore, the Mn atoms, centered between Ga adatoms, are under highly varying strains, ranging from tensile to compressive.

By mapping the observed Mn peak energies onto theoretical energy-strain curves, we can then estimate the expected lattice parameters corresponding to particular energies and compare with the lattice spacing distribution. These results will be discussed as well as the additional discovery of a dependence of the spin anisotropy on the lattice strain.

[1] *Yingqiao Ma, Abhijit V. Chinchore, Arthur R. Smith, María Andrea Barral, and Valeria Ferrari, Nano Letters* **18**, 158 (2018).

2D Materials
Room A226 - Session 2D+EM+MI+MN+NS+QS-WeM

Novel 2D Materials
Moderator: Phil King, University of St Andrews

8:00am 2D+EM+MI+MN+NS+QS-WeM1 A Safari Through Thousands of Layered Materials Guided by Data Science Techniques, *Evan Reed, G. Cheon,* Stanford University **INVITED**
We have utilized data mining approaches to elucidate over 1000 2D materials and several hundred 3D materials consisting of van der Waals bonded 1D subcomponents, or molecular wires. We find that hundreds of these 2D materials have the potential to exhibit observable piezoelectric effects, representing a new class of piezoelectrics. A further class of layered materials consists of naturally occurring vertical hetero structures, i.e. . bulk crystals that consist of stacks of chemically dissimilar van der Waals bonded layers like a 2-D super lattice. We further combine this data set with physics-based machine learning to discover the chemical composition of an additional 1000 materials that are likely to exhibit layered and two-dimensional phases but have yet to be synthesized. This includes two materials our calculations indicate can exist in distinct structures with different band gaps, expanding the short list of two-dimensional phase change materials. We find our model performs five times better than practitioners in the field at identifying layered materials and is comparable or better than professional solid-state chemists. Finally, we find that semi-supervised learning can offer benefits for materials design where labels for some of the materials are unknown.

8:40am 2D+EM+MI+MN+NS+QS-WeM3 2D Ferroelectric Semiconductor α-In₂Se₃ for Non-Volatile Memory Applications, *M. Si, Peide Ye,* Purdue University
α-In$_2$Se$_3$ is a novel two-dimensional (2D) ferroelectric semiconductor. It has a bandgap of ~1.39 eV, room temperature ferroelectricity, the ability to maintain ferroelectricity down to a few atomic layers and the feasibility for large-area growth. Based on the ferroelectric and semiconducting nature of the material, a ferroelectric semiconductor field-effect transistor (FeS-FET) was proposed and experimentally demonstrated [1]. In the FeS-FET, a ferroelectric semiconductor is employed as the channel material while the gate insulator is the dielectric. The two non-volatile polarization states in FeS-FETs exist in the ferroelectric semiconductor channel. Therefore, a high quality amorphous gate insulator can be used instead of the common polycrystalline ferroelectric insulator for Fe-FETs. The fabricated FeS-FETs exhibit high performance with a large memory window, a high on/off ratio over 10^8, a maximum on-current of 862 µA/µm, low supply voltage with scaled gate insulator and the potential to exceed the existing Fe-FETs for non-volatile memory applications.

[1] M. Si, S. Gao, G. Qiu, J. Qin, Y. Duan, J. Jian, H. Wang, W. Wu, and P. D. Ye, "A Ferroelectric Semiconductor Field-Effect Transistor,", arXiv:1812.02933.

9:00am **2D+EM+MI+MN+NS+QS-WeM4 *Ab initio* Informed Theory of Axis-dependent Conduction Polarity in Goniopolar Materials**, *Yaxian Wang*, B. He, M.Q. Arguilla, N.D. Cultrara, M.R. Scudder, J.E. Goldberger, J.P. Heremans, W. Windl, The Ohio State University

NaSn$_2$As$_2$ has recently been synthesized and was found to be an exfoliatable van der Waals Zintl phase, opening new opportunities for electronic design on the few-atom-thick scale. Although the band structure may suggest a range of metal to semi-metal, it shows strong anisotropy especially in its "polarity", characterized by its dominant carrier type, which strongly affects its electronic and thermal properties. We used DFT calculations to investigate bandstructure and Fermi surface. In addition, we employed BoltzTraP code to calculate the transport behavior in in/cross-plane directions, predicting strongly anisotropic carrier transport and directionally dependent polarity –"goniopolarity" – in this layered material. It is confirmed by experimental thermopower measurements. We show from simulations on a model band structure the Fermi surface geometry origin in a single-band toy model, and we utilize the bandwidth concept from a tight-binding model to give an insight of real space orbital contributions and nature of the bonding states in this layered crystal. Based on that, additional candidate materials for goniopolarity can be proposed, and the design space for goniopolar materials in general will be defined.

9:20am **2D+EM+MI+MN+NS+QS-WeM5 In-Plane Mechanical Properties and Strain Engineering of 2D Hybrid Organic-Inorganic Perovskites**, *Qing Tu*, I. Spanopoulos, S. Hao, C. Wolverton, M. Kanatzidis, G. Shekhawat, V. Dravid, Northwestern University

Two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs) are new members of the 2D materials family with wide tunability, highly dynamic structural features and excellent physical properties. Mechanical strain is inevitable in 2D-HOIP-based applications due to materials processing, thermal expansion and substrate deformation. Understanding the mechanical properties and strain engineering of such functional materials are both fundamentally and practically important to achieve high performance and mechanically stable (flexible) devices. Here the in-plane mechanical properties and the impact of in-plane uniaxial tensile strain on the electronic properties of 2D lead iodide perovskites with a general formula (CH$_3$(CH$_2$)$_3$NH$_3$)$_2$(CH$_3$-NH$_3$)$_{n-1}$Pb$_n$I$_{3n+1}$ were reported for the first time. The in-plane Young's modulus and breaking strength of ultrathin 2D HOIP flakes were measured by AFM-based nanoindentation of suspended 2D HOIP membranes.[1] The in-plane Young's moduli of 2D HOIPs are smaller than that of conventional covalently bonded 2D materials like graphene and MoS$_2$ due to the much more deformable [PbI$_6$]$^{4-}$ octahedra structure. Both the Young's modulus and breaking strength first decrease and then plateau as the thickness of 2D HOIP flake increases from monolayer to 4 layers, which is attributed to interlayer slippage during deformation. Ultrathin 2D HOIPs exhibit outstanding breaking strength/Young's Modulus ratio compared to many other widely used engineering materials and polymeric flexible substrates, which renders them suitable for application into flexible electronic devices. Furthermore, the uniaxial tensile strain was found to increase the band gap of 2D HOIPs.[2] Such strain effect on the band gap of 2D HOIPs is fully reversible and depends on the structural unit of the materials. For2D HOIP with n = 5, the strain response of the band gap can be as high as 13.3 meV/%. First-principles simulations show that the strain response of the band gap arises from the rotation of the inorganic [PbI$_6$]$^{4-}$ octahedra and the consequential Pb-I bond stretching and increase of Pb-I-Pb angle. The observed band gap–strain relationship can be harnessed to map the local mechanical strain in 2D HOIP-based devices and allow 2D HOIPs for sensing applications.

References

[1]. Tu Q, Spanopoulos I, Yasaei P, Stoumpos CC, Kanatzidis MG, Shekhawat GS, et al. Stretching and Breaking of Ultrathin 2D Hybrid Organic–Inorganic Perovskites. ACS Nano. 2018;12(10):10347-54.

[2]. Tu Q, Spanopoulos I, Hao S, Wolverton C, Kanatzidis MG, Shekhawat GS, et al. Probing Strain-Induced Band Gap Modulation in 2D Hybrid Organic–Inorganic Perovskites. ACS Energy Letters. 2019;4(3):796-802.

9:40am **2D+EM+MI+MN+NS+QS-WeM6 Collective Electronic States of Epitaxial Monolayer 1T-NbSe$_2$**, *Zhuozhi Ge*, University of Wisconsin; H. Zhang, L. Liu, C. Yan, West Virginia University; M. Weinert, University of Wisconsin; L.L. Li, West Virginia University

At the single layer limit, transition metal dichalcogenides (TMDs) can adopt two different structural variants depending on the anionic environment around the metal ions: the anions are arranged in trigonal prismatic fashion in the 1H polymorph, whereas in 1T the arrangement is octahedral. While bulk 1T NbSe$_2$ doesn't exist in nature, here we show that single layer 1T

NbSe$_2$ polymorph can be grown by molecular beam epitaxy on epitaxial graphene/SiC(0001) substrates. A (Ö13xÖ13) Star-of-David charge density waves is observed by *in situ* scanning tunnelling microscopy, which persists above room temperature. A gap of 0.50 eV is further observed by tunnelling spectroscopy and angle resolved photoemission spectroscopy, indicating that this monolayer 1T phase of NbSe$_2$ is also a Mott insulator, similar to that of bulk 1T TaS$_2$. Our findings indicate that the presence of epitaxial constraints can generate structural configurations that are prohibited in fully-bonded TMD crystals. These findings and their implication on the collective electronic states of single layer 1T-NbSe$_2$ will be discussed at the meeting.

11:00am **2D+EM+MI+MN+NS+QS-WeM10 Magnetic Interfaces of MnSe2 Monolayer**, *Tomas Rojas*, S. Ulloa, Ohio University

Until recently, 2D magnetism was thought to occur together with defects or doping on different substrates. This situation changed drastically, as intrinsic Cr-based ferromagnetic monolayer materials were discovered, namely CrI3 and Cr2Ge2Te6. A different material, MnSe2, was predicted as stable ferromagnetic monolayer by first-principles calculations, and it has been successfully grown on several substrates. In this study, the authors confirm the intrinsic ferromagnetism of the monolayer, while for thicker samples they report an interface of the MnSe2 monolayer with bulk α-MnSe(111). This phase of the material is non-magnetic, and yet the observed magnetic moments are of up to twice the value of those in the monolayer alone. In this work, we present a detailed analysis of the interactions at this interface between the two phases, using the Heyd-Scuseria-Ernzerhof hybrid functional. We have studied the effects on the electronic and magnetic structure of both phases of the material, and the dependence on the sample thickness. We study the role that strain plays at the interface, and how it affects the magnetic moments of the structure.

11:40am **2D+EM+MI+MN+NS+QS-WeM12 Rotationally Controlled van der Waals Heterostructures of 2D Materials**, *Emanuel Tutuc*, K. Kim, G.W. Burg, H.C.P. Movva, The University of Texas at Austin **INVITED**

Heterostructures of atomic layers such as graphene, hexagonal boron-nitride, and transition metal dichalcogenides (TMDs) can serve as testbed for novel quantum phenomena in two-dimensions, and potential device applications. A key ingredient that can add a new dimension to the atomic layer heterostructures palette is the rotational control, and alignment of different two-dimensional (2D) layers. We review here an experimental technique that enables rotationally controlled heterostructures with accurate alignment of the individual layer crystal axes [1]. We illustrate the applicability of this technique to the rotationally aligned double layers of graphene [2], or TMDs [3] separated by a tunnel barrier which display resonant, energy- and momentum-conserving tunneling in vertical transport, consistent with theoretical expectations. When two 2D layers are overlaid with a relative twist, the resulting heterostructure shows a new type of periodicity associated with the moiré superlattice, which are only beginning to be systematically investigated as platform for strongly correlated electron physics. We discuss the electron transport in tunable moiré patterns realized in twisted bilayer [4], and double bilayer graphene heterostructures.

[1] K. Kim *et al., Nano Lett.* **16**, 1989 (2016);

[2] G. W. Burg *et al., Nano Lett.* **17**, 3919 (2017); G. W. Burg *et al., Phys. Rev. Lett.* **120**, 177702 (2018).

[3] K. Kim *et al., Nano Lett.* **18**, 5967 (2018).

[4] K. Kim *et al., Proc. Natl. Acad. Sci. USA* **114**, 3364 (2017).

Electronic Materials and Photonics Division
Room A214 - Session EM+2D+AS+MI+MN+NS+TF-WeM

Nanostructures and Nanocharacterization of Electronic and Photonic Devices

Moderators: Sang M. Han, University of New Mexico, Jason Kawasaki, University of Wisconsin - Madison

8:00am **EM+2D+AS+MI+MN+NS+TF-WeM1 Photonic Thermal Conduction in Semiconductor Nanowires**, *E.J. Tervo, M.E. Gustafson, Z.M. Zhang, B.A. Cola, Michael A. Filler,* Georgia Institute of Technology

We present a practical material system—chains of infrared plasmonic resonators situated along the length of semiconductor nanowires—where near-field electromagnetic coupling between neighboring resonators enables photonic thermal transport comparable to the electronic and phononic contributions. We model the thermal conductivity of Si and InAs nanowires as a function of nanowire diameter, resonator length, aspect ratio, and separation distance by combining discrete dipolar approximation calculations, to determine the relevant dispersion relations, with thermal kinetic theory. We show that photonic thermal conductivities exceeding 1 W m^{-1} K^{-1} are possible for 10 nm diameter Si and InAs nanowires containing repeated resonators at 500 K, more than an order of magnitude higher than existing materials systems and on par with that possible with phonons and electrons. These results highlight the potential for photons in properly engineered solids to carry significant quantities of heat and suggest new ways to dynamic control thermal conductivity.

