

Monday Morning, October 21, 2019

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 MoS₂ on SrTiO₃ Single Crystal Substrates**, *Peiyu Chen, W. Xu, Y. Gao, P. Holdway, J.H. Warner, M.R. Castell*, University of Oxford, UK

Monolayer MoS₂ crystals grown on amorphous substrates such as SiO₂ are randomly oriented. However, when MoS₂ 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 MoS₂ on three different terminations of single crystal strontium titanate (SrTiO₃) substrates: (111), (110), and (001). On all three terminations of SrTiO₃, the monolayer MoS₂ crystals try to align their <2 -1 0>-type directions (i.e., the sulfur-terminated edge directions) with the <-1 -1 0>-type directions on SrTiO₃. This arrangement allows near-perfect coincidence epitaxy between seven MoS₂ unit cells and four SrTiO₃ unit cells. On SrTiO₃(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 MoS₂ monolayers and SrTiO₃ is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this study is that the vdW interaction between MoS₂ and SrTiO₃ substrates determines the supported crystal shapes and orientations by epitaxial relations.

Monolayer MoS₂ 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 MoS₂ supported on SrTiO₃ in ultrahigh vacuum (UHV) because of sulfur loss. MoS₂ was found to degrade on the (111), (110), and (001) terminations of SrTiO₃ 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 MoS₂ crystals (in scanning tunneling microscopy). The sulfur vacancies can be filled by annealing the crystals in a hot sulfur atmosphere, and the optical properties (by Raman spectroscopy and PL) of monolayer MoS₂ can nearly be fully recovered. At higher UHV annealing temperatures, the remaining Mo is oxidized by the SrTiO₃ substrates into MoO₂ and MoO₃. 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 MoS₂ crystal shapes are stable upon annealing until the residual MoO₃ 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 MoS₂.

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), MoS₂ and WS₂, 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, MoS₂ and WS₂ were found to reduce friction in 3D printed PETG and ABS. Graphite being an intrinsically good conductor, while the other 2DLMs explored, specifically MoS₂ and WS₂ 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, MoS₂ and WS₂, 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 WS₂ 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 WS₂ 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 capacitive heterostructure devices were formed with these materials. From this analysis, the photoresponsivity and detectivity of the graphene-WS₂-graphene heterostructure devices were calculated to be ~ 0.86 A/W and ~ 10¹³ 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-WS₂ 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)

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heterostructure devices. Two distinct examples of gate-tunable p-n heterojunctions with anti-ambipolar field effect 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 (MoS₂, WS₂ and WSe₂) 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.

Atomic Scale Processing Focus Topic

Room A214 - Session AP+2D+EM+PS+TF-MoM

Area Selective Deposition and Selective-Area Patterning

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Eric A. Joseph, IBM T.J. Watson Research Center

8:40am **AP+2D+EM+PS+TF-MoM2** **Surface Pre-functionalization of SiN_x and SiO₂ to Enhance Selectivity in Plasma-Assisted Atomic Layer Etching**, *Ryan Gasvoda*, Colorado School of Mines; *Z. Zhang, S. Wang, E.A. Hudson*, Lam Research Corporation; *S. Agarwal*, Colorado School of Mines

To manufacture semiconductor devices in the current sub-7-nm node, stringent processing windows are placed on all aspects in manufacturing including plasma-etching. In recent years, atomic layer etching (ALE) has emerged as a patterning technique that can provide high etch fidelity, directionality, layer-by-layer removal, and selectivity to meet the tight processing windows. Plasma-assisted ALE of SiO₂ and SiN_x is of particular interest since Si-based dielectrics are commonly used throughout the entire fabrication process. Typically, these materials are etched in a cyclic ALE process consisting of two sequential half-cycles: fluorocarbon (CF_x) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Etch selectivity can be achieved through careful manipulation of the plasma and processing parameters. To further increase overall etch selectivity, we have proposed a methodology that selectively pre-functionalizes the SiO₂ or SiN_x surface with hydrocarbons prior to ALE. Recently, we showed that an etch blocking graphitic hydrofluorocarbon film will readily accumulate on a pre-functionalized SiO₂ surface.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* 4-wavelength ellipsometry to monitor the surface reactions, film composition, and net film thickness during the entire ALE process. We show that aldehydes can be used to functionalize SiN_x with extremely high selectivity to SiO₂ surfaces. During ALE on bare SiN_x, a thick graphitic fluorocarbon film accumulates on the surface and can stop all etching after cycle 5. This is attributed to inefficient removal of both the C and N from the surface. To enhance removal and prevent graphitic carbon accumulation, we graft a branched hydrocarbon aldehyde to the SiN_x surface. This branched hydrocarbon provides an abundance of -CH₃ groups which allows for greater C and N removal possibly via HCN formation, thus lowering overall graphitic carbon formation. This retardation of the graphitic hydrofluorocarbon film formation leads to both an overall increase in the etch per cycle and the number of ALE cycles that can be run before an etch stop is observed.

9:00am **AP+2D+EM+PS+TF-MoM3** **Area-selective Atmospheric-pressure Spatial ALD of SiO₂ using Interleaved Back-etch steps Yielding Selectivity > 10 nm**, *A. Mameli*, Holst Centre / TNO, The Netherlands; *F. Roozeboom, Paul Poedt*, Holst Centre / TNO, The Netherlands, Netherlands

Area-selective atomic layer deposition (AS-ALD) has great potential in reducing cost by maskless device manufacturing of patterned layers. Still, in this new *bottom-up* approach the selectivities currently obtained for film growth on patterned growth areas vs. that on the non-growth areas are often very limited. Also the substrate throughput values for conventional low-pressure ALD is too low for industrial acceptance.^(1,2) In this work we present a process for AS-ALD of SiO₂ using intermittent plasma etch-back steps to increase the selectivity above 10 nm film thickness.⁽³⁾ In addition, the deposition process itself is performed in a spatial ALD reactor at atmospheric pressure which allows for achieving high throughput.⁽⁴⁾

AS-ALD of SiO₂ on a substrate with pre-patterned SiO₂ and ZnO areas was demonstrated using a highly chemo-selective inhibitor that chemisorbs preferentially on the non-growth area (ZnO) while allowing the deposition of SiO₂ on the growth area (SiO₂). In order to maximize the process selectivity, a blanket fluorocarbon plasma etch-back step was interleaved after every 110 ALD cycles. This way, selective SiO₂ deposition up to ~ 30 nm film thickness was demonstrated. Furthermore, X-ray Photoelectron Spectroscopy was carried out to verify the selectivity of the process: no Si was detected (detection limit 0.3 at. %) on the non-growth area, demonstrating the high selectivity of the process.

The process presented here combines selective inhibitor chemisorption, plasma-based spatial ALD with high deposition rates and plasma etch-back steps to correct for selectivity loss. This approach is compatible with *roll-to-roll* and *sheet-to-sheet* concepts and can therefore enable high-throughput AS-ALD on large-area and flexible substrates.

[1] A. Mameli, *et al.*, *ACS Nano*, **11**, 9303 (2017).

[2] F.S.M. Hashemi, *et al.*, *ACS Nano*, **9**, 8710 (2015).

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[3] R. Vallat, *et al.*, *J. Vac. Sc. Technol. A*, **35**, 01B104 (2017).

[4] P. Poodt, *et al.*, *Adv. Mater.*, **22**, 3564 (2010).

9:20am **AP+2D+EM+PS+TF-MoM4 Mechanisms of Precursor Blocking during Area-selective Atomic Layer Deposition using Inhibitors in ABC-type Cycles**, *M.J.M. Merckx*, Eindhoven University of Technology, The Netherlands; *D.M. Hausmann*, Lam Research Corporation; *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands; *T.E. Sandoval*, Universidad Técnica Federico Santa María, Chile; *Adrie Mackus*¹, Eindhoven University of Technology, The Netherlands, Nederland

The development of new processes for area-selective atomic layer deposition (ALD) is currently motivated by the need for self-aligned fabrication schemes in semiconductor processing. For example, area-selective ALD processes for dielectric-on-dielectric deposition are being considered for fully self-aligned via (FSAV) fabrication schemes in advanced interconnect technology.

Instead of solely relying on surface functionalization prior to ALD, a novel strategy to area-selective ALD involves the dosing of inhibitor molecules during every cycle in an ABC-type recipe.^{1,2} By using small molecules that can be dosed in vapor-phase as inhibitor, this approach is compatible with industrial process flows. Moreover, the reapplication of the inhibitor molecules during every cycle allows for the use of a plasma as the co-reactant, which broadens the range of materials that can be deposited selectively. In contrast to conventional approaches to area-selective ALD based on self-assembled monolayers (SAMs), very little is known about how small inhibitor molecules can block the ALD growth.

In this contribution, insight into the mechanisms of precursor blocking by inhibitor molecules as obtained from in-situ Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT) calculations will be discussed. Area-selective ALD of SiO₂ using acetylacetone (Hacac) as inhibitor will be described as a model system, illustrating various mechanisms that can contribute to the loss of selectivity. It was found that at saturation, Hacac adsorbs through a mixture of chelate and monodentate bonding configurations. Hacac in monodentate configuration is displaced from the surface when exposed to bis(diethylamino)silane precursor molecules, which limits the selectivity. Strategies for improving the selectivity based on the understanding from these studies will be discussed.

¹ A. Mameli, M.J.M. Merckx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, and A.J.M. Mackus, *ACS Nano* **11**, 9303 (2017).

² A.J.M. Mackus, M.J.M. Merckx, and W.M.M. Kessels, *Chem. Mater.* **31**, 2 (2019).

9:40am **AP+2D+EM+PS+TF-MoM5 Area-Selective Deposition of TiO₂ using Isothermal Integrated Atomic Layer Deposition and Atomic Layer Etching in a Single Reaction Chamber**, *Gregory Parsons*, *S.K. Song*, *H. Saare*, North Carolina State University

INVITED

Several new approaches are emerging where chemical etching is being coupled with atomic layer deposition to achieve area-selective deposition of dielectrics and metals. During ALD, selectivity is generally lost when undesired nuclei form on the targeted non-growth surface. These undesired nuclei can sometimes be removed by periodic etching, improving the overall selectivity. However, it is not known to what extent these coupled deposition/etching sequences can proceed while maintaining good selectivity. As desirable deposition and etching reactions proceed, other changes in the process can occur to enhance unwanted nucleation and/or impede desired etching, thereby limiting the net selectivity. Recent experiments in our lab have used in-situ probes to explore coupled thermal ALD and ALE super-cycles, performed sequentially under isothermal conditions in a single reaction chamber, to achieve area selective deposition of TiO₂ on SiO₂ with hydrogen-terminated silicon (100) as the desired non-growth surface. We find that as ALD/ALE super-cycles proceed, small changes occur in the ALD and ALE reactions, particularly during the transition from ALD to ALE, or from ALE to ALD. Also, modeling studies allow us to quantitatively analyze the ASD results and compare our findings to other known approaches. These insights will be helpful to understand opportunities and challenges in advanced atomic scale reactions and process implementation.