8:20am **EM+2D+AS+MI+MN+NS+TF-WeM2 Electric Field-Induced Defect Migration and Dielectric Breakdown in ZnO Nanowires**, *Hantian Gao, M. Haseman,* Department of Physics, The Ohio State University; *H. von Wenckstern, M. Grundmann,* Universität Leipzig, Felix-Bloch-Institut für Festkörperphysik; *L.J. Brillson,* The Ohio State University

Nanowires of the II-VI compound semiconductor ZnO have generated considerable interest for next generation opto- and microelectronics . Central to nanowire electronics is understanding and controlling native point defects, which can move[1] and lead to dielectric breakdown under applied electric fields. We used nanoscale lateral and depth-resolved cathodoluminescence spectroscopy (DRCLS) with hyperspectral imaging (HSI) in a scanning electron microscope (SEM) to observe defect migration and redistribution directly under applied electric fields and after dielectric breakdown. HSI maps represent lateral intensity distributions of specific features acquired pixel by pixel across SEM-scanned areas and normalized to near band edge (NBE) emissions. A pulsed layer deposited (PLD) ZnO microwire (3 μm diameter) exhibited homogeneous distributions of common luminescence features at 2.0 eV (V$_{Zn}$ cluster) and 2.35 eV (Cu$_{Zn}$) as well as 2.7 and 2.9 eV (V$_{Zn}$) peaks near the wire surface. With increasing electrical bias up to 3×10^5 V/cm between two Pt contacts, these defects systematically redistribute, even at room temperature, moving toward and under one of the contacts, draining the "bulk" nanowire, especially its near-surface region. Since ionized V$_{Zn}$-related and Cu$_{Zn}$ antisite defects are acceptors, their removal reduces the compensation of electron density in the typically n-type ZnO and thus its resistivity.

Besides HSI lateral maps, DRCLS vs. incident beam energy yields depth profiles radially of defects at specific locations along the nanowire. These exhibit high near-surface and wire core densities that biasing reduces. Current voltage measurements with increasing field gradients show a gradual resistivity decrease until an abrupt dielectric breakdown of the microwire at 300 kV/cm (150 V/5 μm). The acceptor removal between the contacts and their accumulation under one of the contacts can both contribute to this breakdown due to the decrease in resistivity and higher current conduction between the contacts and possible defect-assisted tunneling[2] across the increased defect density under the contact, respectively. These electric field-induced defect movements may be of more general significance in understanding dielectric breakdown mechanism not only in ZnO nanostructures but also bulk semiconductors in general.

1. G. M. Foster, et al., Appl. Phys. Lett. **111**, 101604 (2017).

2. J.W.Cox, et al., Nano Lett, **18**, 6974 (2018).

8:40am **EM+2D+AS+MI+MN+NS+TF-WeM3 Characterization of SiGe/Si Multilayer FIN Structures using X-Ray Diffraction Reciprocal Space Maps**, *Roopa Gowda, M. Korde,* SUNY Polytechnic Institute; *M. Wormington,* Jordan Valley Semiconductors Inc.; *A.C. Diebold, V. Mukundan,* SUNY Polytechnic Institute

Nanowire and Nanosheet FET's are potential replacements for FinFET's, mainly beyond sub-10nm CMOS technology nodes, as gate-all-around (GAA) FET device architecture provides improved electrostatics in higher on current (*I* on) and better subthreshold swing. As GAA is one of the best promising device for logic applications for future technology nodes, there is an increased need of characterization technique for such multilayer Si$_{1-x}$Ge$_x$/ Si complex structures. We studied Si$_{1-x}$Ge$_x$/Si/Si$_{1-x}$Gex/Si/Si$_{1-x}$Ge$_x$/Simultilayer FIN structures using X-Ray Diffraction Reciprocal Space Maps (RSM). RSM is one of the most popular technique to study epitaxial thin-films nanostructures due to straightforward analysis of the data. We found RSM simulations showing sensitivity of nanosheet fin structures dimensions such as pitch-walk (PW), Nanosheet thickness (NST), composition and shape. RSM's provide better means to interpret more complex diffraction measurements than real space constructions. RSMs of Si$_{1-x}$Ge$_x$/Si multilayer structure has been simulated using Bruker JV-RADS v6.5.50/HRXRD software. 1D line profiles extracted from RSMs was also used for the analysis of nanostructures dimensions. We obtained multilayer structure dimensions from the published information. We studied the influence of nanostructure parameters PW, NST, Composition and shape on RSMs. Imperfect periodic structures impact the intensity modulation of the grating rods (GRs). We observed that satellite peaks intensity reduces and harmonics peaks intensity enhances as PW increases. Rate of intensity change in higher order peaks is much faster than the lower harmonic peaks. We observed that the spacing between adjacent interference fringes in RSMs is related to the thickness of the layers. The period of fringes is inversely proportional to the thickness of the layer, hence total FIN height can be determined. 1D line profiles along Q$_z$ shows decreased angular width and increase in intensity of the layer peak and interference fringes as NST increases. Symmetric 004 longitudinal RSMs and their line profiles clearly show layer peak shift from substrate peak as composition increases due to increase of SiGe lattice spacing along the growth direction. Cross-shaped GR pattern in RSMs is observed which is due to trapezoidal surface grating caused by SWA. Line profiles indicate that fin shapes influence the modulation of the GRs as a function of Q$_x$. We demonstrate the characterization of complex Si$_{1-x}$Ge$_x$/ Si multilayers using RSMs and their line profiles which are relevant for lateral nanowire and nanosheet FETs. Above findings from RSM simulations clearly indicate the influence of variations in structural dimensions.

9:00am **EM+2D+AS+MI+MN+NS+TF-WeM4 Nanoscale Depth and Lithiation Dependence of V$_2$O$_5$ Band Structure by Cathodoluminescence Spectroscopy**, *Mitchell Walker, N. Pronin,* The Ohio State University; *A. Jarry, J. Ballard, G.W. Rubloff,* University of Maryland, College Park; *L.J. Brillson,* The Ohio State University

Vanadium pentoxide (V$_2$O$_5$) has attracted considerable interest for its potential use as a cathode for solid state lithium ion batteries. While researchers have studied the V$_2$O$_5$ lithiation charge/discharge cycle for over two decades, we are only now able to measure directly its electronic band structure from the surface to the thin film bulk and its changes with Li intercalation on a near-nanometer scale. We used depth-resolved cathodoluminescence spectroscopy (DRCLS) to monitor the changes in electronic structure from the free surface to the thin film bulk several hundred nm below. DRCLS measures optical transitions at 1.8-2, 3.1-3.2, 3.6-3.7, 4.0-4.1, and 4.6-4.7 eV between multiple conduction bands to the pristine (α) V$_2$O$_5$ valence band maximum in excellent agreement with V$_{3d}t_{2g}$ conduction band densities of states (DOS) predicted by density functional theory (DFT).[1] Triplet conduction band states at 1.8, 1.9, and 2 eV correspond to predicted V 3d$_{xy}$–O$_c$ 2p$_x$/2p$_y$ hybridized states resulting from strong deviations of the unit cell VO$_6$ octahedra from cubic coordination correspond to optical absorption edges along the 3 crystallographic axes. With excitation depth increasing from < 10 to 125 nm calibrated by Monte Carlo simulations, the relative amplitudes and energies of these states change, signifying gradual changes in octahedral distortion. The band structure changes significantly with Li intercalation into Li$_x$V$_2$O$_5$ for x = 0, 1, and 2. Lithiation gradually removes the hybridized band and introduces a 2.4-2.7 eV V$_{3d}$ t$_{2g}$ band extending 50 nm (x=1) or 25 nm (x=2) into the surface. Higher (4.0 and 4.4 eV) features possibly related to a secondary phase dominate the spectra deep inside all V$_2$O$_5$ films near the battery electrode. Delithiation reintroduces the 1.8-2 eV split-off band although significantly narrowed by octahedral distortions. Overall, DRCLS shows that

the lithiation cycle alters the V_2O_5 band structure on a scale of 10-100's of nm with lithiation. The direct measure of V_2O_5's electronic band structure as a function of lithiation level provided by DRCLS can help guide future battery engineering work as more efficient lithium ion batteries are developed. In particular, these unique electrode measurements may reveal in what ways lithiation changes V_2O_5 irreversibly, as well as reveal methods to extend solid state battery life. MW and LJB acknowledge support from NSF grant DMR-18-00130. AJ and GR acknowledge Nanostructures for Electrical Energy Storage (NEES), a Department of Energy Office of Science Frontier Research Center.

1. V. Eyert and K.-H. Höck, "Electronic structure of V_2O_5: Role of octahedral deformation," Phys. Rev. B 57, 12727 (1998).

11:00am **EM+2D+AS+MI+MN+NS+TF-WeM10 Hot Electron Emission from Waveguide Integrated Graphene**, *Ragib Ahsan, F.R. Rezaeifar, H.U. Chae, R. Kapadia,* University of Southern California
From free electron laser sources to electronic structure measurements, electron emission devices play an important role in a wide range of areas. Photoemission is one of the basic processes exploited in modern electron emission devices. However, higher-order processes like multiphoton absorption or optical field induced emission are necessary for efficient photoemission from high workfunction metallic emitters. Our work demonstrates a graphene emitter integrated on a waveguide that can evanescently couple with the photons delivered from a CW laser (405 nm) and registers photoemission at a peak power that is orders of magnitude lower than previously published results based on multiphoton and optical field induced emission processes. Coupling FDTD analysis of the waveguide to a rigorous quantum mechanical study of the scattering mechanisms and the tunneling processes in graphene, we have been able to model the emission current from the graphene emitter with good agreement to the experimental data. Our investigation reveals that the photoexcited electrons can go through three mutually competitive processes: (i) electron-electron scattering (ii) electron-phonon scattering and (iii) directly emission into the vacuum. Absorption of a photon causes a reduction in the tunnel barrier seen by the electron and the emission rate increases exponentially. Integration of graphene to the waveguide enables evanescent coupling between electrons and the photons causing almost 100% absorption of the photons. Our integrated photonics approach demonstrates an emission efficiency that is three orders of magnitude greater than free space excitation. These results suggest that integrating photonic elements with low dimensional materials such as 2D materials, nanoparticles, quantum dots, etc. can provide a new domain of efficient electron emission devices and integrated photonics.

11:20am **EM+2D+AS+MI+MN+NS+TF-WeM11 Imaging Candidate Nanoelectronic Materials with Photoemission Electron Microscopy (PEEM)**, *Sujitra Pookpanratana, S.W. Robey,* National Institute of Standards and Technology (NIST)*; T. Ohta,* Sandia National Laboratories
The drive to produce smaller and lower power electronic components for computing is pushing the semiconductor industry to consider novel nanoscale device structures, not based solely on crystalline silicon. Continued innovation and progress towards novel nanoelectronic materials and devices in turn requires metrologies sensitive to electronic properties at these length scales. Tip-based imaging techniques provide electronic contrast with sub-nanometer resolution, however it is a local, scanning-based technique. Photoemission (or photoelectron spectroscopy) is the dominant technique to provide detailed electronic band structure information- level energies, dispersion, polarization dependence, etc. – but typically requires materials with millimeter, or larger, length scales. Photoemission electron microscopy (PEEM) can be employed to allow access to this vital information, providing full-field imaging capabilities sensitive to a variety of electronic contrast mechanisms at 10's of nanometers length scales. Here, we will present our results on imaging the impact of molecular dopants on multilayer tungsten disulfide (WS_2) employing the PEEM at the Center for Integrated Nanotechnologies within Sandia National Laboratories. We will also discuss the commissioning of a recently installed PEEM to perform complementary measurements at NIST-Gaithersburg.

Technological commercialization of transition metal dichalcogenides (TMDs) in nanoelectronics devices requires control of their electronic properties, such as charge carrier type and density, for specific device functionality. Conventional techniques for doping are problematic for atomically thin 2D materials. The sensitivity of mono- to few-layer (TMDs) to their local environment and interfaces can be employed *via* surface doping of molecules on TMDs to provide a promising route toward controllable doping. Investigations of surface doping for one to few layer WS_2 were performed using mechanically exfoliated WS_2 on a SiO_2/Si substrate that was then exposed to tris(4-bromophenyl)ammoniumyl hexachloroantimonate, a p-dopant molecule. PEEM was performed before and after p-dopant exposure. After doping, we find that the contrast of the surface WS_2 physical features change and valence band edge shifts about 0.8 eV away from the Fermi energy, consistent with p-doping. We will discuss the effects of molecular doping in terms of homogeneity and surface features across multiple WS_2 flakes. Lastly, we will discuss commissioning of a new PEEM instrument installed at NIST in 2019, using results of graphene to demonstrate imaging capability and energy resolution of this instrument.

11:40am **EM+2D+AS+MI+MN+NS+TF-WeM12 Comparison of Features for Au and Ir Adsorbed on the Ge (110) Surface**, *Shirley Chiang,* University of California, Davis*; R.K. Xie, H.Z. Xing,* Donghua University, China*; T.S. Rahman,* University of Central Florida*; C.Y. Fong,* University of California, Davis
Two ad-atoms of Au and Ir adsorbed, respectively, on the Ge(110) surface are studied by a first-principles algorithm based on density functional theory. The surface is modeled by a slab consisting of 108 Ge atoms with a 10 Å vacuum region. Hydrogen atoms are used to saturate the dangling orbitals at the other side of the vacuum region. Two cases of Au adsorption and one case of Ir are reported. The case of Ir has a large binding energy because of its small atomic size compared with the Ge atom, and the partially filled d-states. The total energy for each case is given, as are the energies for removing one ad-atom at a time and also both ad-atoms. The binding energy of each case is obtained by simply taking the energy difference between these configurations; this method is more realistic because the experimental data measured by LEEM and STM indicate that the collective motions of the ad-atoms do not allow the surface to relax to its equilibrium state.[1] For a large separation in the case of two Au atoms, there is a smaller binding energy than for one ad-atom. This can relate to the fact that the collective motions seen experimentally do not happen at a full monolayer coverage of ad-atoms.[1] Additional comparisons will be made to an atomic model for Ir/Ge(111) from STM measurements.[2]

[1] B. H. Stenger et al., Ultramicroscopy, 183, 72 (2017).