10:40am **AP+2D+EM+PS+TF-MoM8 Area-Selective Atomic Layer Deposition of Metal Oxides on an Inhibitor-Functionalized SiO₂ Surface**, *Wanxing Xu*, Colorado School of Mines; *P.C. Lemaire*, *K. Sharma*, *D.M. Hausmann*, Lam Research Corporation; *S. Agarwal*, Colorado School of Mines

The continued downscaling of modern semiconductor devices together with the incorporation of 3D architectures places new constraints on conventional lithography techniques. To enable further advances in patterning process, new techniques will be required for next-generation devices to overcome the challenges of limiting the growth of desired materials in a specific area. One method to address these issues is area-selective atomic layer deposition (ALD), which provides the opportunity to build defined patterns from the bottom-up at the atomic-level accuracy. In this study, we will focus on area-selective ALD of metal oxides including ZrO₂ and Al₂O₃ with a metal as the growth surface and inhibitor-functionalized SiO₂ as the non-growth surface. To inhibit ALD, the SiO₂ surfaces were functionalized with aminosilane inhibitors through the vapor phase or with a solution-based method. The functionalized SiO₂ surfaces were characterized by transmission Fourier transform infrared (FTIR) spectroscopy, ellipsometry, and water contact angle measurements. Metal oxides including ZrO₂ and Al₂O₃ were deposited by ALD using metal precursors and H₂O over a temperature range of 150-250 °C. *In situ* attenuated total reflection FTIR spectroscopy was utilized to identify the surface reactions sites and adsorbed surface species during ALD. In addition, the corresponding film growth was measured using *in situ* four-wavelength ellipsometry.

Using *in situ* optical diagnostics, we show the mechanism for the breakdown in selectivity during area-selective ALD on a SiO₂ surface that is functionalized with aminosilanes. The infrared spectra show that aminosilane inhibitors react with almost all of the surface –SiOH groups forming Si–O–Si–R bonds on the surface (see Figure 1). After repeated exposure of the functionalized SiO₂ surface to TEMAZ and ZTB, these precursors react with Si–O–Si bonds without surface –SiOH groups (see Figure 2). Although small growth in the first few ALD cycles is not detected by *in situ* ellipsometry, growth inhibition breaks down after an increased number of ALD cycles. These results suggest that it is an additional requirement to suppress other reactions with a higher activation energy barrier during ALD expect removing main surface reactive sites through surface functionalization. To further impede growth of metal oxides on functionalized SiO₂ surface, a two-step functionalization method was developed to passivate the SiO₂ surface while providing additional steric blocking for the underlying substrates. Comparative studies were carried out to evaluate the effect of different functionalization methods on suppressing the nucleation during ALD.

11:00am **AP+2D+EM+PS+TF-MoM9 Area-selective Deposition Achieved in a Continuous Process using Competitive Adsorption**, *Taewon Suh*, *Y. Yang*, *K.U. Lao*, *R.A. DiStasio, Jr.*, *J.R. Engstrom*, Cornell University

A significant challenge for single-nm fabrication technologies is the development of area selective deposition (ASD) processes, particularly for device structures with exposed metallic and dielectric surfaces on patterned, often three dimensional, substrates. A number of techniques have been proposed and examined for ASD processes, particularly with respect to ALD, and these include the use of “permanent” blocking layers in the form of SAMs, and repetitive deposition/etch cycles. Some success has been reported with these techniques, but they possess potential drawbacks. An ideal ASD process should be fast, preferably vapor phase, and leave no residue on the non-growth surface. One technique that can possibly provide this is the use of competitive adsorption to induce area selective deposition, where a co-adsorbate is chosen that will bind much more strongly to one surface vs. another. A significant challenge concerning this approach is avoiding direct reactions between the co-adsorbate and the thin film precursor in the case of ALD, and also the co-reactant in the case of CVD. We are coupling quantum mechanical calculations of co-adsorbate/thin-film precursor/substrate interactions with experiments using our coupled micro-reactor/UHV surface analysis system. We have examined the effect of a class of unsaturated hydrocarbons as co-adsorbates on the CVD growth of ZrO₂ thin films using a Zr amido-coordination complex as the thin film precursor and O₂ as the co-reactant. The substrates were SiO₂ and Cu, and we examined the effects of both temperature, $T_s = 120-240$ °C, and the partial pressure of the co-adsorbate hydrocarbon. DFT calculations predict that the binding energies of these hydrocarbons are at least a factor of two larger on Cu vs. those on SiO₂. For CVD growth of ZrO₂ thin films as thick as 22 nm (growth rates of ~ 1 nm·s⁻¹), we find that the co-introduction of the hydrocarbon results in

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linear growth with time on a SiO₂ substrate, with no apparent incubation time, while essentially no growth is observed on Cu. *In situ*, post-deposition analysis with XPS reveals ZrO₂ thin films on SiO₂, and only adventitious carbon and less than a monolayer of Zr on the Cu surface. Consistent with a model based on competitive adsorption, we find that selectivity is eventually lost at sufficiently high substrate temperatures or sufficiently low partial pressures of the hydrocarbon co-adsorbate. Finally, we will report on the CVD growth on patterned Cu/SiO₂ substrates where we observe deposition only on those areas covered by SiO₂. We will conclude with a discussion of the promise and challenges of this approach for ASD concerning both ALD and CVD processes.

11:20am **AP+2D+EM+PS+TF-MoM10 Surface Chemistry during Plasma-Assisted ALE: What Can We Learn from ALD?**, *Sumit Agarwal*, Colorado School of Mines **INVITED**

Due to ever decreasing device dimensions and the introduction of 3D device architectures, it is challenging to operate within a narrow processing window using conventional plasma etching. One method to address the demands of the next-generation of devices is atomic layer etching (ALE) which provides high fidelity, selectivity, and directionality, and layer-by-layer removal. Plasma-assisted ALE has been extensively studied for a variety of materials, including Al₂O₃, HfO₂, Si, and Si-based dielectrics. Plasma-assisted ALE of SiO₂ or SiN_x typically uses two sequential steps in a cyclic fashion: CF_x deposition from a C₄F₈/Ar plasma followed by an Ar plasma activation step. However, the surface chemistry during plasma ALE is not well understood. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions, film composition, as well as the net film thickness. Similar to area-selective atomic layer deposition, we show that surface functionalization prior to ALE can be used to alter the etch per cycle. Using this methodology, I will discuss how selective functionalization of SiO₂ or SiN_x can be used to alter the selectivity during plasma-assisted ALE.

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 through in plane interfaces or out of plane in heterostructures.

First, we will examine selective etching with XeF₂ 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 XeF₂ 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 sp³ hybridization of the C atoms binding hydrogen. Moreover, for epitaxial Gr on metals, the substrate-induced Gr corrugation might modulate 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 moiré 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 MoS₂ and WS₂ 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. MoS₂/WS₂ vdW heterostructure arrays produced by this method were characterized, showing coupled photoluminescence between the monolayers. Light-emitting devices using WS₂ 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 MoS₂/Graphene Monolayers, *Yunqiu Kelly Luo*, The Ohio State University; *T. Zhou*, University at Buffalo, State University of New York; *M. Newburger*, The Ohio State University; *R. Bailey-Crandell*, *I. Lyalin*, The Ohio State University; *M. Neupane*, U.S. Army Research Laboratory; *A. Matos-Abiadue*, 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 MoS₂/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. MoS₂ 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 MoS₂ 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 aims to investigate the fundamental nature of bonding of graphene nanoribbons (GNRs) to the edges of MoS₂ 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 MoS₂, 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 MoS₂ 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 synthesise 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 H₂-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}²H_{6n}, C_{18n}²⁻¹⁸ⁿ⁺⁶H_{12n-6}, C_{18n}²⁻³⁰ⁿ⁺¹²H_{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, and J. 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.

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[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 for implementation 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 MoS₂ across cm² areas. Photoluminescence, Raman, XPS, and conductive AFM are used to evaluate DLI grown MoS₂, and indicate high quality material having low defect density, with metrics comparable to or better than exfoliated and chemical vapor deposition grown MoS₂.

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.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science).

3:00pm **2D+AP+EM+MI+NS+PS+TF-MoA5 Area-Selective Atomic Layer Deposition of 2D WS₂ Nanolayers**, *Shashank Balasubramanyam¹*, Eindhoven University of Technology, The Netherlands, Noord Brabant; *M.J.M. Merx*, 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 WS₂ 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 metals¹ and dielectrics² have been successfully demonstrated. However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS₂ nanolayers by using a three-step (ABC-type) plasma-enhanced ALD process.

AS-ALD of WS₂ was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H₂S plasma (C) pulses. This process resulted in immediate growth on SiO₂ while a significant nucleation delay was observed on Al₂O₃, 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 Al₂O₃ surface, blocking precursor adsorption, while little or no inhibitor adsorption was detected on the SiO₂ surface where WS₂ was readily deposited. Furthermore, the area-selective growth was demonstrated on SiO₂ samples with patterned Al₂O₃ on top. On SiO₂, WS₂ could be deposited with angstrom-level thickness control.

To improve the crystallinity, the AS-ALD WS₂ films were annealed at temperatures within the thermal budget of industrial semiconductor processing ($\leq 450^\circ\text{C}$). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS₂. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO₂-Al₂O₃ 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. Mamelì, M.J.M. Merx, 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

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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 $\sim 1030^\circ\text{C}$ 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 ($\sim 20\ \mu\text{m}$) 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 discuss 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/acsp Photonics.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 $\text{B}_2\text{O}_3/\text{Si}$ with an average growth rate of $\sim 1.4\ \text{\AA}/\text{cycle}$, 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 $>1000\ \text{K}$. 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 \AA , 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. Yaliso, **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 $< 10^\circ$ 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 $0.76\text{-}0.78\ \text{\AA}/\text{cycle}$. 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 $\sim 7\text{-}15\ \text{\AA}$ 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.