[2] M. van Zijll et al., Surf. Sci. 666, 90, (2017).

Support from NSF DMR-1710748 (SC, CYF); NSF DMR-1710306 (TSR); National Natural Science Foundation of China Grants 61376102, 11174048 and computational support from Shanghai Supercomputer Center (RKX, HZX).

12:00pm **EM+2D+AS+MI+MN+NS+TF-WeM13 Reference Materials for Localization Microscopy**, *C.R. Copeland, R.G. Dixson, L.C.C. Elliott, B.R. Ilic,* National Institute for Science and Technology (NIST)*; D. Kozak, K.-T. Liao,* FDA, National Institute for Science and Technology (NIST)*; J.A. Liddle,* NIST Center for Nanoscale Science and Technology*; A.C. Madison,* National Institute for Science and Technology (NIST)*; J.-H. Myung,* FDA*; A. Pintar, Samuel Stavis,* National Institute for Science and Technology (NIST)
As the diffraction limit fades away into the history of optical microscopy, new challenges are emerging in super-resolution measurements of diverse systems ranging from catalysts to therapeutics. In particular, due to common limitations of reference materials and microscope calibrations, many localization measurements are precise but not accurate. This can result in gross overconfidence in measurement results with statistical uncertainties that are apparently impressive but potentially meaningless, due to the unknown presence of systematic errors that are orders of magnitude larger. To solve this fundamental problem in measurement science, we are optimizing and applying nanofabrication processes to develop reference materials for localization microscopy, and demonstrating their use in quantitative methods of microscope calibration.

Our program consists of two complementary approaches. In the first, involving applied metrology, we are developing reference materials such as aperture arrays that can serve as standalone artifacts for widespread deployment. This approach will require the application of critical-dimension metrology to establish the traceability of master artifacts, and their use to calibrate a super-resolution microscope for high-throughput characterization of economical batches of reference materials. In the second approach, involving fundamental research, we are demonstrating the application of reference materials and calibration methods in our own experimental measurements. Most interestingly, achieving vertical integration of our two approaches and the unique capabilities that result, we are building reference materials into measurement devices for in situ calibration of localization measurements for nanoparticle characterization.

.

Magnetic Interfaces and Nanostructures Division
Room A210 - Session MI+2D-WeM

Emerging Multifunctional Magnetic Materials I and Magnetocaloric Materials

Moderator: Greg Szulczewski, University of Alabama

8:00am MI+2D-WeM1 Spin-dependent Electron Reflection at Materials with Strong Spin-orbit Interaction, *Markus Donath, C. Angrick, A. Reimann, C. Datzer, A. Blob,* Muenster University, Germany; *J. Braun,* LMU München,, Germany; *H. Ebert,* LMU München, Germany

The reflection of electrons at surfaces becomes spin dependent due to exchange interaction in the case of ferromagnets or due to spin-orbit interaction in the case of heavy elements. It can be used for spin-polarization analysis, e.g., in angle-resolved photoelectron spectroscopy in a single-channel mode or in multi-channel-mode detectors by using the scattering target as a spin-polarizing mirror. In addition, the understanding of the spin-dependent scattering properties provides information about the surface barrier. We present a combined experimental and theoretical study of the spin-dependent electron reflection at surfaces with strong spin-orbit interaction. We performed spin-dependent very-low-energy electron diffraction (VLEED) experiments on Au(111), Bi_2Se_3, and W(110) over a wide range of energies and angles of incidence. We derived maps for the reflectivity, the Sherman function, and the figure of merit and compare them with *ab-initio* calculations. In addition, we discuss possible working points for the use as scattering targets in spin-polarization analyzers.

8:20am MI+2D-WeM2 Competitive and Cooperative Electronic States in $Ba(Fe_{1-x}T_x)_2As_2$, *Q. Zou, M. Fu, Z. Wu, L. Li, A.-P. Li, D.S. Parker, A. Safat, Zheng Gai,* Oak Ridge National Laboratory

The electronic structure inhomogeneity in Ni, Co and Ni doped $BaFe_2As_2$ 122 single crystals are compared using scanning tunneling microscopy/spectroscopy (STM/S) at atomic level within the pure superconducting (SC) dome, coexisting of SC and antiferromagnetic (AFM) phase, and non-SC phase regions. K-means clustering statistic method is utilized to categorize the various nanometer-size inhomogeneous electronic states described here as 'in-gap', 'L-shape' and 'S-shape' states immersed into the SC matrix for Ni-and Co-doped 122, and L-shape and S-shape states into metallic matrix for Cr-doped 122. Although the relative percentages of in-gap, L-shape and S-shape states various in three samples, the total volume fraction of the three electronic states is quite similar, coincident with the electron ($Ni_{0.04}$ and $Co_{0.08}$) and hole ($Cr_{0.04}$) numbers doped into the 122 compound. By combining the volume fractions of the three states, local density of the states (LDOS), field dependent behavior and global properties in these three sets of samples, the in-gap state in SC crystals is confirmed as magnetic impurity state from Co or Ni dopants, the L-shape state is identified as the spin density wave (SDW) which competes with the SC phase, and the S-shape state is found to be another form of magnetic order which constructively cooperates with the SC phase rather than competing with it. The comparison of the vortex structures indicates that those inhomogeneous electronic states serve as pinning centers for stabilizing the hexagonal vortex lattice.

8:40am MI+2D-WeM3 Microscopic Origin of High Temperature Magnetism in Multiferroic Superlattices $(LuFeO_3)_m/(LuFe_2O_4)_1$, *Janice Musfeldt, S. Fan, K.A. Smith,* University of Tennessee Knoxville; *H. Das, A.F. Rebola,* Cornell University; *B.S. Holinsworth,* University of Tennessee Knoxville; *J.A. Mundy,* University of California at Berkeley; *C. Brooks, M. Holtz,* Cornell University; *R. Ramesh,* University of California at Berkeley; *D.A. Muller, D.G. Schlom, C.J. Fennie,* Cornell University; *S.A. McGill,* National High Magnetic Field Laboratory **INVITED**

Multiferroics are fascinating materials in which ferroelectric and magnetic orders coexist and spatial inversion and time-reversal symmetries are simultaneously broken. Outstanding challenges that currently prevent widespread application in memory and logic devices as well as neuromorphic computing include requirements for (i) a large coupling coefficient and (ii) room temperature operation. The development of a homologous series of superlattices with formula $(LuFeO_3)_m:(LuFe_2O_4)_n$ offers a path forward, although questions still exist about the microscopic origin of the high-temperature magnetism and the nature of the charge ordering pattern. In order to resolve these issues and provide additional insight into how external stimuli like magnetic fields can control behavior, we combined optical spectroscopy, magnetic circular dichroism, and first

principles calculations to reveal the response of the $(LuFeO_3)_m:(LuFe_2O_4)_n$ superlattice. Each of the unique iron centers has excitations at slightly different energies, so by analyzing features in the dichroic rotation - which are proportional to net magnetization - and the character of the optical hysteresis loops at these energies, we reveal the magnetic field - temperature (H - T) behavior and how spin in the $LuFe_2O_4$ layer is the most significant contributor to the overall magnetic response. We also find that trends in the coercive field can be interpreted in terms of how the exchange strength depends upon the Fe site. The techniques developed here open the door to the microscopic analysis of materials with multiple metal centers and strong charge, spin, orbital, and lattice entanglement.

9:20am MI+2D-WeM5 Hidden Local Spin-polarized Electronic States investigated by Spin- and Angle-resolved Photoelectron Spectroscopy, *Taichi Okuda,* Hiroshima University, Japan **INVITED**

Spin-polarized electronic states caused by spin-orbit interaction (SOI) have been attracted much attention recently because of the potential application for next-generation spintronic devices. In order to realize spintronic devices for various applications, it is necessary to search various kinds of new materials and systems possessing spin-polarized states. Although it was believed that the breaking of structural inversion symmetry is necessary to emerge the spin-polarized electronic states by SOI, the possibility of spin-polarized states by the inversion symmetry breaking at the local structure of crystals has been suggested recently[1]. Since the spin-polarization of the local structure of the other side of the crystal is opposite to maintain the zero net spin-polarization of materials, it is difficult to observe the local spin-polarization by macroscopic measurement and the spin-polarized states are, so to speak, hidden states.

Spin- and angle-resolved photoelectron spectroscopy(spin-ARPES) is one of the most powerful tools to investigate the spin-polarized electronic states caused by SOI since it can measure directly the *k*-dependent spin-polarization of electrons in the crystal (= spin-resolved band structure). Recent realization of high-efficiency, high-resolution and three-dimensional vector analysis in spin-ARPES measurement and the characteristic of the moderate proving depth of photoemission process enabled to investigate such hidden spin-polarized states. In this talk, some examples of the observation of the hidden spin-polarized states of layered materials (MoS_2, $PtSe_2$, and $LaOBiSe_2$, etc.)[2-4] will be presented. The finding of new materials possessing hidden spin-polarized states largely expands the variety of spin-polarized materials and will contribute to the future application for the spintronic devices.

[1] X. Zhang, Q. Liu, J.-W. Luo, A. J. Freeman, and A. Zunger, Nat. Phys. **10**, 387 (2014).

[2] R. Suzuki, M. Sakano, Y. J. Zhang, R. Akashi, D. Morikawa, A. Harasawa, K. Yaji, K. Kuroda, K. Miyamoto, T. Okuda, K. Ishizaka, R. Arita, and Y. Iwasa, Nat. Nanotechnol. **9**, 611 (2014).

[3] W. Yao, E. Wang, H. Huang, K. Deng, M. Yan, K. Zhang, T. Okuda, L. Li, Y. Wang, H. Gao, C. Liu, W. Duan, and S. Zhou, Nat. Commun. **8**, 14216 (2017).

[4] S.-L. Wu, K. Sumida, K. Miyamoto, K. Taguchi, T. Yoshikawa, A. Kimura, Y. Ueda, M. Arita, M. Nagao, S. Watauchi, I. Tanaka, and T. Okuda, Nat. Commun. **8**, 1919 (2017).

11:00am MI+2D-WeM10 Compositional Tuning of Magnetic Exchange Interactions and Interpretation of the Pressure Dependence of the Magnetic Curie Temperature in High Entropy Alloys., *Michael Mchenry,* Carnegie Mellon University **INVITED**

Magnetocaloric effect (MCE) materials are of interest in a more efficient technology than conventional gas compression refrigeration.MCE cooling is environmentally friendly since ozone depleting refrigerants are not used. Critical rare earths metals (REs) and compounds have large MCE response and working temperatures near room temperature. However, their scarcity, high price and corrosion limit their use. Recently, transition metal based high entropy alloys (HEAs) are studied for MCE applications due to convenient tunability of Curie temperatures,use of inexpensive components and tuning of the breadth of the magnetic phase transformation by distributing pair-wise magnetic exchange interations on a single fcc crystalline lattice. I will present our understanding of Curie temperature, T_c, engineering in metals with direct exchange interactions as rooted in the famous Bethe-Slater curve semi-empirically derived from considerations of the chemical bond and the constraints of the Pauli exclusion principle.

The Bethe-Slater curve predicts the dependence of the magnetic exchange interactions on D/d where D is the transition metal interatomic spacing and d is the spatial extend of the magnetic d-orbitals. The Bethe-Slater

curveguides alloy design to optimize T_c's through distribution of exchange interactions in MCE HEAs. I will present results for the composition and pressure dependence of the Curie temperature along with Mossbauer spectra, for which the average hyperfine field is proportional to an average pairwise exchange interaction and by inference T_c. Within this formalism, we consider J(D/d), i.e. the exchange interaction(s) as a function of D/d the variable for which the Bethe-Slater curve is parameterized. The P-dependence of T_c will be interpreted for FeCoNiMnCu 5-component HEAs with a room temperature T_c.

11:40am MI+2D-WeM12 Epitaxy of Novel Co$_{1.5}$Ti$_{0.5}$FeGe Heusler Alloy Thin Films, *Shambhu KC[1]*, *R. Mahat, T.J. Evans, S. Budhathoki, G.J. Mankey, A. Gupta, P. LeClair,* The University of Alabama

While the half-metallic ferromagnets are considered ideal candidates to be used for efficient spintronics devices, a single-phase microstructure with promising half-metallic character is recently reported in a bulk Co$_{1.5}$Ti$_{0.5}$FeGe Heusler alloy[1]. This alloy has Ti substitution for Co atoms in the parent Co$_2$FeTiGe alloy, where the parent alloy does not exhibit half-metallic behavior[2]. However, the Ti substitution is useful not only to stabilize single-phase behavior but also to tune half-metallicity by the Fermi level shift. In this work, successful growth of epitaxial thin films of this novel Co$_{1.5}$Ti$_{0.5}$FeGe alloy on a-plane sapphire and MgAl$_2$O$_4$(100) by using DC magnetron sputtering will be reported. In-situ reflection high energy electron diffraction shows that the films grow epitaxially with smooth surfaces. X-ray diffraction analysis confirms the epitaxial relation and lattice parameters within a few percent of the reported bulk value. Presence of finite size Laue oscillations in the XRD pattern and 0.035˚ full width at half maximum of rocking curve obtained in case of films grown on a-plane sapphire describe excellent quality of the films. The presence of superlattice peaks; (200) and (111), indicate a strong tendency to form the L2$_1$ structure. The degree of B2 ordering is estimated to be as high as 0.92 showing that intermixing between the atoms in the octahedral and tetrahedral sites is limited. Atomic force microscopy shows that the films grown on MgAl$_2$O$_4$(100) are atomically smooth with a rms roughness of 0.2 nm. Magnetic measurements of films grown at 800ºC show that the saturation magnetization is in close agreement with the bulk value. Angle-dependent magnetization measurements show the symmetry of the coercivity is consistent with a magnetocrystalline anisotropy. Temperature-dependent transport measurements show metallic behavior and an ordinary magnetoresistance as high as 1.55 % is obtained at 100 K. All the above results describe the feasibility of growing good quality epitaxial films of novel Co$_{1.5}$Ti$_{0.5}$FeGe alloy with the structural and magnetic properties consistent with reported bulk properties.

1. KC et al., Tunable Properties and Potential Half-Metallicity in (Co$_{2-x}$Ti$_x$)FeGe Heusler Alloys; an Experimental and Theoretical Investigation, submitted to Phys. Rev. Materials.

2. Kumar et al., First-principles Calculation and Experimental Investigations on Full-Heusler Alloy Co$_2$FeGe, IEEE Transactions on Magnetics 45, 3997 (2009).

12:00pm MI+2D-WeM13 Spin Transport in NiO Measured with Ferromagnetic Resonance, *G.J. Mankey, T.J. Evans, S. KC, Arjun Sapkota, T. Mewes,* The University of Alabama

Recently, a measured spin diffusion length of approximately 22 nm was reported for spin current transmission through polycrystalline NiO.[1] The diffusion length is inferred by referencing the effective Gilbert damping constant in NiO/Fe$_{20}$Ni$_{80}$ bilayers as a function of NiO and Fe$_{20}$Ni$_{80}$ thickness. We present results using a different approach to determine the spin diffusion length, using trilayers of Fe$_{20}$Ni$_{80}$/NiO/Pt with FMR measurements covering the frequency range of 4 GHz to 50 GHz. The Pt serves as a spin sink when deposited directly on Fe$_{20}$Ni$_{80}$ and strongly increases the effective damping parameter. With NiO between the Pt spin sink and the ferromagnetic Fe$_{20}$Ni$_{80}$, the increase in damping parameter is diminished, and the decay length is extracted from measurements as a function of NiO thickness. Our preliminary measurements show that the decay length is smaller than 15 nm consistent with a decay length of approximately 4 nm determined from inverse spin hall effect measurements of Y$_3$Fe$_5$O$_{12}$/NiO/Pt structures.[2] In addition, at lower FMR frequencies (4 GHz as compared to 22 GHz) multiple resonances are observed for polycrystalline NiO, suggesting that ferromagnetic impurities are present in the antiferromagnet.

Results for polycrystalline and epitaxial trilayers will be presented, showing the effect of processing conditions on the spin diffusion length. These

measurements will be correlated with microstructural and morphological characterization of the samples.

References

1 Tetsuya Ikebuchi, Takahiro Moriyama, Hayato Mizuno, Kent Oda, and Teruo Ono, Appl Phys Express **11** (7), 073003 (2018).

2 Yu-Ming Hung, Christian Hahn, Houchen Chang, Mingzhong Wu, Hendrik Ohldag, and Andrew D. Kent, AIP Advances **7** (5), 055903 (2017).

Complex Oxides: Fundamental Properties and Applications Focus Topic
Room A220-221 - Session OX+EM+MI+SS-WeM

Electronic and Magnetic Properties of Complex Oxide Surfaces and Interfaces

Moderators: Yingge Du, Pacific Northwest National Laboratory, Vincent Smentkowski, GE-Research

8:00am OX+EM+MI+SS-WeM1 Charge Transfer in Lanthanum Ferrite-Strontium Nickelate Superlattices, *Le Wang, Z. Yang, M.E. Bowden,* Pacific Northwest National Laboratory*; J.W. Freeland,* Argonne National Laboratory*; Y. Du, S.A. Chambers,* Pacific Northwest National Laboratory

Charge transfer at oxide interfaces can drive emergent phenomena that do not occur in the bulk, thereby significantly enriching our fundamental understanding of these material systems and their applications. Designing oxide heterostructures and seeking new and novel interfacial phenomena has been an active area of research for some time. We have synthesized a series of [(LaFeO$_3$)$_m$/(SrNiO$_{3-d}$)$_n$]$_z$ ([(LFO)$_m$/(SNO)$_n$]$_z$) superlattices (SLs) (z = 7 to 21) by oxide molecular beam epitaxy on (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) (001) substrates. *In situ* RHEED patterns and x-ray diffraction measurements reveal a high degree of structural quality in the SLs. X-ray photoemission spectroscopy (XPS) shows that the Fe is Fe^{4+} in the (LFO$_1$/SNO$_1$)$_{21}$ SL. However, the Fe 2p binding energy shifts to lower values with increasing LFO layer thickness in (LFO$_m$/SNO$_1$)$_z$ SLs, suggesting that the volume averaged Fe valence decreases. Fe L-edge X-ray absorption spectroscopy (XAS) measurements corroborate the XPS results, indicating that Fe is 4+ for the (LFO$_1$/SNO$_1$)$_{21}$ SL and mostly 3+ for the (LFO$_5$/SNO$_1$)$_{10}$ SL. On the other hand, Ni L-edge XAS shows that Ni valence is Ni^{3+} for the (LFO$_1$/SNO$_1$)$_{21}$ SL as is also true for insulating NdNiO$_3$, suggesting that the Ni layers in this SL are insulating, which is consistent with our in-plane transport measurements. However, for the (LFO$_5$/SNO$_1$)$_{10}$ SL, the Ni valence is larger than 3+. The measured energy shifts suggest that Ni is close to 4+. The thicker LFO layer in the (LFO$_5$/SNO$_1$)$_{10}$ SL may result in a larger band offset and create a potential well to trap the holes in the Ni layer, inducing the formation of Ni^{4+}. Our ongoing studies are probing the impact of the SNO layer thickness on material structure as well as the evolution of the Fe and Ni valences in (LFO$_5$/SNO$_n$)$_z$ SLs. Additional planned experimental and theoretical investigations will address how charge transfer from Fe to Ni occurs at the LFO/SNO interface, and how to stabilize the unusual high 4+ valence in Fe^{4+} and Ni^{4+} by means of interfacial engineering.

8:20am OX+EM+MI+SS-WeM2 Self-healing Growth of LaNiO$_3$ on Mixed-terminated (LaAlO$_3$)$_{0.3}$-(Sr$_2$AlTaO$_6$)$_{0.7}$, *Friederike Wrobel, H. Hong, S. Cook, T.K. Andersen, D. Hong, C. Liu, A. Bhattacharya, D.D. Fong,* Argonne National Laboratory

Epitaxial LaNiO$_3$ (LNO) thin films and superlattices are known to be antiferromagnetic and weakly insulating for LNO thicknesses of 2 unit cells but paramagnetic and metallic for higher LNO thicknesses [1]. The quality of the single-crystal substrate surface, and in particular the chemical composition of the surface, is known to be a key factor governing the quality of the deposited thin film. For SrTiO$_3$ (001) substrates, there are well-established preparation methods to ensure that the surface is TiO$_2$-terminated and atomically smooth; the only features that appear with atomic force microscopy are the regular steps and terraces associated with crystal miscut. SrTiO$_3$ is therefore often preferred as a substrate over other materials like (LaAlO$_3$)$_{0.3}$-(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT), whose surface composition is harder to control. Interestingly, for unknown reasons, the highest quality LaNiO3 thin films have been grown on mixed-terminated, untreated LSAT (001) substrates [2, 3]. At present, very few detailed studies have been conducted regarding the precise influence of the substrate on thin film growth behavior due to the need for an in-situ, atomic-scale characterization technique. Exploiting an in-situ, oxide molecular beam epitaxy (MBE) chamber at the Advanced Photon Source, we were able to monitor the deposition of thin films of LNO on LSAT (001) substrates with

---
[1] **Falicov Student Award Finalist**

Wednesday Morning, October 23, 2019

different surface compositions. Both non-resonant and resonant (Sr K-edge) X-ray scattering measurements were conducted at several points during the growth process. We observed the formation of atomically smooth, high-quality LNO films regardless of the initial substrate surface composition, suggesting that any excess, non-stoichiometric material on the initial LSAT substrate rises to the surface during deposition. With atomic layer-by-atomic layer MBE under the right conditions, we can therefore achieve self-healing growth behavior of complex oxides on top of mixed-terminated substrates. We will discuss details of the in-situ growth measurements and the methods used to determine the atomic and chemical structures.

1. Frano, A., et al., *Orbital Control of Noncollinear Magnetic Order in Nickel Oxide Heterostructures.* Physical Review Letters, 2013. **111**(10): p. 106804.

2. Liu, C., et al., *Counter-thermal flow of holes in high-mobility LaNiO3 thin films.* Physical Review B, 2019. **99**(4): p. 041114.

3. Wrobel, F., et al., *Comparative study of LaNiO3/LaAlO3 heterostructures grown by pulsed laser deposition and oxide molecular beam epitaxy.* Applied Physics Letters, 2017. **110**(4): p. 041606.

8:40am OX+EM+MI+SS-WeM3 Optoelectronics with Oxides and Oxide Heterostructures, *Alexander Demkov,* University of Texas at Austin **INVITED**

Si photonics is a hybrid technology combining semiconductor logic with fast broadband optical communications and optical information technologies. With the increasing bandwidth requirement in computing and signal processing, the inherent limitations in metallic interconnection are seriously threatening the future of traditional IC industry. Silicon photonics can provide a low-cost approach to overcome the bottleneck of the high data rate transmission by replacing the original electronic integrated circuits with photonic integrated circuits. The development has proceeded along several avenues including mounting optical devices based on III-V semiconductors and/or LiNbO$_3$ (LNO) on Si chips, incorporation of active optical impurities into Si, and utilization of stimulated Raman scattering in Si. All these approaches have had limited success. Recently, another path to Si photonics through epitaxial integration of transition metal oxide films was demonstrated when an effective electro-optic (Pockels) coefficient of BaTiO$_3$ (BTO) films epitaxially grown on Si *via* an SrTiO$_3$ buffer was reported to be an order of magnitude larger than that in commercially-available LNO modulators. More generally, epitaxial growth of SrTiO$_3$ on Si(001) enables monolithic integration of many functional perovskite oxides on Si, including ferroelectric BTO, ferromagnetic LaCoO$_3$, photocatalytic TiO$_2$ and CoO, and many others.

In this talk, I will focus on two materials systems integrated on Si (001) and well-suited for implementation in the next-generation optical technologies: SrTiO$_3$/LaAlO$_3$ quantum wells and Pockels-active BTO thin film heterostructures. Both materials systems are promising for use in a wide variety of optical and electro-optical devices central to integrated photonic technologies, including quantum cascade lasers, photodetectors, electro-optic modulators and switches. The resulting devices achieve refractive index tuning with power consumption many orders of magnitude less than previously reported. Taken together, these two approached will hopefully open the door for the development of new kinds of optical and electro-optical devices for use in integrated photonics technologies.

9:20am OX+EM+MI+SS-WeM5 Medard W. Welch Award Lecture: Defect-Mediated Coupling of Built-in Potentials at Buried Interfaces Involving Epitaxial Complex Oxides, *Scott. A Chambers*[1], Pacific Northwest National Laboratory **INVITED**

Semiconductor-based devices are of broad importance, not only in electronics, but also in energy technology. Internal electric fields dictate the flow of charge that occurs both laterally and vertically. The associated potential profiles can be approximated from electronic transport data, and also calculated via Poisson-Schrodinger modeling, provided the properties of the constituent materials and interface structures are sufficiently well understood. These approaches work well for heterostructures involving, for instance, III-V semiconductors. However, when complex oxides are involved, they become unreliable because of poorly understood defects that can be present. There is, therefore, a critical need for new methods to enable the determination of band-edge profiles in heterostructures involving these materials.

The SrTiO$_3$/Si(001) interface has been a prototypical system for understanding the materials physics and electronic structure of crystalline

oxides on semiconductors. Thinner films (a few unit cells, u.c.) are known to result in flat-band heterojunctions in which the valence (conduction) band offset is large (small). However, we have recently found that thicker films (~30 u.c.) of SrNb$_x$Ti$_{1-x}$O$_3$ (0 ≤ x ≤ 0.2) on intrinsic Si(001) result in completely different electronic structures. Transport data suggest sharp upward band bending in the Si, leading to hole gas formation at the interface, and a large (~2 eV) built-in potential in the SNTO, along with surface depletion. We have probed these buried interfaces using hard x-ray photoelectron spectroscopy (HAXPES). The resulting core-level spectra exhibit unusual features not seen in thinner films, and not credibly ascribed to secondary phases or many-body effects. In order to interpret these line shapes, we hypothesize that they result from large built-in potentials within the system. We have developed an algorithm to extract these potential profiles by fitting heterojunction spectra to linear combinations of spectra from phase-pure, flat-band materials, summed over layers within the probe depth, each with a binding energy characteristic of the potential at each depth. This approach leads to excellent agreement with experiment and band-edge profiles completely consistent with those from transport data. Moreover, we find that the built-in potentials extracted from HAXPES on the Si side of the interface are in quantitative agreement with those resulting from solving Poisson's equation using the SIMS profile for in-diffused oxygen from the STO. Oxygen is a shallow donor in Si, and assuming 100% donor ionization, along with the ^{18}O SIMS depth profile, leads to near-perfect agreement with HAXPES.