Thin Films Division

Room A124-125 - Session TF+2D+AP+EL+SS-MoA

ALD and CVD: Nucleation, Surface Reactions, Mechanisms, and Kinetics

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

1:40pm TF+2D+AP+EL+SS-MoA1 ALD on Particles: What is Different from Wafers?, **Ruud van Ommen**, Delft University of Technology, Netherlands

INVITED

Advanced materials, often relying on nanostructured particles as building blocks, are crucial in meeting grand challenges in energy and health. Atomic layer deposition (ALD) is an excellent technique to make such nanostructured particles: particles of which the surface is either covered by an ultrathin film or by nanoclusters. Although the underlying mechanisms are similar, there are quite some differences between ALD processing of wafers and ALD processing of particles. This presentation will discuss recent developments and insights in the field of applying ALD to particles, with an emphasis on reactor technology, precursor utilization, operating conditions, and scaling up. I will show that ALD is suited to produce

nanostuctured particles with very high precision. Moreover, it is scalable such that large amounts of such particles can be produced.

2:20pm TF+2D+AP+EL+SS-MoA3 Insights into Particle ALD Peculiarities from In- and Ex-Situ Characterization, Benjamin Greenberg, American Society for Engineering Education; *J.A. Wollmershauser, B. Feygelson,* U.S. Naval Research Laboratory

Particle atomic layer deposition (pALD) is an increasingly popular technique for mass production of core/shell nanoparticles (NPs). In a typical pALD process, NP powders are agitated in a fluidized bed or rotary reactor, and conformal coating of the entire powder surface—often $> 100 \text{ m}^2$ in lab-scale reactors—is attempted via prolonged precursor exposures and purges. Over the past 2+ decades there have been many reports of highly encouraging results, including TEM images of NPs individually encapsulated by shells of uniform thickness. Nevertheless, several fundamental questions about pALD mechanisms and behavior remain challenging to answer. For example, how does the pALD growth per cycle (GPC) deviate from the corresponding ALD GPC on a flat substrate, and why? Or more importantly, what conditions are required to maximize the fraction of powder that attains an ideal core/shell structure (individual NP encapsulation) rather than a coated-agglomerate structure in which cores are glued together? In this work, using a commercial rotary pALD reactor to coat various NPs with oxide shells, we employ a wide array of characterization techniques to shed light on these issues and inform process optimization. *In situ*, we experiment with relatively uncommon techniques such as high-speed video analysis and pyrometry of the agitated NP powder, as well as conventional techniques such as mass spectrometry (RGA). High-speed videos in particular reveal aspects of the process often undiscussed (and sometimes difficult to convey) in the pALD literature, including changes in the powder motion as surface chemistry evolves. *Ex situ*, we characterize the coated NPs via TEM, XRD, SAXS, XPS, and N_2 -adsorption surface area measurements (BET method).

3:00pm TF+2D+AP+EL+SS-MoA5 Controlling the Nucleation of CVD Cobalt Films on SiO_2 : Combining an Amido-based Nucleation Promotor with an Amine-based Growth Inhibitor to Afford Atomically-smooth Surfaces, Zhejun Zhang, G.S. Girolami, J.R. Abelson, University of Illinois at Urbana-Champaign

Cobalt films are of interest for the back-end metallization and transistor contact in microelectronics because cobalt has a greater electromigration resistance and a lower diffusion rate in dielectrics compared with copper. However, few-nanometer thick Co films deposited by CVD on dielectrics are usually non-continuous – they consist of islands with pinholes and significant roughness – which renders them unsuitable for nanoscale device fabrication. A nucleation layer, such as TiN, can be pre-deposited to improve the area density of Co nuclei; this approach eliminates the problem of islanding, but it subtracts cross-sectional area from the plug or line, thus increasing the electrical resistance.

Here, we solve the Co nucleation problem in CVD using a two-pronged approach. First we expose the SiO_2 surface to a tetrakis(dimethylamido)(transition metal) precursor at low temperature. This affords a self-limiting, submonolayer coverage of an intermediate, similar to the behavior of such molecules in ALD processes. The adsorbate layer then enhances the nucleation of cobalt from the $\text{Co}_2(\text{CO})_8$ precursor, such that a large area density of nanoscale islands forms with essentially no nucleation delay. Using this approach, the rms surface roughness for a 1.5-nm-thick Co film decreases from 2.5 to 1.0 nm.

Second, we further improve the surface morphology by adding a co-flow of ammonia together with the carbonyl precursor; this serves as a growth inhibitor that reduces the steady-state growth rate of Co films by 50%. The presence of the inhibitor does not alter the nucleation rate, however, the rms roughness of a 1.5-nm-thick film is further reduced to only 0.4 nm. We suggest that the roughness is due to a better valley-filling at low precursor reaction probability, consistent with the literature. In summary, our approach enables the use of CVD to afford excellent Co films for nanofabrication.

3:20pm TF+2D+AP+EL+SS-MoA6 Plasma-assisted Atomic Layer Epitaxy of Indium Aluminum Nitride Studied Using *in situ* Grazing Incidence Small-angle X-ray Scattering, Jeffrey M. Woodward, ASEE (residing at US Naval Research Laboratory); *S.G. Rosenberg,* American Society for Engineering Education (residing at US Naval Research Laboratory); *S.D. Johnson, N. Nepal,* U.S. Naval Research Laboratory; *Z.R. Robinson,* SUNY Brockport; *K.F. Ludwig,* Boston University; *C.R. Eddy,* U.S. Naval Research Laboratory

Indium aluminum nitride (InAlN) is an attractive material for power electronic applications. However, conventional methods of epitaxial growth of InAlN are challenged by a large miscibility gap and the significant differences in optimal growth conditions for the constituent aluminum nitride (AlN) and indium nitride (InN) binary compounds. Despite these challenges, the epitaxial growth of InAlN alloys throughout the entire compositional range has been demonstrated using plasma-assisted atomic layer epitaxy (ALEp)¹, a variant of atomic layer deposition in which relatively higher temperatures are utilized. In the ALEp growth of InAlN, the desired alloy compositions are achieved by forming ultra-short period superlattices of alternating InN and AlN layers, referred to as digital alloys (DA). In order to further advance these empirical efforts, significant research is needed to better understand the nucleation and growth kinetics of ALEp DA growth. To this end, we employ *in situ* grazing incidence small angle X-ray scattering (GISAXS) for the real-time study of the evolving ternary InAlN surfaces as has been done previously for binary InN² and AlN³.

Here we present *in situ* GISAXS studies of ALEp growth of InN, AlN, and a range of InAlN DAs on GaN (0001) substrates, which were performed at Brookhaven National Laboratory's NSLS-II using a custom reactor. The InAlN DAs studied include $\text{In}_{0.19}\text{Al}_{0.81}\text{N}$ (3 AlN cycles and 2 InN cycles per supercycle), $\text{In}_{0.5}\text{Al}_{0.5}\text{N}$ (1 AlN cycle and 3 InN cycles per supercycle), $\text{In}_{0.64}\text{Al}_{0.36}\text{N}$ (1 AlN cycle and 5 InN cycles per supercycle) and $\text{In}_{0.83}\text{Al}_{0.17}\text{N}$ (1 AlN cycle and 14 InN cycles per supercycle). Preliminary analysis of the data suggests that while the pure InN and AlN grew in 3D and 2D modes, respectively, the InAlN growth mode did not follow a simple trend as the nominal composition was tuned from InN to AlN. Instead, select compositions (50% and 83% In) exhibited predominantly 3D growth, while others (19% and 64% In) exhibited 2D growth. We also present complementary ALEp growth studies using a commercial Ultratech/Cambridge Nano Tech Fiji 200 and *ex situ* characterization methods, including high resolution X-ray diffraction, X-ray reflectivity, and atomic force microscopy.

¹ N. Nepal, V.R. Anderson, J.K. Hite, and C.R. Eddy, *Thin Solid Films* **589**, 47 (2015)

² J.M. Woodward, S.G. Rosenberg, A.C. Kozen, N. Nepal, S.D. Johnson, C. Wagenbach, A.H. Rowley, Z.R. Robinson, H. Joress, K.F. Ludwig Jr, C.R. Eddy Jr, *J. Vac. Sci. Technol. A* **37**, 030901 (2019)

³ V.R. Anderson, N. Nepal, S.D. Johnson, Z.R. Robinson, A. Nath, A.C. Kozen, S.B. Qadri, A. DeMasi, J.K. Hite, K.F. Ludwig, and C.R. Eddy, *J. Vac. Sci. Technol. A* **35**, 031508 (2017)

4:00pm TF+2D+AP+EL+SS-MoA8 Real-time Monitoring of the Surface Chemistry of Atomic Layer Deposition by Ambient Pressure X-ray Photoelectron Spectroscopy, Joachim Schnadt, P. Shayesteh, Lund University, Sweden; *R. Tsyshkevskiy,* University of Maryland; *J.-J. Jean-Jacques, F. Bournel,* Sorbonne Université, France; *R. Timm,* Lund University, Sweden; *A.R. Head,* Brookhaven National Laboratory; *G. D'Acunto, F. Rehman, S. Chaudhary,* Lund University, Sweden; *R. Sánchez-de-Armas,* Uppsala University, Sweden; *F. Rochet,* Sorbonne Université, France; *B. Brena,* Uppsala University, Sweden; *A. Mikkelsen, S. Urpelainen, A. Troian, S. Yngman, J. Knudsen,* Lund University, Sweden

INVITED
Atomic layer deposition (ALD) and chemical vapour deposition (CVD) are very important methods that enable a highly controlled growth of thin films [1]. The surface chemistry of the underlying processes remains, however, little understood. While idealised reaction mechanisms have been developed, they represent postulates rather than models based on the factual identification of surface species and kinetics [2]. New *in situ* and *operando* methods offer the prospect of gaining a much more thorough understanding of the involved molecular and atomic surface processes and (dynamic) structures, which, in turn, means that a much better knowledge basis can be achieved for the future improvement of materials and growth recipes (see, e.g. [3,4]). One such *operando* method, which can be applied to the investigation of ALD and CVD, is synchrotron-based ambient pressure x-ray photoelectron spectroscopy (APXPS). While conventional x-ray photoelectron spectroscopy (XPS) is limited to vacuum pressures of 10^{-5} mbar and below, APXPS can be carried out at realistic pressure. Today,

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most APXPS machines can operate at pressures up to the 10 mbar regime, which is an ideal match to the pressure regime used in standard ALD reactors.