11:20am OX+EM+MI+SS-WeM11 Structural and Dielectric Characterization of Epitaxial Entropy-Stabilized Oxide Thin Films, *George Kotsonis, J.-P. Maria,* Pennsylvania State University

The emergence of entropy-stabilized oxides (ESOs) represents a new paradigm for complex oxide engineering. The large configurational entropy of ESOs facilitates mixing of chemically dissimilar cations in significant proportions. ESO research continues to intensify as the oxide community works toward a thorough understanding of structure-property-synthesis relationships. Due to inherent metastability, high energy, non-equilibrium synthesis techniques are well suited for ESO fabrication. In particular, laser ablation has excelled at producing high quality epitaxial ESO thin films, which provide a platform for fundamental characterization.

We present the growth and characterization of Ba(Ti$_{0.2}$Sn$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$)O$_3$ and similar Barium-based perovskite structured ESO thin films grown by laser ablation. Crystal structure, surface morphology, and optical properties are characterized by X-ray diffraction, atomic force microscopy, and ellipsometry respectively. Epitaxial thin film capacitor structures were fabricated to characterize the frequency, voltage, and temperature dependence of electrical properties.

By exploiting the entropy-stabilized nature of ESOs, we demonstrate the incorporation of significant amounts of aliovalent cation pairs (*e.g.* Sc^{3+}Ta^{5+}) in hopes of producing nano-polar regions supporting a dispersive dielectric response similar to relaxor ferroelectrics. Additionally, we explore compositional space in search of a phase boundary between a high-symmetry ESO phase and a lower symmetry end-member. Compositions at such a boundary may exhibit phase instability and enhanced dielectric functionality similar to compositions at or near a morphotropic phase boundary. The compositional degrees of freedom available in ESO systems provide new avenues for property tuning and studying the effects of extreme chemical disorder on dielectric properties.

11:40am OX+EM+MI+SS-WeM12 Oxygen Vacancy-Mediated Epitaxy: TiO$_2$(111)/Al$_2$O$_3$(0001) and Ferromagnetic Cr$_2$O$_3$(0001)/TiO$_2$(111), *C. Ladewig, F. Anwar, Jeffry Kelber,* University of North Texas; *S.Q.A. Shah, P.A. Dowben,* University of Nebraska-Lincoln

The formation of all-oxide heterostructures comprising multiferroic oxides interfaced with appropriate semiconducting substrates is a promising path towards low power, voltage-switchable spintronics, including non-volatile memory and multi-functional logic devices. At the same time, the necessary scaling of film thicknesses to the nm range can induce structures and properties sharply different than those of the bulk. We report here in situ XPS, LEED, EELS and ex-situ MOKE data on the growth and properties of Cr$_2$O$_3$(0001) on TiO$_{1.7}$(111) on Al$_2$O$_3$(0001). The data indicate that the presence of O vacancies during film growth can mediate the further growth of oxides with unusual structures and properties. These data show that (a) O vacancies during initial stages of film growth yield a TiO$_2$ film of an unusual crystallographic orientation and structure; and that (b) this leads to growth of an epitaxial Cr$_2$O$_3$ layer exhibiting magnetic ordering above the expected Néel temperature of thin film chromia - indicative of a strained chromia lattice due to epitaxial growth on a substrate with a

---

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

Wednesday Morning, October 23, 2019 27 *8:00 AM*

lattice constant of 5.1 Å, compared to the bulk chromia lattice constant of 4.9 Å. Molecular beam epitaxy (MBE) of Ti at 500 K in 10^{-6} Torr O_2 on Al_2O_3(0001) initially yields $TiO_{1.7}$(111) with the structure of corundum phase Ti_2O_3 (a = b=5.1 Å). Further deposition and annealing in O_2 results in stoichiometric TiO_2(111), but with the same lattice structure and orientation as Ti_2O_3(111), and with a total thickness of 5 nm. This is sharply different from the generally observed growth of TiO_2(001) on Al_2O_3(0001). MBE of ~ 1 monolayer of Cr on TiO_2(111) yields hexagonally-ordered Cr_2O_3 and the formation of titania oxygen vacancies. MOKE measurements confirm that this chromia layer is magnetically ordered at 280 to 315 K, likely antiferromagnetically ordered, with exchange bias coupling to the $TiO_{1.7}$(111) substrate. O vacancies in the TiO_2(111) lattice exhibit weak ferromagnetic behavior, as is evident in the In-plane MOKE, enhancing the canting of the magnetism away from the thin film normal, which is expected for the Cr_2O_3(0001) alone. These data demonstrate that careful control of initial growth conditions and film stoichiometry during oxide MBE can template the subsequent growth of stoichiometric oxide heterostructures with non-bulk like structures and properties.

12:00pm **OX+EM+MI+SS-WeM13 Incorporation of Ti into Epitaxial Films of Magnetite**, *Tiffany Kaspar, S.R. Spurgeon, D.K. Schreiber, S.D. Taylor, M.E. Bowden, S.A. Chambers,* Pacific Northwest National Laboratory

Magnetite, Fe_3O_4, exhibits metallic conductivity via electron hopping between Fe^{2+} and Fe^{3+} occupying octahedral sites in the spinel lattice. As Ti^{4+} is doped into the octahedral sites of magnetite (the titanomagnetite series), an equal fraction of Fe^{3+} is reduced to Fe^{2+} to maintain charge neutrality. The site occupancies of Fe^{2+} and Fe^{3+} determine the transport properties of the titanomagnetite series; the end-member ulvöspinel, Fe_2TiO_4, exhibits *p*-type semiconducting transport properties. The Fe^{2+}/Fe^{3+} site occupancy remains controversial, but is likely in part a function of the lattice strain induced by doping smaller Ti^{4+} into the lattice. Here, we have deposited titanomagnetites and ulvöspinel as well-defined epitaxial thin films on MgO, $MgAl_2O_4$, and Al_2O_3 substrates by oxygen-plasma-assisted molecular beam epitaxy. The incorporation of Ti into the magnetite lattice is found to depend strongly on deposition conditions and substrate orientation. We have characterized the crystalline structure, phase segregation, and surface morphology with XRD, STEM/EDS, APT, and AFM, and related these to the kinetic and thermodynamic factors determined by the deposition conditions. The Fe valence state is evaluated with *in situ* XPS. The impact of film structure and Fe oxidation state on the electrical transport properties of the films will be discussed.

Magnetic Interfaces and Nanostructures Division
Room A210 - Session MI+2D-WeA

Emerging Multifunctional Magnetic Materials II

Moderators: Valeria Lauter, Oak Ridge National Laboratory, Axel Hoffmann, Technical University of Berlin

2:20pm MI+2D-WeA1 Field and Current Control of the Electrical Conductivity of an Artificial Two-Dimensional Honeycomb Lattice, *Deepak Singh,* University of Missouri **INVITED**

Two-dimensional magnetic nanostructured geometry, such as an artificial magnetic honeycomb lattice, provides facile platform to explore many novel properties of magnetic materials in one system. Originally envisaged to explore the physics of effective magnetic monopoles and magnetic field-induced avalanche of Dirac string, artificial magnetic honeycomb lattice has emerged as a key playground to discover new and exotic magnetic phases, such as magnetic charge ordered state and the spin solid state, in disorder free environment. We have created a new artificial permalloy honeycomb lattice of ultra-small connected element, with a typical length of ~ 12 nm, in this pursuit. Using neutron scattering and complementary measurements on the newly created honeycomb lattice, we have investigated emergent phenomena of short-range quasi-spin ice and long range spin solid order. Additionally, two new properties of Wigner crystal type state of magnetic charges and magnetic diode-type rectification are discovered in the newly created artificial honeycomb lattice. The new findings create a new vista for the next generation design of spintronics devices in this two-dimensional frustrated geometry. Research at MU is supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Grant No. DE-SC0014461.

3:00pm MI+2D-WeA3 Emergence and Dynamics of Magnetic Order in Metamagnetic Nanostructures, *Vojtech Uhlir,* CEITEC BUT, Brno University of Technology, Czech Republic **INVITED**

The advantage of ferromagnetic materials is the nonvolatility of the information encoded in the internal magnetic configuration, which can be used for memory storage, logic and sensing devices. Antiferromagnets are another class of magnetic materials that features nonvolatile magnetic ordering, yet its applications have been largely overlooked until recently [1]. In materials featuring a first-order metamagnetic phase transition between the antiferromagnetic (AF) and ferromagnetic (FM) states, the nature of the phase transition can be tuned by strain, pressure, chemical doping, temperature, as well as magnetic and electric fields, potentially offering very high recording densities and huge changes in the order parameters controlled with very low power.

Moreover, metamagnetic materials are outstanding candidates for finding and exploiting new functionalities and emergent phenomena on the mesoscale [2,3]. For instance, the transition from the AF order to FM order in sub-micron-wide FeRh wires becomes greatly asymmetric when comparing the heating and cooling cycles [3,4]. This recovery of the abrupt transition in nanostructures could lead to low-energy, efficient routes to control magnetic properties, leading to potential applications, for instance, in spintronics.

Furthermore, we show the dynamic response of the electronic and magnetic order to ultrafast laser excitation can be followed by time-resolved photoemission electron spectroscopy [5], which unlike techniques probing the total magnetization in the sample provides a direct comparison to the dynamic response of the structural order.

[1] T. Jungwirth, X. Marti, P. Wadley, and J. Wunderlich, *Nature Mater.* **11**, 231 (2016).

[2] F. Pressacco *et al., Sci. Rep.* **6**, 22383 (2016).

[3] V. Uhlíř, J. A. Arregi, and E. E. Fullerton, *Nat. Commun.* **7**, 13113 (2016).

[4] J. A. Arregi *et al.,J. Phys. D: Appl. Phys.* **51**, 105001 (2018).

[5] F. Pressacco *et al., Struct. Dyn.* **5**, 034501 (2018).

4:20pm MI+2D-WeA7 Time Dependence in La$_{0.7}$Sr$_{0.3}$MnO$_3$ Thin Films with Magnetic Competition, *Mikel B. Holcomb, R.B. Trappen, N.M. Mottaghi, S.F. Yousefi, G. Cabrera, G. Bhandari, M.S.S. Seehra,* West Virginia University

La$_{0.7}$Sr$_{0.3}$MnO$_3$ is a strongly correlated ferromagnetic system, commonly proposed for many magnetoresistance applications. Utilizing many techniques (bulk magnetometry, neutron reflectometry and resonant x-ray magnetic scattering), we observe magnetic competition between different magnetic phases in many samples under various growth conditions. This competition results in inverted hysteresis loops (common in superparamagnetic nanoparticles) and negative remanent magnetization. While transmission electron microscopy images show pristine epitaxial growth, the data supports that there are regions of different magnetic order. This results in interesting magnetic measurements, that share similarities with ferrimagnets with competing magnetic lattices. In this talk, the time, field and temperature dependence of these samples will be discussed to help understand this phenomenon. Sample growth and optimization were supported by NSF (DMR-1608656), national facility measurements and theory were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0016176, and optical measurements by American Chemical Society (PRF #56642-ND10). **We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.**

4:40pm MI+2D-WeA8 Optically Induced Magnetization through Spin States at Perovskite/Ferromagnetic Interface Revealed by Neutron Magnetoreflectivity Studies, *Bin Hu,* University of Tennessee Knoxville **INVITED**

This presentation reports an optically induced magnetization at perovskite/ferromagnetic interface realized at room temperature. By using neutron magnetoreflectivity measurement, it was found that a circularly polarized light of 405 nm induces a magnetization with the thickness up to 5 nm into the surface of perovskite (MAPbBr$_3$) film underneath of ferromagnetic Co layer at room temperature. On contrast, a linearly polarized light does not generate any detectable magnetization within the perovskite surface in the MAPbBr$_3$/Co sample during the neutron magnetoreflectivity measurement. This observation provides an evidence to show optically induced magnetization on the perovskite surface in contact with Co surface. Furthermore, the MAPbBr$_3$/Co interface demonstrates a magneto-capacitance phenomenon, indicating that the electrical polarization on perovskite surface is coupled with magnetic polarization on the Co surface. On the other hand, a circularly polarized light leads to spin states in hybrid perovskites through photoexcitation. The observed magnetization indicates that circularly polarized light-generated spin states can directly interact with electric-magnetic coupling, leading to an optically induced magnetization.

5:20pm MI+2D-WeA10 Effect of Interlayer and Underlayers on the Microstructure and Magnetic Softness in FeGa-based Ferromagnetic Composites, *Adrian Acosta, K. Fitzell,* University of California, Los Angeles*; C. Dong,* Northeastern University*; M. Zurbuchen, N.X.S. Sun, J.P. Chang,* University of California, Los Angeles

Magnetoelectric materials provide the ability to efficiently control magnetism with electric fields, which is key to circumvent the size and efficiency limitations of traditional electric dipole antennas. Strain-mediated multiferroic antennas, composed of individual ferromagnetic and piezoelectric phases, have recently generated a lot of interest due to the potential to reduce the size of antennas by up to 5 orders of magnitude through the coupling of magnetization and electric polarization via strain at the interface. However, this requires a low-loss magnetic material with strong magnetoelastic coupling at high frequencies.