Here, I will report on our recent efforts to apply density functional theory (DFT)-assisted synchrotron-based APXPS to the ALD/CVD of oxides (TiO₂, SiO₂, and HfO₂) on semiconductor (InAs and Si) and oxide surfaces (TiO₂, RuO₂) [3-5]. I will show that APXPS allows the identification of the surface species occurring during thin film growth and the real-time monitoring of their evolution with a time resolution of down into the millisecond regime. Here, DFT is an important tool for pinpointing the nature of the chemical species and for providing deeper insight in the surface chemical processes. I will also report on our efforts to further improve instrumentation with the goal of achieving a much closer match of the APXPS sample environment with the geometries used in conventional ALD reactors. The development will also open for the use of a wider range of precursors and growth protocols.

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- [2] F. Zaera, *Coord. Chem. Rev.* 257 (2013) 3177.
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- [4] K. Devloo-Casier et al., *J. Vac. Sci. Technol.* 32 (2014) 010801.
- [3] S. Chaudhary et al., *J. Phys. Chem. C* 119 (2015) 19149.
- [4] A. R. Head et al., *J. Phys. Chem. C* 120 (2016) 243.
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4:40pm **TF+2D+AP+EL+SS-MoA10 Kinetics during TMA-H₂O ALD: The Possible Role of Cooperative Surface Reactions**, *Brent Sperling, B. Kalanyan, J.E. Maslar*, National Institute of Standards and Technology (NIST)

Until recently, the CH₃ groups produced by surface reactions of trimethylaluminum (TMA) during atomic layer deposition were widely believed to always be highly reactive toward H₂O, but *in situ* measurements have shown this is not the case below about 200 °C.[1] At these temperatures, some CH₃ groups react slowly, and a significant amount persists from cycle to cycle under typical growth conditions. Interestingly, these persistent CH₃ groups are not incorporated as carbon impurities. We have observed these CH₃ groups using *in situ* reflection infrared spectroscopy and have confirmed low carbon concentrations in our films using *ex situ* XPS. Furthermore, we have measured the kinetics of the reaction with H₂O and have found them to be well-described by a double-exponential decay function. A simple Monte Carlo simulation that incorporates cooperative effects by clustered surface reactants (as suggested by DFT calculations[2]) reveals that a double-exponential decay of coverage can result even when only one species of reactant is present. Furthermore, the short-range distributions of coverage that result in the simulation differ from purely random ones. This difference implies that measurements sensitive to dipole-dipole interactions when combined with an independent measurement of surface coverage could be used to confirm or disprove the cooperative reaction model.

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- [2] M. Shirazi and S. D. Elliott, *Nanoscale*7 (2015) 6311.

5:00pm **TF+2D+AP+EL+SS-MoA11 Atomic Layer Deposition of Metal Sulfides: Growth and Surface Chemistry**, *Xinwei Wang*, Shenzhen Graduate School, Peking University, China

Atomic layer deposition (ALD) of metal sulfides has recently aroused great interest, and many new sulfide ALD processes have emerged during the past several years. Surface chemistry plays a key role in ALD, but it remains yet to be investigated for many recently developed sulfide ALD processes. In this representation, I will report our study on the growth and surface chemistry of the ALD of nickel, iron, and cobalt sulfides, using various *in situ* characterization techniques of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), quartz crystal microbalance (QCM), and quadrupole mass spectrometry (QMS). For instance, nickel sulfide (NiS) can be deposited from a Ni amidinate precursor (Ni(amd)₂) and H₂S by ALD (*Chem. Mater.* (2016) 28, 1155), but the surface chemistry of this process is found to deviate from the conventional ligand-exchange ALD scheme, and a formation of a nonvolatile acid-base complex from acidic surface sulfhydryl and basic amidine is suggested during the H₂S half-cycle (*J. Phys. Chem. C* (2018) 122, 21514). The initial ALD growth of NiS on a SiO_x surface is also intriguing, as the initial growth mechanism is found to be rather different from that in the later steady film growth. In the initial ALD cycles, the XPS results show a drastic cyclic variation of the signals for the Ni-O

bonds, with prominently observable Ni-O signals after each Ni(amd)₂ dose but almost negligible after the subsequent H₂S dose. These results suggest that the Ni-O bonds are first formed on the surface in the Ni(amd)₂ half-cycles and then mostly converted to NiS in the following H₂S half-cycles. To describe this initial ALD growth process, a reaction-agglomeration mechanistic scheme is proposed (*Chem. Mater.* (2019) 31, 445). Surface thermolysis study of the Ni amidinate precursor further reveals the temperature-dependent behavior of the film growth.

Energy Transition Focus Topic

Room A212 - Session TL+2D+HC+SS-MoA

Surface Reaction Mechanisms in Energy Conversion (ALL INVITED SESSION)

Moderators: Marie Turano, Loyola University Chicago, Sarah Zaccarine, Colorado School of Mines

1:40pm **TL+2D+HC+SS-MoA1 Selective Photo-driven Organic Reactions on the Surfaces of Colloidal Quantum Dots**, *Y. Jiang, K. McClelland, C. Rogers, Emily Weiss*, Northwestern University

INVITED

Colloidal quantum dots present a unique opportunity not only to power chemical reactions with sunlight but to control those chemical reactions through various templating strategies. This talk will explore demonstrations of chemo-, regio-, and stereoselective reactions photocatalyzed by quantum dots.

2:20pm **TL+2D+HC+SS-MoA3 Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood In Silico**, *Charles Sykes*, Tufts University

INVITED

In this talk I will discuss a new class of metallic alloy catalysts called *Single Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.¹⁻⁵ These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between the atomic scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. Over the last five years the concepts derived from our surface science and theoretical calculations have been used to design *Single Atom Alloy* nanoparticle catalysts that can perform industrially relevant reactions at realistic reaction conditions in collaboration with Maria Flytzani-Stephanopoulos at Tufts. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective chemical reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis and Michaelides at UCL that predicts reactivity trends of 16 different *Single Atom Alloy* combinations for important reaction steps like activation of H-H, C-H, N-H, O-H and C=O bonds. This project illustrates that the field of surface science is now at the point where it plays a critical role in the design of new heterogeneous catalysts.

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- [2] Marcinkowski et al. *Nature Materials* **12**, 523 (2013).
- [3] Lucci et al. *Nature Communications* **6**, 8550 (2015).
- [4] Liu et al. *JACS* **138**, 6396 (2016).
- [5] Marcinkowski et al. *Nature Chemistry* **10**, 325 (2018).

3:00pm **TL+2D+HC+SS-MoA5 Understanding Fundamental Energy Conversion Mechanisms: How Surface Science Can Help**, *Ulrike Diebold*, Institute of Applied Physics, TU Wien, Austria

INVITED

As we move to a more sustainable society, current energy conversion schemes need to be improved and novel ones designed. The relevant charge transfer processes and chemical transformations all occur at interfaces, so insights into fundamental mechanisms are needed to provide a scientific basis for these developments.

Using the frontier tools of surface science, I will discuss how we can directly inspect charge transfer to molecules, investigate the influence of the local environment on the reactivity of active sites, or probe the acidity of individual hydroxyls. Together with first-principles computations such experiments give crisp and clear insights into surface processes. I will also discuss the steps that are necessary to the transfer the knowledge gained from model systems to more complex environments.

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4:00pm **TL+2D+HC+SS-MoA8 Atomically-defined Model Interfaces in Energy-related Catalysis, Electrochemistry, and Photoelectrochemistry, Jörg Libuda**, University Erlangen-Nuremberg, Germany **INVITED**

The transformation between chemical energy, solar energy, and electrical energy occurs at interfaces. Therefore, functional interfaces are the key to the development of new materials in energy technology and energy-related catalysis. In our work, we explore model systems, which provide detailed insight into the chemistry and physics at such functional interfaces. Complex, yet atomically-defined model systems are studied both under 'ideal' surface science conditions and under 'real' conditions, i.e., in contact with gases, liquids, in electrochemical, and in photoelectrochemical environments. We illustrate the approach in three examples from our recent research.[1-5]

First, we consider new noble-metal-efficient catalysts for fuel cell applications.[1] We show that precious noble metals such as Pt can be anchored to nanostructured oxide supports. The resulting materials show very high noble metal efficiency and high stability. Surface science studies on model catalysts provide insight into the functionality of these systems. Electronic metal support interactions modify the reactivity of the catalytic surfaces but also stabilize sub-nanometer-sized Pt nanoparticles against sintering and deactivation.

Secondly, we report on the development of atomically defined model systems for oxide-based electrocatalysts, which can be studied under true operation conditions, i.e., in liquid environments and under potential control. We describe how such model electrodes are prepared by surface science methods and, subsequently, are studied in liquid electrolytes preserving their atomic structure. We investigate the role of particle size effects and identify the origin of metal-support interactions.

In the third part, we scrutinize the role of organic-oxide hybrid interfaces in energy transformation. Particularly fascinating are organic layers of molecular photoswitches, which provide an extremely simple solution for solar energy conversion and storage. We show that it is possible to assemble fully operational solar-energy-storing hybrid interfaces by anchoring tailor-made norbornadiene photoswitches to atomically defined oxides. Interestingly, the activation barrier for energy release in these systems is not affected by the anchoring reaction. Finally, we demonstrate that solar energy storage and release in such systems can also be controlled electrochemically with high reversibility.

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[5] F. Faisal et al., *Nat. Mater.*, 17 592 (2018)

4:40pm **TL+2D+HC+SS-MoA10 Controlling Ultrafast Photochemical Reactions in Photocatalysis, Annemarie Huijser**, University of Twente, The Netherlands, The Netherlands **INVITED**

The transition from fossil to renewable energy is one of the most important challenges of our society. Solar devices are widely considered as a highly promising option, as the energy provided by the sun to the earth by far exceeds global needs. We are investigating the use of nanostructured materials for application in solar energy conversion. The overall efficiency relies on the complex interplay of many elementary process, occurring at different time scales and also dependent on the nanostructure. In this presentation I will show how a combination of methods for ultrafast spectroscopy can shed light on the nature of photoinduced processes and provide mechanistic information valuable for the design of novel materials.

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 Synchrotron 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 MnPS₃ 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 MnPS₃. 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:

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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].

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9:20am **2D+AS+MI+NS-TuM5 Low-Energy Electron Induced Disorder 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 H₂S 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 H₂S 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°C the Si atoms decouple from the underlying surface and form a weakly buckled silicene layer with the $\sqrt{3} \times \sqrt{3}$ 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°C) 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 3d, S 2p, and O 1s 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 3d, S 2p, and O 1s 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. Maffitt, 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.