Galfenol (Fe81Ga19 or FeGa) is a promising candidate material due to its large magnetostriction (~275 ppm in polycrystalline bulk) and large piezomagnetic coefficient (>2 ppm/Oe) but is highly lossy at high microwave frequencies. Previously, nanoscale laminates were fabricated via DC magnetron sputtering of FeGa with NiFe as an interlayer material resulting in a composite with a small coercive field (<20 Oe), narrow FMR linewidth (<35 Oe), and high relative permeability (>1000) [1]. In this work, the enhancement in soft magnetic properties is correlated to the microstructure of these composites by TEM analysis where the nanolayering strategy promotes the formation smaller grain sizes. Optical magnetostriction measurements displayed an enhanced magnetostriction beyond that expected from averaging the individual FeGa and NiFe phases, indicating an interfacial contribution present leading to increase of the overall magnetostriction. The magnetostriction sensitivity peaks at a lower magnetic field (23 Oe for FeGa/NiFe multilayers vs 56 Oe for FeGa). To delineate the impact of the microstructure of FeGa on the soft and functional magnetic properties, FeGa was sputter deposited onto several materials (NiFe, Ta, Cu, and Al$_2$O$_3$) as underlayers on a Si substrate which can directly influence the polycrystalline structure and enhance its soft magnetic properties [2]. XRD and AFM are used to show the dependence of the coercivity, FMR linewidth, and magnetostriction on the texture,

internal stress, grain size, and surface roughness of the FeGa film with the different underlayer materials.

Integration of these engineered composites into a strain-mediated multiferroic shear wave antenna design further demonstrates the potential of FeGa-based laminates for use in microwave communications systems for implantable medical devices.

References:

[1] Rementer, C. R., et al. (2017). *Applied Physics Letters* 110(24): 242403.

[2] Jung, H., et al. (2003). *Journal of Applied Physics* 93(10): 6462-6464.

5:40pm **MI+2D-WeA11 Tunable Spin-polarized Edge Effects in Transition Metal Dichalcogenides on FM and AFM Substrates**, *N. Cortes,* Universidad Tecnica Federico Santa Maria, Chile*; Oscar Avalos-Ovando,* Ohio University*; L. Rosales, P. Orellana,* Universidad Tecnica Federico Santa Maria, Chile*; S. Ulloa,* Ohio University

We explore proximity-induced ferromagnetism (FM) and antiferromagnetism (AFM) on transition metal dichalcogenide (TMD), focusing on molybdenum ditelluride (MoTe2) ribbons with zigzag and/or armchair edges, deposited on either a FM or an AFM substrate, e.g. such as FM europium oxide and AFM manganese oxide. A three-orbital tight-binding model allows to model MoTe2 monolayer structures in real space, incorporating the exchange and Rashba fields induced by proximity to the substrate. For in-gap Fermi levels, electronic modes in the nanoribbon are strongly spin-polarized and localized along the edges, acting as 1D conducting channels with tunable spin-polarized currents. We also study the effect of atomic defects on the 1D conducting channels and on the spin-polarized currents, finding that even in the presence of either Te and/or Mo vacancies, the spin-polarized current is nonvanishing. Hybrid structures such as the MoTe2/FM-substrate and/or MoTe2/AFM- substrate configuration can serve as building blocks for spintronic devices and provide versatile platforms to further understand proximity effects in diverse materials systems.

[1] N. Cortes et al, Phys. Rev. Lett. 122, 086401 (2019).

[2] N. Cortes et al, in preparation (2019).

6:00pm **MI+2D-WeA12 Magnetocaloric Properties of Thin Film La$_{0.7}$Sr$_{0.3}$MnO$_3$: Magnetic Field Dependence and Effects of Superparamagnetism**, *Navid Mottaghi*[1], *M.S.S. Seehra, C.-Y. Huang, S. Kumari, S. Yousefi Sarraf, G. Cabrera, G. Bhandari, R.B. Trappen, M.B. Holcomb,* West Virginia University

La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) with Curie temperature $T_C \approx 370$ K is one of the manganites which has been of interest for applications in magnetic memory devices and spintronics.[1] The magnetic properties of LSMO thin films are also known to depend on the thickness of the films.[2] Recent magnetic investigations of a 7.6 nm LSMO film grown by pulsed laser deposition (PLD) showed it to have a $T_C \approx 290$ K with a magnetic dead layer $d \approx 1.4$ nm which demonstrated behavior consistent with containing superparamagnetic (SPM) spin clusters with blocking temperature $T_B \approx 240$ K.[3,4] Here we report magnetocaloric properties of this LSMO thin film for temperatures $T \leq T_C$ in magnetic fields H up to 4 kOe. In particular, magnetic entropy $S_M(T, H)$ is evaluated from the isothermal plots of magnetization (M) vs. H at different temperatures (Fig. 1) using the Eq. $\Delta S_M (T,H) = \sum_i [(M_{i+1} (T_{i+1}, H) - M_i (T_i, H))/(T_{i+1}-T_i)] \Delta H$. The H-dependence of $\Delta S_M (T,H)$ is analyzed using the relation $(-\Delta S_M)=aH^n$, where a is a constant and $n = 2/3$ is expected at $T = T_C$.[5] Our fit of the data to this Eq. for several $T \leq T_C$ in Fig. 2 shows $n \sim 1$ for $T < T_C$ with the magnitude of n increasing for $T > T_C$. This deviation of n from $n = 2/3$ is likely due to presence of SPM spin clusters in the dead layer for $T < T_C$. The larger magnitudes of n for $T > T_C$ is due to the Curie-Weiss variation of the magnetization in this regime.[5]

References

[1] N. Izyumskaya, Y. Alivov, and H. Morkoç, Crit. Rev. Solid State Mater. Sci. **34**, 89 (2009).

[2] M. Huijben, L.W. Martin, Y.-H. Chu, M.B. Holcomb, P. Yu, G. Rijnders, D.H.A. Blank, and R. Ramesh, Phys. Rev. B **78**, 94413 (2008).

[3] N. Mottaghi, R.B. Trappen, S. Kumari, C.Y. Huang, S. Yousefi, G.B. Cabrera, M. Aziziha, A. Haertter, M.B. Johnson, M.S. Seehra, and M.B. Holcomb, J. Phys. Condens. Matter **30**, 405804 (2018).

[4] N. Mottaghi, M.S. Seehra, R. Trappen, S. Kumari, C.-Y. Huang, S. Yousefi, G.B. Cabrera, A.H. Romero, and M.B. Holcomb, AIP Adv. **8**, 056319 (2018).

[5] M. Pękała, J. Appl. Phys. **108**, 113913 (2010).

---

[1] **Falicov Student Award Finalist**

2D Materials

Room A216 - Session 2D+EM+MI+NS+QS+SS-ThM

Dopants, Defects, and Interfaces in 2D Materials
Moderator: Evan Reed, Stanford University

8:00am 2D+EM+MI+NS+QS+SS-ThM1 Interfacial Engineering of Chemically Reactive Two-Dimensional Materials, *Mark Hersam,* Northwestern University **INVITED**
Following the success of ambient-stable two-dimensional (2D) materials such as graphene and hexagonal boron nitride, new classes of chemically reactive layered solids are being explored since their unique properties hold promise for improved device performance [1]. For example, chemically reactive 2D semiconductors (e.g., black phosphorus (BP) and indium selenide (InSe)) have shown enhanced field-effect mobilities under controlled conditions that minimize ambient degradation [2]. In addition, 2D boron (i.e., borophene) is an anisotropic metal with a diverse range of theoretically predicted phenomena including confined plasmons, charge density waves, and superconductivity [3], although its high chemical reactivity has limited experimental studies to inert ultrahigh vacuum conditions [4-7]. Therefore, to fully study and exploit the vast majority of 2D materials, methods for mitigating or exploiting their relatively high chemical reactivity are required [8]. In particular, covalent organic functionalization of BP minimizes ambient degradation, provides charge transfer doping, and enhances field-effect mobility [9]. In contrast, noncovalent organic functionalization of borophene leads to the spontaneous formation of electronically abrupt lateral organic-borophene heterostructures [10]. By combining organic and inorganic encapsulation strategies, even highly chemically reactive 2D materials (e.g., InSe) can be studied and utilized in ambient conditions [11].

[1] A. J. Mannix, *et al.*, *Nature Reviews Chemistry*, **1**, 0014 (2017).

[2] D. Jariwala, *et al.*, *Nature Materials*, **16**, 170 (2017).

[3] A. J. Mannix, *et al.*, *Nature Nanotechnology*, **13**, 444 (2018).

[4] A. J. Mannix, *et al.*, *Science*, **350**, 1513 (2015).

[5] G. P. Campbell, *et al.*, *Nano Letters*, **18**, 2816 (2018).

[6] X. Liu, *et al.*, *Nature Materials*, **17**, 783 (2018).

[7] X. Liu, *et al.*, *Nature Communications*, **10**, 1642 (2019).

[8] C. R. Ryder, *et al.*, *ACS Nano*, **10**, 3900 (2016).

[9] C. R. Ryder, *et al.*, *Nature Chemistry*, **8**, 597 (2016).

[10] X. Liu, *et al.*, *Science Advances*, **3**, e1602356 (2017).

[11] S. A. Wells, *et al.*, *Nano Letters*, **18**, 7876 (2018).

8:40am 2D+EM+MI+NS+QS+SS-ThM3 Effects of Mn Doping on the Surface Electronic Band Structure and Bulk Magnetic Properties of ZnS and CdS Quantum Dot Thin Films, *Thilini K. Ekanayaka[1], G. Gurung,* University of Nebraska-Lincoln*; G. Rimal,* Rutgers University*; S. Horoz,* Siirt University, Turkey*; J. Tang, T. Chien,* University of Wyoming*; T. Paudel, A.J. Yost,* University of Nebraska-Lincoln
Semiconducting quantum dots (QDs) are desirable for solar cells due to the ability to tune the band gap by changing the QD size without changing the underlying material or synthesis technique. Doping QDs with a transition metal is one way of further tailoring the electronic band structure and magnetic properties of QDs in order to improve overall device performance. Understanding the mechanisms causing the change in the electronic band structure and magnetic properties due to transition metal doping is important to device-by-design schemes. In this study, we measure the effects of Mn dopants on the surface electronic band structure of ZnS and CdS QDs using scanning tunneling microscopy/spectroscopy and photoemission spectroscopy. In both the ZnS and CdS systems, a decrease in band gap upon introduction of Mn is observed. Additionally, a rigid band shift was observed in ZnS upon Mn doping It is argued, using X-ray photoemission spectroscopy, that the rigid band shift is due to a hole-doping mechanism caused by the formation of Zn vacancies accompanied by a Mn^{3+} oxidation state which leads to the reduction in total S vacancies as compared to the undoped ZnS system. No band shift was observed in CdS upon Mn doping, but a strong sp-d hybridization takes place which results in a significant band gap reduction. Furthermore, induced midgap states originating from the Mn dopant appear in the surface electronic band structure of Mn: CdS. Measurements of the magnetization of Mn doped and undoped ZnS and CdS confirms the

presence of d^0 ferromagnetism. The magnetization is reduced and the coercive field is increased post Mn doping which suggests the anti-ferromagnetic alignment of Mn dopant atoms. Density Functional Theory calculations support the Mn anti-ferromagnetic alignment hypothesis and a ground state with Mn in the 3^+ valence. This study provides important information on the role of dopants and vacancies in dilute magnetic semiconductor quantum dot materials for applications in photovoltaics and spintronics.

9:00am 2D+EM+MI+NS+QS+SS-ThM4 Interaction of Molecular O₂ with Organolead Halide Nanorods by Single-Particle Fluorescence Microscopy, *Juvinch Vicente, J. Chen,* Ohio University
The photoluminescence (PL) of organolead halide perovskites (OHPs) is sensitive to its surface conditions, especially surface defect states, making the PL of small OHP crystals an effective way to report their surface states. At the ensemble level, when averaging a lot of nanocrystals, the photoexcitation of OHP nanorods under inert nitrogen (N_2) atmosphere leads to PL decline, while subsequent exposure to oxygen (O_2) results to reversible PL recovery. At the single-particle level, individual OHP nanorods photoblinks, whose probability is dependent on both the excitation intensity and the O_2 concentration. Combining the two sets of information, we are able to quantitatively evaluate the interaction between a single surface defect and a single O_2 molecule using a kinetic model. This model provides fundamental insights that could help reconcile the contradicting views on the interactions of molecular O_2 with OHP materials and help design a suitable OHP interface for a variety of applications in photovoltaics and optoelectronics.

9:20am 2D+EM+MI+NS+QS+SS-ThM5 Complementary Growth of 2D Transition Metal Dichalcogenide Semiconductors on Metal Oxide Interfaces, *T.E. Wickramasinghe, Gregory Jensen, R. Thorat,* Nanoscale and Quantum Phenomena Institute*; S.H. Aleithan,* Nanoscale and Quantum Phenomena Institute, Saudi Arabia*; S. Khadka, E. Stinaff,* Nanoscale and Quantum Phenomena Institute
A chemical vapor deposition (CVD) growth model will be presented for a technique resulting in naturally formed 2D transition metal dichalcogenide (TMD) based metal-oxide-semiconductor structures. The process is based on a standard CVD reaction involving a chalcogen and transition metal oxide-based precursor. Here however, a thin metal oxide layer, formed on lithographically defined regions of a pure bulk transition metal, serves as the precursor. X-ray diffraction and cross -sectional SEM studies show insight into the type and thickness of the metal oxide created during optimal growth conditions. The chalcogen reacts with the metal oxide, forming TMD material which migrates outward along the substrate, leading to lateral growth of highly-crystalline, mono-to-few layer, films. In addition to displaying strong luminescence, monolayer Raman signatures, and relatively large crystal domains, the material grows deterministically and selectively over large regions and remains connected to the bulk metallic patterns, offering a scalable path for producing as-grown two-dimensional materials-based devices.