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12:00pm **2D+AS+MI+NS-TuM13 Characterization of Catalytic Active Sites on the Surface of MoS₂ 2-D Materials, Miguel Jose Yacamán**, 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 TiSe₂, TiTe₂, and VSe₂. 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 TiSe₂, 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 TiTe₂ is driven into a charge-ordered phase in the monolayer which is not stable in the bulk at all. In VSe₂, 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.

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

²Feng *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. *Ab 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 electronic transitions. These peaks are double indirect 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-MnSe₂ with Topological Insulator Bi₂Se₃, 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 Bi₂Se₃. Monolayer of MnSe is grown on Bi₂Se₃ 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-MnSe₂ on Bi₂Se₃ surface. By performing spin-polarized STM measurement with Cr tip, we observed directly the magnetic signal from 1T-MnSe₂ on Bi₂Se₃. The growth of 1T-MnSe₂ on Bi₂Se₃ further leads to the MBE synthesis of magnetic topological insulator Bi₂MnSe₄, 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.

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11:00am **2D+EM+MI+MN+NS+QS-TuM10 Sign-change Pairing Symmetry in Single Layer FeSe/SrTiO₃ 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 SrTiO₃(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 pairing states, such as sign-persevering s_{\pm} -wave, sign-changing nodeless d -wave and s_{\pm} -wave have been suggested,

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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/SrTiO₃ 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/SrTiO₃ 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 down to the single atomic layer limit. High quality single layer FeTe_{1-x}Se_x films are grown on SrTiO₃(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. Chen¹, 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. Schneeloch⁴, R.D. Zhong⁴, G.D. Gu⁴, Liang Fu⁵, Hong Ding^{1,2,3}.

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

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Electronic Materials and Photonics Division Room A214 - Session EM+2D+AP+NS+PS-TuM

New Devices and Materials for Electronics and Photonics

Moderators: Sean W. King, Intel Corporation, Michelle M. Paquette, University of Missouri-Kansas City

8:00am **EM+2D+AP+NS+PS-TuM1 Performance Modeling and Design for Spintronic Logic and Memory Devices, Azad Naeemi, Georgia Institute of Technology INVITED**

As scaling conventional logic and memory devices becomes more and more challenging, there is a global search for novel materials and devices that can augment mainstream technologies used for data storage and processing. To this end, spintronic materials and devices are promising candidates as they provide dense non-volatile storing elements that enable novel computing paradigms such as in memory-computing and neural networks.

This talk will present physical models for various read and write spintronic mechanisms and quantifies the potential performances of Boolean circuits based on various spintronic logic devices. It will be shown that without major breakthroughs such circuits will not be able to compete with their CMOS counterparts. However, novel circuit paradigms that take advantage of the physics of these devices can potentially provide significant benefits. For example, cellular neural networks based on spintronic devices are projected to perform better compared to their analog CMOS implementation.

While spin-transfer-torque random access memory (STT-RAM) is becoming commercially available, it suffers from relatively large switching currents that limits its density and causes reliability challenges. Novel read and write mechanisms such as spin-orbit torque or magneto-electric effects can potentially address or partially mitigate some of these challenges. In this talk, the array-level potential performance of various magnetic memory devices will be quantified and benchmarked.

8:40am **EM+2D+AP+NS+PS-TuM3 High Yield, Low Variability HfO₂ 1T1R Cells Fabricated in 65nm CMOS, J.H. Hazra, M.L. Liehr, K. Beckmann, Nathaniel C. Cady, SUNY Polytechnic Institute**

Hafnium Oxide (HfO₂) based Resistive Random Access Memory (ReRAM) devices are promising candidates for non-volatile memory, having a wide variety of applications in neuromorphic computing, artificial intelligence and future memory solutions. Stochastic conductive filament (CF) generation and rupture processes, however, contribute to high variability resistive switching in these devices. In order to address this issue, an extensive characterization of HfO₂ 1 transistor 1 RRAM (1T1R) cells was performed to investigate switching yield and cell-to-cell variability. 1T1R devices were integrated into a 300mm wafer platform utilizing the IBM 65nm 10LPe process technology, in which the memristor device stack is implemented between the M1 and M2 metallization layers, using a custom designed FEOL compatible process flow. The ReRAM device stack is comprised of a TiN bottom electrode followed by conformal deposition of the HfO₂ switching layer, Ti oxygen scavenging layer and TiN top electrode. The HfO₂ switching layer was deposited using an atomic layer deposition (ALD) process with an organic precursor. For statistical significance, the performance of 50 different 1T1R cells was compared for cell-to-cell variability in operating voltage and resistance in the on and off state. An impressive 100% switching yield and low cell-to-cell switching variability were observed for these devices. 1T1R cells were also investigated for long term endurance and high temperature retention, exhibiting excellent endurance of up to 1 billion switching cycles with an average R_{off}/R_{on} ratio of 10:1. As compared to 1T1R cells that we have fabricated with alternative ALD precursors/methods, these devices show superior yield and performance. We are currently performing compositional and structural comparisons between these sets of devices, to elucidate the impact of ALD precursor choice and processing methods on yield and electrical performance.

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9:00am **EM+2D+AP+NS+PS-TuM4 Heat Transfer Proximity Effects in Resistive Memory Crossbar Arrays**, *Marius Orlowski, M.S. Al-Mamun*, Virginia Tech

Evidence for thermal cross talk in resistive RAM memory arrays is presented. Frequent switching of a resistive memory cell (Cu/TaO_x/Pt) may lead to a considerable local accumulation of Joules heat. The heat generated in a stressed device spreads via common electrode lines to the neighboring cells impacting their switching behavior. As a probe into degraded performance of the neighbor cells we choose the cell itself set into the on-state under specific conditions. The cell is set at a critical compliance current I_{cc} that allows repeated switching for no more than ~15 cycles. After the maximum number of cycles the on-state becomes volatile. For a lower I_{cc} , the cell produces a volatile on-state, and for higher I_{cc} the cell switches for hundred of times with a stable on-state. We find that the cells in close proximity of the heated device display various degrees of degradation indicated by a reduced number of cycles of the probed cell. The 1st neighbor cell experiences the greatest, and the 4th neighbor cell the smallest degradation. This indicates the spread of the heat from the heated device to its neighbors. After a sufficient cooling off period (10 minutes or longer), all the neighboring cells and the heated device display again the maximum number of cycles i.e. 15, when set under the critical compliance current and reset, repeatedly. Also cells that don't share any of the common electrode metal lines with the heated source cell, may degrade provided that the intermediate cells are set to on-state, thus enabling a continuous thermal conduction path between the heated cell and the probed cell. The heat dissipation from the heated device is slower for narrow and thin metal electrode lines than for wide and thick metal lines. However, in case of wide and thick metal lines more distant neighbor cells are affected by the parasitic cell-to-cell heat transfer.

We have performed the characterization of the neighboring cells along the Cu and Pt electrode lines. We find that the performance degradation of the neighboring cells along the Cu line is significantly stronger than along the Pt metal line. This observation is consistent with the much better heat conductivity of Cu lines (385W/(mK) and 150nm thick) than the Pt (72W/(mK) and 50nm thick) lines, but is at odds with the assumption of the standard electro-chemical metallization model postulating a conical shape of the Cu filament with a broad base of the cone at the Pt electrode and a tip at the Cu electrode. We discuss the extant controversial experimental evidence and models for the filament's shape and propose an hour-glass shape for the filament reconciling the extant findings and our thermal results.

9:20am **EM+2D+AP+NS+PS-TuM5 High Performance Memristive Action in Methylammonium Bismuth Iodide([MA]3BiI9) Films**, *P. Cheng*, Vanderbilt University; *G. Luo*, Washington University in St. Louis; *Z. Gao*, University of Central Florida; *A. Thind*, *R. Mishra*, Washington University in St. Louis; *Parag Banerjee*, University of Central Florida

We demonstrate high performance (ON/OFF ~ 2.4x10⁵) resistive switching in methylammonium bismuth iodide ((CH₃NH₃)₃BiI₉ or, MBI) thin films.¹ MBI has a post-perovskite structure and consists of 2D layers of face-shared

BiI₆ octahedra. This talk focuses on the structure, composition and associated defect chemistry that is critical for memristive behavior in MBI films.

Memristors are formed by contacting MBI films with aluminum electrodes. The switching for a 200 nm film is observed at voltages ~ 0.5 V. High frequency performance of these memristors shows a peak ON/OFF ratio 2.4x10⁵ at 50 KHz. The ON state retention is maintained at 50C for > 10⁶ seconds. Stable room temperature endurance is noted for up to 1000 cycles. Energy dispersive x-ray spectroscopy on planar memristor devices show that, postswitching,

a detectable change in the I- concentration is observed closer to the anode side. Density-functional theory (DFT) calculations show low activation barrier for iodine migration in agreement with the experimental results. The DFT calculations also provide insights about the migration pathway and strategies to control this behavior.

From a synthesis perspective, MBI films can be deposited using solution as well as low temperature (< 200C), atmospheric CVD technique.² The compounds are air stable. This family of ternary compounds offers a large compositional and structural tunability; unlike binary metal oxides commonly used for memristors. As opposed to recent 2D MoS₂ based planar, tunneling RAM devices³, the vertical stack of the 2-terminal memristor bodes well for scalability. Thus, we propose that hybrid organic-

inorganic thin films may offer strategic materials and design advantages together with seamless process integration into current Si-based devices.

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9:40am **EM+2D+AP+NS+PS-TuM6 Mechanism of Chalcogen Passivation of GaAs Surfaces**, *Takayuki Suga*, *S. Goto*, UEC-Tokyo, Japan; *A. Ohtake*, *NIMS*, Japan; *J.N. Nakamura*, UEC-Tokyo, Japan

GaAs surfaces are stabilized by surface treatments with Se or S through the reduction of the dangling bond density [1,2]. It has long been thought that the Se- or S-treated GaAs(111)B-(1x1) surface has a simple structure; the outermost As atoms of the ideal (111)B surface are completely replaced by Se or S atoms, the Se- or S-terminated model [3]. In general, the structural stability of compound semiconductor surfaces can be explained in terms of the so-called electron-counting rule (ECR) [4]. The Se- or S-terminated model, however does not satisfy ECR. Recently, the atomic structure of the Se-treated GaAs(111)B surface has been revisited [5] and another structure model has been proposed, where the Se atoms substitute 3/4 of the topmost surface As atoms in a (2x2) unit [6]. This mixed Se/As-terminated model satisfies ECR, being electronically stable [6]. We have depicted phase diagrams of Se- or S- treated GaAs(111)B surface at 0K as functions of the chemical potentials of Se ($\Delta\mu_{\text{Se(S)}}$) and As ($\Delta\mu_{\text{As}}$). The (2x2) As-trimer and the mixed Se(S)/As-terminated surfaces appear under Se poor condition. It is noted that the Se- or S-terminated surface also becomes stable as $\Delta\mu_{\text{Se}}$ or $\Delta\mu_{\text{S}}$ increases, respectively, even though these surfaces are not qualified for ECR.