9:40am 2D+EM+MI+NS+QS+SS-ThM6 Kagome-type Lattice Instability and Insulator-metal Transition in an Alkali-doped Mott Insulator on Si(111), *Tyler Smith, H. Weitering,* University of Tennessee Knoxville
The 1/3 ML monolayer (ML) 'alpha phase' of Sn on Si(111) is a remarkable platform for the study of strong correlations in a spin ½ triangular adatom lattice. In this work, we employ an adatom doping scheme by depositing potassium onto the triangular Sn lattice. The K-atoms destabilize the parent Mott insulating phase and produce a charge-ordered insulator, revealing a rare Kagome lattice at the surface. Scanning Tunneling Microscopy and Spectroscopy reveal a phase transition from an insulating kagome lattice to a metallic triangular lattice at about 200 K. DFT band structure calculations for this kagome system [J. Ortega et al., unpublished] reveal the presence of a flat-band just below the Fermi level, making this novel system a compelling platform for hole-doping studies of magnetic and/or superconducting instabilities.

11:00am 2D+EM+MI+NS+QS+SS-ThM10 Chemical Migration and Dipole Formation at TMD/TI Interfaces, *Brenton Noesges, T. Zhu,* The Ohio State University*; D. O'Hara,* University of California, Riverside*; R. Kawakami, L.J. Brillson,* The Ohio State University
Proximity effects at the interface between two materials can induce physical properties not present in either material alone. Topological insulators (TIs) such as Bi_2Se_3 with non-trivial surface states are sensitive to interface proximity effects where overlayers and adsorbates can act as a dopant source, chemically interact with the TI surface, or couple across the

---

[1] **National Student Award Finalist**

TI surface states leading to novel quantum phases. Transition metal dichalcogenides (TMDs), a class of 2D van der Waals materials, are a promising candidate to control this interface given the shared general hexagonal symmetry and wide range of TMD properties. However, the interface between TMDs and Bi_2Se_3 can be more complex than the ideal van der Waals interface. Chemical species exchange like metal cation exchange and selenium migration from substrate to growing film can impact the structure and properties of either layer. Self-assembly mechanisms have also been observed where complete metal monolayers form inside the Bi_2Se_3 quintuple layer [1]. We used x-ray photoelectron spectroscopy (XPS) connected in vacuo via UHV suitcase to a molecular beam epitaxy (MBE) system to investigate chemical interaction at the interface between selenide TMDs and Bi_2Se_3. Air-free transferring is crucial to minimize contamination at the interface and prevent oxidation in the air-sensitive TMDs. We compare the effects of ultrathin pure Mn metal overlayers and monolayer $MnSe_x$ on Bi_2Se_3 to pristine Bi_2Se_3. In the case of pure Mn metal on Bi_2Se_3, Bi core levels exhibit a 1.7 eV shift toward lower binding energies while the Mn core levels also show signs of Mn-Se bonding. These core level changes indicate that, in the absence of excess Se during growth, Mn pulls Se from the substrate leaving behind Bi_2 bilayers near the surface. Depositing a monolayer of $MnSe_x$ produces very different results than the pure metal case. Bi_2Se_3 core levels measured below the monolayer $MnSe_x$ film exhibit a rigid 0.8 eV chemical shift toward higher binding energies indicative of surface/interface dipole formation. The presence of this dipole is likely due to growth of primarily α-MnSe instead of the $1T$-$MnSe_2$ 2D phase [2]. Scanning tunneling microscopy (STM) height maps and spectroscopy data provide further evidence of majority α-MnSe formation. XPS core level analysis combined with controlled depositions, air-free transfers and surface analysis can provide a consistent explanation of chemical diffusion and dipole formation at a TMD/TI interface. This work is supported by NSF MRSEC under award number DMR-1420451.

[1] J. A. Hagmann et al., New J. Phys. 19, 085002 (2017).

[2] D.J. O'Hara et al. Nano Lett., 18(5), 3125-3131 (2018).

11:20am **2D+EM+MI+NS+QS+SS-ThM11 Atomically Resolved Electronic Properties of Defects in the in-plane Anisotropic Lattice of ReS_2**, *Adina Luican-Mayer*, University of Ottawa, Canada

Among the layered transition metal dichalcogenides, the compounds that exhibit in-plane anisotropy are of particular interest as they offer an additional tuning knob for their novel properties. In this talk, we present experimental evidence of the lattice structure and properties of semiconducting ReS_2 by using scanning tunneling microscopy and spectroscopy (STM/STS). We demonstrate that rhenium atoms form diamond-shaped clusters, organized in disjointed chains and characterize the semiconducting electronic band gap by STS. When imaging the surface of ReS_2, we encounter "bright" or "dark" regions indicating the presence of charged defects that will electrostatically interact with their environment. By spatially mapping the local density of states around these defects, we explore their origin and electrostatic nature. Experimental results are compared with ab-initio theory.

12:00pm **2D+EM+MI+NS+QS+SS-ThM13 Size-independent "Squeezed" Shape of Metal Clusters Embedded Beneath Layered Materials**, *A. Lii-Rosales*, Ames Laboratory and Iowa State University; *S. Julien, K.-T. Wan,* Northeastern University; *Y. Han,* Ames Laboratory and Iowa State University; *K.C. Lai,* Iowa State University; *M.C. Tringides, J.W. Evans, Patricia A. Thiel,* Ames Laboratory and Iowa State University

We have developed a continuum elasticity model for metals embedded beneath the surfaces of layered materials. The model predicts that the equilibrated cluster shape is invariant with size, manifest both by constant side slope and by constant aspect ratio (width:height ratio). This prediction is rationalized by dimensional analysis of the relevant energetic contributions. The model is consistent with experimental data for Cu and Fe clusters embedded in graphite, especially in the limit of large clusters. For comparison, we have performed a Winterbottom analysis of the equilibrium shape of an uncovered Cu cluster supported on top of graphite. The aspect ratio of the embedded cluster is about an order of magnitude higher than that of the supported cluster. Analysis of key energetics indicates that this is due to the strain energy (resistance to deformation) of the top graphene membrane, which effectively squeezes the metal cluster and forces it to adopt a relatively low, flattened shape. These insights may be useful for developing components such as metallic heat sinks or electrodes in electronic devices that use two-dimensional or layered materials.

Magnetic Interfaces and Nanostructures Division
Room A210 - Session MI+2D+AS+EM-ThM

Novel Magnetic Materials and Device Concept for Energy efficient Information Processing and Storage

Moderators: Mikel B. Holcomb, West Virginia University, Markus Donath, Westfälische Wilhelms-Universität Münster, Germany

8:00am **MI+2D+AS+EM-ThM1 Using Novel Magnonic Device Concepts for Efficient Information Processing**, *Burkard Hillebrands,* Technical University Kaiserslautern, Germany **INVITED**

In the field of magnonics, wave-based logic devices are constructed and studied based on the utilization of spin waves and their quanta - magnons. The field is developing rapidly due to its potential to implement innovative ways of data processing as a CMOS complementary technology. Basic building blocks of magnonics have already been realized. Examples are linear and nonlinear spin-wave waveguide structures, magnonic logic, as well as magnonic amplifiers such as the magnon transistor and parametric amplification.

In this talk, I will give an overview about the fundamentals and the current trends in magnonics. One topic is the realization of new functionalities and devices by using novel concepts borrowed from integrated optics and combining them with the specific advantages found in magnetic systems. Examples are directional couplers and quantum-classical analogy devices, such as a magnonic Stimulated Raman Adiabatic Passage (STIRAP) device.

Another important direction is to use fundamentally new macroscopic quantum phenomena such as a Bose-Einstein condensate (BEC) at room temperature as a novel approach in the field of information processing technology. Very promising is the use of magnon supercurrents driven by a phase gradient in the magnon BEC. I will demonstrate evidence of the formation of a magnon supercurrent along with second magnonic sound, and its spatiotemporal behavior, which is revealed by means of time- and wavevector-resolved Brillouin light scattering (BLS) spectroscopy. I will conclude with an outlook.

8:40am **MI+2D+AS+EM-ThM3 Spin-Polarized Scanning Tunneling Microscopy of <10 nm Skyrmions in $SrIrO3$/$SrRuO3$ Bilayers**, *Joseph Corbett, J. Rowland, A. Ahmed, J.J. Repicky,* The Ohio State University; *K. Meng,* The Ohio State Univesity; *F.Y. Yang, M. Randeria, J.A. Gupta,* The Ohio State University

We imaged isolated <10 nm sized skyrmions in $SrIrO_3$ on $SrRuO_3$ by spin-polarized scanning tunneling microscopy. We fabricated bilayers of 2 unit cells of $SrIrO_3$ atop of 10 unit cells of $SrRuO_3$ via off-axis sputtering. This thickness combination was selected because it showed a strong topological hall signal. We observed a granular morphology of $SrIrO_3$ mounds with rare patches of exposed $SrRuO_3$. We can distinguish $SrIrO_3$ from $SrRuO_3$ by scanning tunneling spectroscopy where, $SrIrO_3$ grains show a gap-like feature, while $SrRuO_3$ have states near the Fermi level. The height histogram of the observed granular structures is consistent with an average of 2 unit cells of $SrIrO_3$. The grains of the $SrIrO_3$ appear to act as a nucleation for skyrmion formation. Similarly, we've imaged skyrmions under applied +/- 1 T fields demonstrating their magnetic character by observing an inversion in magnetic contrast. We found that the number of $SrIrO_3$ unit cells did not determine skyrmion formation, but the size of the skyrmion was linked to the grain size, i.e. the skyrmion formed roughly the size of the grain. Furthermore, we've been able to manipulate the skyrmions by utilizing the influence of the tip. On-going investigations into the mechanism of the magnetic manipulation of the skyrmion are underway, as well theoretical modeling of the isolated skyrmion to ascertain the local Dzyaloshinskii-Moriya interaction constant.

9:00am **MI+2D+AS+EM-ThM4 Relieving YIG from its Substrate Constraints - YIG Resonators on Various Crystalline Substrate Materials**, *Georg Schmidt,* Martin-Luther-Universität Halle-Wittenberg, Germany **INVITED**

We have recently demonstrated the fabrication of free-standing 3D yttrium iron garnet (YIG) magnon nano-resonators with very low damping [1]. At first the resonators were fabricated on gallium gadolinium garnet (GGG) substrates which are most suitable for epitaxial deposition of YIG. The process involves room temperature deposition and subsequent annealing. Transmission electron microscopy investigation of the bridge-like structures shows that the span of the bridge is almost monocrystalline while some defects nucleate at the transitions from the span to the posts of the bridge which are epitaxially bound to the substrate. This suggests that the quality of the span may only indirectly depend on the quality of the feet, the latter being largely determined by the lattice matching of the

substrate material to the YIG. Being able to grow YIG structures on substrate materials other than GGG would not only be interesting because of availability and price but also because the high frequency properties of GGG are less than ideal while other materials like MgO or Sapphire would be preferred for high frequency applications. We have fabricated YIG bridges on various substrate materials including yttrium aluminium garnet (YAG), MgO, and sapphire. In most cases we achieve high crystalline quality of the span even for non-matching substrates. For some of the materials time resolved magneto optical Kerr microscopy even reveals magnon resonances with reasonable linewidth.

[1] F. Heyroth et al. cond-mat.1802.03176

9:40am MI+2D+AS+EM-ThM6 Magnetic Textures in Chiral Magnet MnGe Observed with SP-STM, *Jacob Repicky*, J.P. Corbett, T. Liu, R. Bennett, A. Ahmed, The Ohio State University*; J. Guerrero-Sanchez,* National Autonomous University of Mexico*; R. Kawakami, J.A. Gupta,* The Ohio State University

Materials with non-centrosymmetric crystal structures can host helical spin states including magnetic skyrmions. Bulk MnGe hosts a short period magnetic state (3 nm), whose structure depends strongly on atomic lattice strain, and shows a large emergent transport signature associated with the skyrmion phase. Here, we use low-temperature (5 K) spin-polarized scanning tunneling microscopy (SP-STM) to image the magnetic textures in MnGe thin films grown via molecular beam epitaxy and study the influence of the surface on those textures. Most microscopic locations show a spin spiral phase with a 6-8 nm period and a propagation direction that is influenced by step edges and surface termination. We also report the presence of isolated target skyrmions which have a triangular shape that appears to be set by the in-plane lattice vectors, and a core size of approximately 15 nm. We observe the target state is significantly more sensitive to magnetic fields than the spiral phase, and that local voltage and current pulses with the STM tip imply the texture can be 'switched' between states with different topological charge. Detailed analysis of atomic resolution STM images is used to probe the role of small lattice strain on the distinct textures. To fully understand the magnetic textures in MnGe we will expand this study by investigating films of different thicknesses to vary the magnetic anisotropy and strain.

Funding for this research was provided by the Defense Advanced Research Projects Agency Grant No. 18AP00008

11:00am MI+2D+AS+EM-ThM10 Dzyaloshinskii-Moriya Interaction in Magnetic Multilayers, *Hans Nembach,* National Institute of Sandards and Technology (NIST) **INVITED**

The Dzyaloshinskii-Moriya Interaction (DMI) gives rise to chiral magnetic structures, which include chiral spin-chains and skyrmions. The latter have recently received much attention, especially for their potential application for magnetic data storage. Each skyrmion would represent a bit and would be moved along a racetrack. DMI requires broken inversion symmetry and can exist in the bulk as well as at interfaces, for example at interfaces between a ferromagnet and a material with large spin-orbit coupling like heavy metals. More recently it has been shown that interfacial DMI can also exist at interfaces with graphene and oxides.