The Se(S)-treated GaAs(111)B surface is prepared experimentally by molecular beam epitaxy under a finite temperature and a gas pressure. Therefore, it is necessary to consider the free energy of a molecule in vapor phase. In this study, we investigate the stabilization of the Se- or S-treated GaAs(111)B surface structures by considering the beam equivalent pressure of As and Se(S) in a growth temperature using the first-principles calculations within the density functional theory. The chemical potentials of molecules are derived from the partition functions for the translation, the rotation, and the vibrational motions.

In the phase diagram for the actual experiment condition, T=800K, the mixed Se/As terminated surface appears in the Se pressure of 10⁻¹⁵-10⁻⁵ Torr, being consistent with the recent experiment [5]. Surprisingly, the Se-terminated surface also becomes stable as the Se pressure increases. We will discuss the stabilization mechanism of the chalcogen-treated GaAs surfaces.

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11:00am **EM+2D+AP+NS+PS-TuM10 Combining 2D and 1D Atomic Scale Tailored Nanowire Surfaces for Novel Electronics and Photonics**, *Anders Mikkelsen*, Lund University, Sweden

INVITED

The III-V nanowire (NW) technology platform has reached a level of advancement that allows atomic scale control of crystal structure and surface morphology as well as flexible device integration. In particular, controlled axial stacking of Wurtzite (Wz) and Zincblende (Zb) crystal phases is uniquely possible in the NWs. We explore how this can be used to affect electronic, optical and surface chemistry with atomic scale precision opening up for 1D, 2D and 3D structures with designed local properties.

We have previously demonstrated atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) on a wide variety of these III-V NWs and on operational NW devices[1-4]. We now use these methods for studying atomic scale crystal phase changes, the impact on local electronic

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properties and demonstrating full atomic resolution STM during device operation[5-7]. We explore the surface alloying of Sb into GaAs NWs with controlled axial stacking of Wz and Zb crystal phases[5] demonstrating a simple processing-free route to 1D and 2D compositional control at the monolayer level. Further we show how Bi can form unique 1D and 2D structures in particular on the unique Wz GaAs NW segments. Using 5K STM/S we measure local density of states of Zb crystal segments in Wz InAs NWs down to the smallest possible atomic scale crystal lattice change [6], which is effectively a small 2D material segment in a 1D structure. We find that the general Zb electronic structure is preserved locally in even the smallest segments and signatures of confined states in them.

Characterization to the atomic scale during electrical and optical operation is necessary to understand and develop the functionality of structures as discussed above. We demonstrate a novel device platform allowing STM/S with atomic scale resolution across a III-V NW device simultaneously with full electrical operation and high temperature processing in reactive gases[7]. Using 5-15 femtosecond laser pulses combined with PhotoEmission Electron Microscopy (PEEM) we explore local dynamic response of carriers in the 1D Wz and Zb crystal phases down to a few femtoseconds temporally and a few tens of nanometer spatially[8].

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11:40am **EM+2D+AP+NS+PS-TuM12 Nanoflower Decorated GaN and AlGaIn/GaN based Catalyst-free CO Sensors**, *Monu Mishra, G. Gupta*, National Physical Laboratory, India

III-Nitride semiconductors owing unique material properties have proven their potential in the detection of light, chemical, biomolecules and toxic/explosive gases. Despite of numerous advantages viz. biocompatibility, high temperature/frequency tolerance and harsh/adverse environmental condition sustainability, the use of expensive catalysts (e.g. platinum) and higher operation temperature (>250°C) for gas sensing has plagued the development of GaN based cost-effective sensing technology. Upto the best of our knowledge, literature lacks any scientific report on the development of catalyst-free CO sensors operating at room-temperature using GaN or AlGaIn/GaN structures indicating the necessity of dedicated scientific attention in this area. Therefore, we report the fabrication of nanoflowers-decorated GaN and AlGaIn/GaN heterostructure based catalyst-free CO sensors operating at lower (including room) temperature. Planar as well as nanostructured GaN & AlGaIn/GaN thin films were employed for sensors fabrication which exhibited significant CO sensing associated with its superior surface and interface properties. For in-depth understanding, the obtained results were thoroughly analyzed and correlated to investigate the underlying science/phenomenon which revealed that CO sensing on GaN (and AlGaIn/GaN) is governed by the chemical nature of ambient-oxidation induced amorphous oxide (O₂, O²⁻ or OH⁻ species) layer grown on the surface and acting as a donor/acceptor state. Besides, electron accumulation at AlGaIn/GaN interface influenced the critical parameters like Schottky barrier height, ideality factor etc. perturbed the effective carrier transport and ultimately the device performance. The study demonstrates that development of catalyst-free room temperature operating GaN based CO sensors is feasible using nanostructured surfaces, though further research is required for optimization of device performance.

12:00pm **EM+2D+AP+NS+PS-TuM13 Surface Transfer Doping of Diamond by Complex Metal Oxides for Power Electronics: A Combined Experimental and Simulation Study**, *Vihar Georgiev, A.J. Moran, A. McGhee*, University of Glasgow, UK

Diamond has unique properties that make it an attractive wide band-gap material to produce future high-performance electronic devices. With a wide band-gap of 5.5eV, a thermal conductivity 5 times greater than 4H-SiC, a high breakdown field and high hole and electron carrier velocities, diamond is a clear stand out candidate for high frequency and high power devices. However, the lack of a suitable doping mechanism has hindered

the application of diamond in electronic devices. Conventional substitutional doping techniques are limited as it is difficult to substitute atoms into the diamond crystal lattice.

Surface Transfer Doping (STD) gives the use of diamond for such applications more promise. For STD to occur there are typically two prerequisites: hydrogen terminated diamond (H-diamond) and an electron accepting material in intimate contact with the H-diamond surface. The hydrogen termination gives the diamond a negative electron affinity which facilitates the transfer of electrons from the diamond to the electron-accepting material, creating a shallow, quasi two-dimensional hole gas (2DHG) in the diamond. This doping process traditionally relies upon interfacial electron transfer between the diamond valence band and favourable energy states provided by atmospheric molecules dissolved in a water layer naturally adsorbed on the diamond surface. However, the stability of this atmospheric layer, upon which the transfer doping process relies, has been a significant limiting factor in the production of high-power handling and robust operation devices.

One of the materials that can improve the performance and stability of STD in diamond are the metal oxides such as MoO₃ which acts as an alternative electron acceptor medium on the H-diamond surface. In order to validate and understand the physical and the chemical process in such STD, in this work we have combined experimental and simulation studies. The electrical characterisation is done by high temperature Hall measurements. Those experimental results are compared to numerical simulation based on the first principle methods such as Density Functional Theory. Comparing the simulation and experimental results revealed that the electrons are transferred from the diamond to the metal oxides, leading to formation of a sub-surface 2DHG in the diamond. Due to this transfer of electrons to the oxide the hole carrier concentration increases in comparison to the air-exposed H-diamond. Our work shows the potential to improve the stability and performance of hydrogen-terminated diamond electronics devices through incorporation of high electron affinity transition metal oxides.

Surface Science Division

Room A220-221 - Session SS+2D+HC-TuM

Atom Manipulation and Synthesis/Oxide Surface Reactions & Flash Session

Moderators: Liney Arnadottir, Oregon State University, Stephen McDonnell, University of Virginia, Martin Setvin, TU Wien, Austria

8:00am **SS+2D+HC-TuM1 Angstrom Scale Chemical Analysis of Metal Supported *Trans*- and *Cis*-Regioisomers by Ultrahigh Vacuum Tip-Enhanced Raman Mapping**, *S. Mahapatra, J. Schultz, L. Li, Nan Jiang*, University of Illinois at Chicago

Real space chemical analysis of two structurally very similar components i.e. regioisomers lies at the heart of heterogeneous catalysis reactions, modern-age electronic devices and various other surface related problems in surface science and nanotechnology. One of the big challenges in surface chemistry is to identify different surface adsorbed molecules and analyze their chemical properties individually. Herein, we report a topological and chemical analysis of two regioisomers, *trans*- and *cis*-tetrakis(pentafluorophenyl)porphodilactone (*trans*- and *cis*-H₂F₂₀TPPDL) molecules by high resolution scanning tunneling microscopy (STM), and ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Both isomeric structures are investigated individually on Ag(100) at liquid nitrogen temperature. Following that, we have successfully distinguished these two regioisomeric molecules simultaneously through TERS with an angstrom scale (8 Å) spatial resolution. Also, the two-component organic heterojunction has been characterized at large scale using high resolution two-dimensional (2D) mapping. Combined with time-dependent density functional theory (TDDFT) simulations, we explain the TERS spectral discrepancies for both isomers in the fingerprint region.

8:40am **SS+2D+HC-TuM3 On-surface Synthesis by Atom Manipulation Studied with Atomic Force Microscopy**, *Leo Gross*, IBM Research - Zurich, Switzerland

INVITED

Elusive molecules are created using atomic manipulation with a combined atomic force/scanning tunneling microscope (AFM/STM). Employing high-resolution AFM with functionalized tips provides insights into the structure, geometry, aromaticity, charge states and bond-order relations of the molecules created and into the reactions performed [1].

We created radicals, diradicals [2], non-Kekulé molecules [3] and polyynes [4] and studied their structural and electronic properties. We recently

showed that the reorganization energy of a molecule on an insulator can be determined [5]. In addition, we expanded the toolbox for the synthesis of molecules by atomic manipulation, demonstrating reversible cyclisation reactions [2], skeletal rearrangements [4] and controlled reactions on insulating substrates by electron attachment/detachment [6].

On insulating substrates we can control the charge state of molecules and resolve changes within molecular geometry, adsorption and aromaticity related to the oxidation state.

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9:20am **SS+2D+HC-TuM5 The Large Effect of Solvents on Heats of Adsorption versus Gas Phase Explained with a Simple Bond-additivity Model: A Case Study with Phenol on Pt(111) in Water, Charles T. Campbell**, University of Washington; *N. Singh*, University of Michigan; *J.R. Rumpitz*, University of Washington

The low-coverage heat of adsorption of phenol on Pt(111) facets of a Pt wire in aqueous phase is approximately 21 kJ/mol (relative to aqueous phenol)¹, much smaller than the heat for gas phase phenol adsorption at this same low coverage on single-crystal Pt(111) in ultrahigh vacuum (200 kJ/mol from adsorption calorimetry²). Here we quantitatively analyze the individual contributions that give rise to this large solvent effect using a simple pairwise bond-additivity model, taking advantage of experimental data from the literature to estimate the bond energies. The dominant contribution to the lowering in heat when adsorbing phenol in water is the energy cost to break the strong bond of liquid water to Pt(111) ($E_{\text{adhesion}} = \sim 116$ kJ per mole of phenol area). The water-phenol bonding is lost on one face of the phenol and this costs ~ 50 kJ/mol, but this is nearly compensated by the new water-water bonding (~ 53 kJ/mol of phenol area). The results indicate that the intrinsic bond energy between phenol and Pt(111) is not very different when in gas versus aqueous phase, provided one takes into consideration the expectation that water forces phenol into 2D islands of high local coverage even at low average coverage (for the same reason that oil and water don't mix). This also explains the lack of a strong coverage dependence in the heat of adsorption when measured in aqueous phase, whereas it decreases by ~ 60 kJ/mol with coverage when measured in gas phase. This bond-additivity analysis can be extended to other surfaces and solvents for any flat adsorbate. It clarifies why catalysis with molecules like phenol which have very strong bonding to Pt group metals can proceed rapidly at room temperature in liquid solvents like water, but would never proceed in the gas phase at room temperature due to irreversible site poisoning. We also present many new measurements of solvent / metal adhesion energies that will aid future analyses of solvent effects in adsorption.

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9:40am **SS+2D+HC-TuM6 Atomic-Scale Growth Mechanisms of Niobium Hydrides on Hydrogen Infused Nb(100), Rachael Farber, D.R. Veit, S.J. Sibener**, The University of Chicago

Particle accelerator technology and science, while commonly associated with fundamental high-energy physics applications, is also a crucial component in biological, chemical, and industrial scientific technologies. In order to increase the accessibility and applicability of accelerator-based technologies in multiple sectors, it is imperative to develop technologies that will enable the production of a more intense particle beam at a lower price point. As such, it is essential to identify structural and chemical features that inhibit beam intensity and develop methods to suppress such surface features.

Niobium (Nb) is the current standard for superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance (R_s) and high cavity quality factor (Q) at operating temperatures of ~ 2 K. It is known

that SRF cavity surface composition and contaminant incorporation is directly related to Q , and much work has been done to understand factors influencing SRF cavity performance for the clean and oxidized Nb surface. Hydrogen incorporation, which results in the formation of Nb hydrides, has been identified as a major source of decreased Q . There is not, however, a fundamental understanding of the growth mechanism for Nb hydrides. In this work, we have investigated the atomic-scale growth mechanism of Nb hydrides on oxidized Nb(100) under ultra-high vacuum (UHV) conditions using temperature programmed desorption (TPD), low-temperature scanning tunneling spectroscopy (LT-STM), and scanning tunneling spectroscopy (STS). The incorporation of relevant concentrations of hydrogen into the Nb(100) crystal was confirmed using TPD, LT-STM experiments revealed novel, real space information regarding the atomic-scale growth mechanism of Nb hydrides, and STS was used to elucidate the relationship between Nb hydride formation and the surface density of states.

11:00am **SS+2D+HC-TuM10 Water induced restructuring of Vanadium oxide clusters, Kræn Christoffer Adamson, J.V. Lauritsen, S. Chiriki, B. Hammer**, Aarhus University, Denmark

Fundamental knowledge of catalytic processes for NO_x removal (Selective Catalytic reaction, SCR) is important for improving existing catalysts and developing new. In the SCR cycle, NO_x is known to react from gas-phase on adsorbed ammonia on a VO_x/TiO₂ based catalysts. It is well established that vanadium in the V⁵⁺-state is most catalytic active state, though is still debated whether it is a hydroxylated- or an unhydroxylated- species that is most active species. Here we investigate the structure of vanadium oxide (V₂O₅) before, under and after exposure of water.

By evaporation of Vanadium in an oxygen-rich atmosphere (10⁻⁶ mBar) on an anatase-TiO₂ (101) substrate, we can create well-dispersed single V₂O₅–clusters. Confirm the oxidation state of vanadium with X-ray Photo electron Spectroscopy (XPS) and image the size and structure with high resolution Scanning Tunneling Microscopy (STM). Prior to water exposure V₂O₅ – clusters appear predominately as elongated features extending across two bridging oxygen rows of the anatase-TiO₂ (101) substrate. Utilizing the high scanning speed of the Aarhus STM we can follow the water induced restructuring of the clusters in situ. We observe a clear change in appearance of the vanadium oxide cluster, where a vanadium atom moves across on of the bridging oxygen rows of the a-TiO₂ substrate. Removal of water causes another change in appearance, but re-exposure of water the previous appearance is restored. We therefore observe a reversible reaction with exposure and removal of water, however with several hour of pumping we cannot return to the initial state directly after evaporation.

Together with Theoreticians, we are able to suggest structure models of the interactions between the vanadium oxide and water. We are able to explain both the irreversible restructuring in the first water exposure and the reversible restructuring with re-exposure of water. Understanding the structure and its dynamical behavior under water exposure bring us closer to understand the catalyst under working conditions.

11:20am **SS+2D+HC-TuM11 Hydrogenation of Titanium Dioxide with Low-energy Hydrogen Ions and Atomic Hydrogen, N. Nagatsuka, Y. Ohashi**, Institute of Industrial Science, The University of Tokyo, Japan; *M. Fujimoto, M. Matsumoto*, Tokyo Gakugei University, Japan; *Katsuyuki Fukutani*, Institute of Industrial Science, The University of Tokyo, Japan

Interaction of hydrogen with TiO₂ surfaces is of interest and importance in view of photocatalytic H₂ generation and hydrogen sensors. Furthermore, hydrogenated TiO₂ has recently acquired much attention due to its excellent photocatalytic activity [1]. In our previous study, we have investigated the interaction of hydrogen with the rutile TiO₂(110) surface with nuclear reaction analysis (NRA) and ultraviolet photoemission (UPS) [2]. Whereas the former allows us to quantify hydrogen in the sample in a depth-resolved manner [3], the latter provides us with the information on the electronic states. In the present study, we have studied interaction of low-energy hydrogen ions with TiO₂ single-crystal surfaces, where the hydrogen ion penetrates the surface being distributed in the near-surface region [4]. We also report atomic hydrogen interaction with TiO₂ nanoparticles in relation with hydrogenation of TiO₂.

When the rutile TiO₂(110) and anatase TiO₂(101) surfaces are exposed to atomic hydrogen, NRA shows adsorption of hydrogen on the surfaces with a coverage of about 0.5 monolayer [2]. When the rutile TiO₂(110) surface is exposed to a hydrogen ion beam at 500 eV, on the other hand, NRA reveals a maximum at a depth of about 1 nm extending to ~ 30 nm with an average concentration of 5.6 at. % and UPS shows an in-gap state (IGS) at ~ 0.8 eV below the Fermi level with a downward band-bending by 0.5 eV. The IGS

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intensity is about ten times as large as that of the H-adsorbed surface. Upon annealing at 673 K, the IGS intensity is reduced by about 40 % and H with a coverage of 1.4 monolayer remains in the near-surface region, which suggests stable H occupation of subsurface sites. When the H-ion-irradiated surface is exposed to oxygen molecules, on the hand, the hydrogen distribution remains unchanged although the IGS intensity is substantially reduced. The effect of hydrogen in the near-surface region on the surface electronic state is discussed.

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11:40am **SS+2D+HC-TuM12 Direct Observation of Atomic Exchange during Surface Self-diffusion**, *Matthew Koppa, P.R. Schwoebel, D.H. Dunlap*, University of New Mexico

The growth of crystals from the vapor phase is widely used in many technological applications, ranging from the microfabrication of microprocessors to the development of biological sensors. The dynamics of processes such as the surface diffusion of adatoms are key phenomena governing mass transport and the resulting crystal growth. Atomic exchange with substrate atoms during surface self-diffusion has been inferred from previous field ion microscope(FIM)-based experiments by mapping adatom visitation sites. Here iridium enriched to >93% ^{191}Ir was deposited onto an atomically clean and smooth *Ir(100)* plane as observed in an atom-probe field ion microscope. Following thermally activated surface self-diffusion the adatom was field desorbed and mass analyzed. Observation of the ^{193}Ir isotope in one-half of the cases demonstrates conclusively that atomic exchange can occur during surface self-diffusion.

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].

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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 WSe₂/graphene heterostructure devices. Spatial maps demonstrate long-lived spin/valley lifetimes on the bare WSe₂ but reveal a quenching of spin-valley signal at the WSe₂/graphene interfaces. Time delay scans show these interface lifetimes to be quenched up to 3 orders of magnitude in comparison to bare WSe₂. Furthermore, photoluminescence mapping exhibits quenching at the interfaces while photoconductivity is enhanced in these regions, demonstrating efficient charge transfer from WSe₂ 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 MoS₂ 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 MoS₂ 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 MoS₂; 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 MoS₂. A series of gas exposure studies demonstrate a clear correlation between PL brightening and the presence of water. We propose that H₂O molecules passivate sulfur vacancies in the CVD-grown MoS₂, 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.

This research was performed while S.V.S and M.R.R held a National Research Council fellowship and H.-J.C. held an American Society for Engineering Education fellowship at NRL.

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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 SiO_2/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 monolayer $MoSe_2$ 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.

Materials and Processes for Quantum Information, Computing and Science Focus Topic
Room B231-232 - Session QS+2D+EM+MN+NS-TuA

Materials for Quantum Sciences

Moderators: Matthew R. Rosenberger, U.S. Naval Research Laboratory, Robert Walko, The Ohio State University

2:20pm **QS+2D+EM+MN+NS-TuA1 Electrically Detected Electron Nuclear Double Resonance Study of Defects in 4H-SiC Bipolar Junction Transistors**, *Ryan Waskiewicz*, *B.R. Manning*, *D.J. McCrory*, *P.M. Lenahan*, Pennsylvania State University

There is growing interest in the possibilities of SiC in spin-based quantum computation. The development of such spin-based quantum computation will require a fundamental understanding of spin physics of paramagnetic defects in SiC including both electron and nuclear paramagnetism. We utilize electrically detected magnetic resonance (EDMR) detection through spin dependent recombination (SDR). In this study we demonstrate relatively high signal to noise electron nuclear double resonance (ENDOR) in a single fully processed SiC pn junction at room temperature. The electrically detected ENDOR (EDENDOR) involves nitrogen nuclei in close proximity to deep level centers within the depletion region of the pn junction; the deep levels are almost certainly silicon vacancies.