We use Brillouin Light Scattering spectroscopy (BLS) to determine the DMI from the non-reciprocal frequency-shift Damon-Eshbach spin-waves. In order to gain deeper insight into the underlying physics of DMI, we prepared several sample series to study different aspects of the DMI. First, we prepared two samples series to study the relationship between the DMI and the Heisenberg exchange. One series was a $Ni_{80}Fe_{20}$ thickness series on a Pt layer and for the other series we introduced a Cu dusting layer at the interface between a CoFeB layer and Pt to disrupt the Heisenberg exchange directly at the interface. For both sample series, we found that the Heisenberg exchange and the DMI are proportional to each other as it has been predicted by theory. Next, we prepared a $Cu/Co_{90}Fe_{10}$ and a $Pt/Co_{90}Fe_{10}$ sample series, which were in-situ oxidized for different times and subsequently capped to prevent any further oxidation. Density functional theory calculations have shown that the hybridization and the associated charge transfer is important for the DMI and that interfaces with an oxide can have DMI. Our BLS measurements showed that oxide interfaces have DMI. Moreover, we showed that the spectroscopic splitting factor g, which we determined with ferromagnetic resonance spectroscopic, is correlated to the DMI. This is an indirect confirmation of the theory predictions regarding the role of hybridization and charge transfer.

So far, most work on DMI has been carried out for highly symmetric interfaces. Low symmetry systems can have anisotropic DMI and can potentially support anti-skyrmions. We prepared a Pt/Fe(110) sample and found that the DMI is anisotropic with the strongest DMI along the [001] direction, which coincides with the magnetic easy axis.

Finally, we studied the impact of He^+ ion irradiation on DMI for the Ta/CoFeB/Pt system. We found that the DMI increases with the dose before it drops for the highest does. This is in contrast to the perpendicular anisotropy, which continuously decreases with ion-irradiation.

11:40am MI+2D+AS+EM-ThM12 Transport in Goniopolar and (pxn) Metals, *Joseph Heremans, B. He, L. Zheng, Y. Wang, M.Q. Arguilla, N.D. Cultrara, M.R. Scudder, J.E. Goldberger, W. Windl,* The Ohio State University **INVITED**

semiconductors that have *p*-type conduction along some crystallographic directions and *n*-type conduction along others due to a particular topology of their Fermi surface. The electrical and thermoelectric transport of one member of this class, $NaSn_2As_2$, will be presented. A second class of materials have similar transport properties due to different mechanisms: some, like Be and Cd, have Fermi surfaces that contain both electron and hole pockets that have partial thermopowers of opposite polarities, but very anisotropic mobilities, so that one carrier type dominates the total thermopower in one direction, and the other carrier type dominates the thermopower in the other direction. A new member of this class, the semimetal bismuth doped p-type with Sn, will be described in this talks as well. In practice, a third class of artificial materials made of separate layers of p-type and of n-type semiconductors can be made to have a similar behavior in transport as well; the last two classes are called (pxn)-materials.

The electrical conductivity and thermopower tensors in goniopolar and (pxn) materials can be made to have off-diagonal components, which cause exciting new properties like zero-field Hall and Nernst-Ettingshausen effects. These materials can be used in single-crystal transverse thermoelectrics.

[1] He, B. et al , *Nat. Mater.* (published online doi.org/10.1038/s41563-019-0309, 2019)

[2] Zhou, C. et al. *Phys. Rev. Lett.* **110**, 227701 (2013).

Magnetic Interfaces and Nanostructures Division
Room Union Station B - Session MI-ThP

Magnetic Interfaces and Nanostructures Poster Session

MI-ThP1 Room Temperature Skyrmion in Alternative Layer Molecular Beam Epitaxial Grown B20 Fe-rich $Fe_{1.2}Ge$ Films, *Tao Liu*, R. Bennett, S. Chen, A. Ahmed, R. Kawakami, The Ohio State University
Magnetic Skyrmions are localized, topological spin textures that arise from competition between exchange interaction and Dzyaloshinskii-Moriya interaction (DMI) in magnetic materials with broken inversion symmetry. Their topological stability, small size, and the ability to be very energy efficiently written, read and manipulated, put them at the forefront of candidates for next generation storage technology. However, it is still challenging to find a material which can achieve skyrmion at room temperature with size no more than 10 nm, which has already become a major bottleneck of their developments. In order to realize this goal, it requires strong exchange interaction strength J, which sets the temperature scale, and a large DMI strength D that determines skyrmion stability and size, Ja/D (a is the atomic lattice spacing). Current skyrmion research is focused on two classes of materials: metallic multilayers and B20 crystals. Neither of them can meet this challenge. Metallic multilayers can meet the criteria of room temperature operations, but with small DMI arising from surface inversion symmetry broken. B20 crystals have a large bulk DMI and nanoscale skyrmions with sizes down to 3 nm, but cannot achieve room temperature operations.

In this work, we successfully synthesized Fe-rich $Fe_{1.2}Ge$ films by alternative layer molecular beam epitaxy at room temperature and adding extra Fe atoms at the Fe-sparse atomic layers. As shown in figure 1, the cross sectional TEM result indicated that the Fe-rich $Fe_{1.2}Ge$ film is B20 structure. Its XRD peak position shift to a lower angle relative to FeGe film, which might be good evidence indicating the extra Fe atoms went into the B20 structure rather than formed another stucture phase. The Curie Temperature of the Fe-rich $Fe_{1.2}Ge$ film has been pushed above room temperature (RT), and the observing of clear topological Hall resistance with maximum value around $H=\pm1.5$ kOe could be the result of stabilization of RT skymrmion.

MI-ThP2 Investigation of Exchange Bias in $L1_0$- MnGa/ θ-MnN/MgO Bilayers, *Sneha Upadhyay*, Ohio University; *K. Meng, F.Y. Yang,* The Ohio State University; *D. Ingram, A.R. Smith,* Ohio University
Exchange bias, a shift in the center for the magnetic hysteresis loop of a magnetic material, has gained a lot of attention due to its application in spintronics. Generally, exchange bias is observed in layered magnetic structure like antiferromagnetic/ferromagnetic bilayers. In this work, the $L1_0$ MnGa (T_c= 590K) / θ-MnN (T_N= 660K) bilayer on MgO substrate was studied for the investigation of exchange bias motivated by the recent report of giant exchange bias using MnN as the antiferromagnet.[1]

These bilayers were prepared using molecular beam epitaxy, and the growth was monitored by *in-situ* RHEED. Three samples were grown with MnN thickness of 47 nm while $L1_0$ MnGa thicknesses were varied from 15nm, 3nm and 1 nm. During the growth, RHEED images were taken which showed some disorder and roughness on the surfaces especially for thinner ones. In order to observe exchange bias, these samples were field cooled through the Néel temperature and the hysteresis was taken at a specific applied field using SQUID. The measurements showed the presence of a small but finite exchange bias in the case of the 3 nm L10 MnGa/θ-MnN sample in the *in-plane* direction only, and the amount of loop shift from the origin was estimated to be 300 Oersted. The results were compared with the recent publication for the case of CoFeB/ θ-MnN which showed giant exchange bias (3600 Oersted).

Although the field cooling procedure is important to observe exchange bias, in our previous measurements, we were unable to field cool through the high Néel temperature of MnN. Currently, we are working on a new field cooling capability in our MBE chamber and further plan to study the sample using *in-situ* spin-polarized scanning tunneling microscopy under an applied magnetic field. We also plan to repeat the SQUID measurements as well with the high-temperature, field-cooled sample.

[1] P. Zilske, D. Graulich, M. Dunz, and M. Meinert, "Giant perpendicular exchange bias with antiferromagnetic MnN," *Appl. Phys. Lett.* **110**, 192402 (2017).

MI-ThP3 Investigating a Possible Kondo Resonance for Iron-induced Islands on Chromium Nitride (001), *K. Alam, Y. Ma, Shyam Chauhan, S.R. Upadhyay, A.R. Smith,* Ohio University
Chromium and iron surfaces have been of intense interest due to their high technological importance. Stroscio *et al.* investigated the electronic states of Fe(001) and Cr(001) surfaces using room temperature scanning tunneling spectroscopy, finding surface state peaks at +170 meV and -50 meV, respectively, relative to the Fermi level and enabling a chemical identification of surface elemental species in FeCr alloys.[1] Later, Hanke *et al.* measured the temperature-dependent spectroscopy on Cr(001) surfaces and found that both orbital Kondo effect and single-particle models could be used to reasonably interpret the observed temperature-dependent Cr(001) surface peak seen at 20 meV above E_F.[2]

Recently, we have carried out a study of Fe on CrN(001) surfaces exhibiting a step-terrace morphology as grown by molecular beam epitaxy. These CrN samples are antiferromagnetic below 270 K.[3] We performed STS spectroscopy on, and between, nanometer-sized islands resulting from sub-ML Fe deposition. Spectroscopy on the clean CrN regions displays a broad dip near E_F and a peak at 125 meV, similar to the oxygenated Cr surface reported by Hanke et al. Whereas spectroscopy on the islands displays sharp spectral features exactly at, or within a few meV of, E_F. We make a case for interpreting these spectra in terms of a Kondo resonance.

[1] Stroscio et al., Phys. Rev. Lett. **75**, 2960 (1995).

[2] Hanke et al., Phys. Rev. B **72**, 085453 (2005).

[3] Alam et al., Phys. Rev. B **96**, 104433 (2017).

MI-ThP5 Characteristics of a Single Molecule Magnet on Graphene: A DFT Study, *Rainier Berkley*, Z. Hooshmand, T.S. Rahman, University of Central Florida
Single-molecular magnets (SMMs) are molecules that function as nanoscale magnets below their blocking temperature. These systems have become of increasing interest due to their potential applications for magnetic technologies, since they display many unique quantum phenomena and their structures can be tuned to modify their magnetic and quantum properties. However, in order for SMMs to be applicable for magnetic technology they must retain stability both in their structures and their magnetic moments during and after the deposition process. Due to the complicated nature of magnetic interactions with substrates, the effects of magnetic materials on substrates are not fully understood. Therefore, in order to fully understand these systems a study of the interactions between a well-characterized SMM and substrate at the most fundamental level is required. For this purpose, we have studied the interactions of a [Mn3]2 dimer1 with graphene using Density Functional Theory (DFT) calculations. The [Mn3]2 dimer can exhibit two different ground states: ferromagnetic (FM) and anti-ferromagnetic (AFM). Our calculations for the spin of both the FM and AFM configurations of the isolated [Mn3]2 dimers in gas phase, agree with experimental results (S=12 and 0 respectively)1 only when the dimers are charged (+2). More importantly, our calculations reveal that graphene is inert; thus, hardly affecting the magnetic properties of the FM and AFM dimers and that both dimers display the same spin as in their isolated gas phase structures after deposition. These results are further confirmed by charge redistribution analysis in which there are no strong charge distribution from/to molecules to/from graphene and the spin density remains almost intact after interactions of molecules with substrate. Our results provide insights into the design of coupled SMM/substrate systems, namely [Mn3]2 dimer on graphene.

1 Nguyen et al. J. Am. Chem. Soc. 2015, 137, 7160–7168.

* This work is supported by DOE-DE-SC0019330

MI-ThP6 Molecular Conductivity Switching via Voltage Controlled Spin Crossover at a Ferroelectric Interface, *Aaron Mosey*, Indiana University-Purdue University Indianapolis; *G. Hao,* University of Nebraska-Lincoln; *A.T. N'Diaye,* Lawrence Berkeley National Laboratory; *A.S. Dale,* Indiana University-Purdue University Indianapolis; *U. Manna,* Illinois State University; *P.A. Dowben,* University of Nebraska-Lincoln; *R. Cheng,* Indiana University-Purdue University Indianapolis
The scale of new micro and nano magneto-electronic devices is bounded by thermal and quantum constraints as predicted by Moore's Relation. This necessitates a push into the limits of harnessable natural phenomena to facilitate a post-Moore's era of design. Thermodynamic stability at room temperature, fast (Ghz) switching, and low energy cost narrow the list of candidates. Molecular electronic frontier orbital structure of Fe ions in octahedral fields will split in response to the local energetic environment, giving rise to the e_g and t_{-2g-} suborbitals. The energetic scale between these

two orbitals as a result of this deformation yields a low spin diamagnetic state or an S=2 high spin paramagnetic state. Spin crossover complex [Fe(II)(H$_2$B(pyz)$_2$(bipy))$_2$] will show locking of its spin state well above the transition temperature, with an accompanied change of conductivity, when placed in a polar environment. Here we show voltage controllable, room temperature, stable locking of the spin state, and the corresponding conductivity change, when molecular thin films of [Fe(II)(H$_2$B(pyz)$_2$(bipy))$_2$] are deposited on a ferroelectric polyvinylidene fluoride hexafluropropylene substrate. This opens the door to the creation of a thermodynamically stable, room temperature, multiferroic gated voltage device.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index

Author Index

Zheng, L.: MI+2D+AS+EM-ThM12, 33
Zhou, T.: 2D+AP+EM+MI+MN+NS+PS+TF-MoA5, 7
Zhu, M.: 2D+EM+MI+MN+NS+QS-TuM5, 13

Zhu, T.: 2D+EM+MI+MN+NS+QS-TuM5, **13**; 2D+EM+MI+NS+QS+SS-ThM10, 31
Zieve, R.J.: AC+LS+MI-MoM5, **2**
Zou, Q.: 2D+EM+MI+MN+NS+QS-TuM11, **14**; MI+2D-WeM2, 25

Zurbuchen, M.: MI+2D-WeA10, 29
Zutic, I.: 2D+AP+EM+MI+MN+NS+PS+TF-MoA5, 7
Zwicknagl, G.E.: AC+LS+MI-MoM8, **3**