We believe these observations are of importance for at least two reasons: (1) they demonstrate that the enormous analytical power of ENDOR can be extended to the study of problems in conventional solid-state electronics and (2) the results demonstrate a way to directly monitor small numbers of nuclear spins through the measure of electronic currents.

In our EDMR measurements, a slowly varying magnetic field and an oscillating microwave frequency magnetic field are applied to the sample inside a microwave cavity. As in conventional EPR, energy is absorbed by paramagnetic sites when the resonance condition is met. For a simple case, this resonance condition is $h\nu = g\mu_B B \pm \sum_i m_i A_i$, where h is Planck's constant, g is an orientation dependent number typically expressed in a g-tensor, μ_B is the Bohr magneton, B is the magnetic field, m_i is the spin quantum number of the i^{th} nucleus, and A_i is the hyperfine interaction of the i^{th} magnetic nucleus. In EDMR, the EPR response is detected through a change in device current, in our case due to SDR.

The devices in this study are 4H-SiC BJTs. The EDMR response obtained on these BJTs is very similar to an EDMR spectrum that has been linked to a silicon vacancy in 4H-SiC MOSFETs. To perform the EDENDOR measurement, the magnetic field is held constant and an NMR frequency sweep is applied to the device. The device current is measured and a large response is measured at what is unambiguously the nuclear frequency of nitrogen. These results demonstrate the analytical power of the EDENDOR measurement, measuring nitrogen in the vicinity of the silicon vacancy defect centers that are measured with EDMR.

This work was supported by the Air Force Office of Scientific Research under award number NO. FA9550-17-1-0242.

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2:40pm **QS+2D+EM+MN+NS-TuA2 Scanning Tunneling Microscopy Studies of Er Adatoms on GaAs (110)**, *Rebekah Smith, A. Benjamin, J.A. Gupta*, The Ohio State University

Rare earth dopants in III-V semiconductors are of interest as high quality optical sources due to the preservation of sharp intra- f -shell transitions. The long optical coherence lifetime and narrow energy width of these transitions, at 1.54 μm , make them a candidate for quantum communication. Here we investigate Er interactions with host GaAs (110) surface with atomic resolution using STM. Er atoms were deposited via electron beam evaporation onto the GaAs surface at 5 K. We find three different Er_{ad} configurations with varying abundance upon deposition, each with a different surface site location. All three configurations exhibit long-range depressions in STM topographic images, attributed to band bending associated with a positive adatom charge state. Individual Er adatoms can be switched between these states by applying a positive voltage pulse with the STM tip. Tunneling spectroscopy on Er adsorbed at the interstitial sites reveals prominent states within the GaAs bandgap, but no evidence of sharp f -shell transitions inferred from bulk optical studies. We also form substitutional Er_{Ga} by applying a larger positive voltage pulse. Substitutional Er appears neutral, which we attribute to it being isoelectronic with Ga. This work acknowledges funding from the DOE (DE-SC0016379).

3:00pm **QS+2D+EM+MN+NS-TuA3 Defect-based Quantum Systems in Hexagonal Boron Nitride**, *Trong Toan Tran*, University of Technology Sydney, Australia
INVITED

Engineering solid state quantum systems is amongst grand challenges in realizing integrated quantum photonic circuitry. While several 3D systems (such as diamond, silicon carbide, zinc oxide) have been thoroughly studied, solid state emitters in two dimensional (2D) materials are still in their infancy. In this talk I will introduce hexagonal boron nitride (hBN) as a promising layered material that hosts ultra bright quantum emitters. I will present several avenues to engineer these emitters in large area hBN multilayers and monolayers using chemical vapour deposition techniques. I will then show unique tuning experiments and promising results for controlling the emission wavelength of these quantum emitters. At the second part of my talk, I will discuss promising avenues to integrate the emitters with plasmonic and photonic cavities to achieve improved collection efficiency and Purcell enhancement. These are fundamental experiments to realize integrated quantum photonics with 2D materials. I will summarize by outlining challenges and promising directions in the field of quantum emitters and nanophotonics with 2D materials and other wide band gap materials.

4:20pm **QS+2D+EM+MN+NS-TuA7 Specific Placement of V_{Si} in 4H-SiC for Quantum Technologies using Li^+ Implantation**, *S.P. Pavunny, Rachael L. Myers-Ward, D.K. Gaskill*, U.S. Naval Research Laboratory; *E.S. Bielejec*, Sandia National Laboratories; *H.B. Banks, A.L. Yeats*, U.S. Naval Research Laboratory; *M.T. DeJard, Raytheon*; *S.G. Carter*, U.S. Naval Research Laboratory

Silicon carbide has been a material of interest in the quantum technology field for future applications in communication and sensing due in part to the long spin ($S = 3/2$) coherent lifetime of the Si vacancies (V_{Si}). Additional benefits to using SiC for quantum technologies is wafer scalability and fabrication capability using standard processing techniques, making it a favorable material. To improve emission rates of photoluminescence from the vacancies, exact placement of the V_{Si} within microcavities is necessary. Here we show implanted Li^+ into Si-face, 4H-SiC homoepitaxy creates V_{Si} in desired locations. The epitaxial material had no measurable V_{Si} prior to Li^+ implantation. The dose of 100 keV Li^+ ranged from $10^{12} - 10^{15} \text{ cm}^{-2}$ and was directed using a maskless focused ion beam technique with a positional accuracy of $\sim 25 \text{ nm}$. The arrays were characterized with high-resolution scanning confocal fluorescence microscopy. Using a 745 nm excitation source, the photoluminescence ranging from 860 – 975 nm produced the characteristic $V1'$, $V1$ and $V2$ lines, with the $V1'$ zero-phonon line being consistent for all measurements. In addition, the $V1'$ intensity showed a linear dependence with implantation dose. Moreover, near single photon emission is obtained from V_{Si} at the lowest doses.

Research at NRL is supported by the Office of Naval Research. Ion implantation was performed at Sandia National Laboratories through the Center for Integrated Nanotechnologies, an Office of Science facility operated for the DOE (contract DE-NA-0003525) by Sandia Corporation, a Honeywell subsidiary.

4:40pm **QS+2D+EM+MN+NS-TuA8 Silicon Vacancy Point Defect in High-quality Nanobeam Photonic Crystal Cavities in 4H Silicon Carbide**, *Mena Gadalla, X. Zhang, A.S. Greenspon*, Harvard University; *D.O. Bracher*, Harvard GSAS; *R.K. Defo, E. Hu*, Harvard University

Silicon carbide (SiC) has recently found promise and applications in the quantum world, because of various fluorescent point defects that serve as an intriguing platform for solid-state quantum information and quantum sensing technologies. One such native point defect is the negatively charged silicon vacancy (V_{Si}^-) in the 4H polytype of SiC. This color center can occupy two inequivalent lattice sites, resulting in two distinct zero-phonon-lines (ZPL) at 862nm and 916nm. V_{Si}^- possesses good spin coherence properties, with spin states that can be initialized and read out optically. Unfortunately, low branching ratio is a characteristic of the V_{Si}^- spectrum where a small fraction of the total emission is coupled into the ZPL and the rest is emitted into the phonon sideband. This low emission fraction limits the ability to employ V_{Si}^- in various quantum information schemes. To increase the fraction of light emitted into the ZPL and increase the defect emission rate, we fabricated high-quality factor nanophotonic crystal cavities designed to match the ZPL frequency. Through tuning of the cavity into resonance with the ZPLs, we have demonstrated a 75-fold Purcell enhancement at 4K. This talk will describe the fabrication process for 1D nanobeam photonic crystal cavities, leading to quality factors in excess of 10^4 . The highest cavity-defect interactions depend on resonance in frequency and high spatial overlap of the defect with the maximum electric field within the cavity. Using the cavity as a “nanoscope”, revealing defect position, we used laser irradiation annealing at varying times and different laser frequencies to infer the diffusive motion of defects within the cavity. We showed that a systematic and controlled laser annealing can increase the ZPL of the implanted cavity mode by a factor of 4.

5:00pm **QS+2D+EM+MN+NS-TuA9 Tailoring the Heterogeneities in 2D Materials by Controlled Synthesis and Processing**, *Kai Xiao, X. Li, K. Wang, A. Oyedele, M. Yoon, S. Xia, M. Mahjouri-Samani, C.M. Rouleau, A.A. Puzetky, L. Liang, R.R. Unocic, D. Geohagan*, Oak Ridge National Laboratory

Two-dimensional (2D) materials are intrinsically heterogeneous, therefore controlling defects, understanding the impact of boundaries and interfaces and developing means to exploit these heterogeneities is a transformative opportunity that could underpin future technologies and energy applications. In this talk, I will discuss the fundamental understanding of the roles of heterogeneities including defects, dopants, edges, strain, and phases in 2D materials on their optoelectronic properties. Through isoelectronic doping in monolayer of MoSe_2 , the Se vacancies are effectively suppressed and photoluminescence is significantly enhanced. In addition, we demonstrate the non-equilibrium, bottom-up growth approach not only can tailor the defect density far beyond intrinsic levels in monolayers of 2D MoSe_2 , but also create new antisite defects in monolayers of WS_2 during the synthesis. The build-in localized strain in 2D crystals directly grown on patterned curved surface can tune the bandgap of 2D crystals for possible quantum emitting applications. The bottom up synthesis of 2D materials discussed here provides excellent control over the heterogeneity in 2D materials, which can modulate the optical and electrical properties in 2D materials and their heterostructures for ultra-thin and flexible electronics.

Acknowledgment: Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:20pm **QS+2D+EM+MN+NS-TuA10 Epitaxial Al Films for Plasmonic and Quantum Computing Applications**, *Ka Ming Law, S. Budhathoki, S. Ranjit, F. Martin, A.J. Hauser*, The University of Alabama

Superconducting resonators are important for application in quantum computing but require high quality factors. Much work has been done on superconducting resonators fabricated from aluminum thin films on sapphire, and superconducting Josephson tunnel junctions made from aluminum are used as the basis for quantum bit designs. In addition, epitaxial aluminum films has attracted attention in plasmonics due to their superior performance in the UV regime compared to Au and Ag, and their compatibility with current CMOS technology. Sapphire substrates are chemically stable and have low lattice mismatch with aluminum, allowing higher film quality without the need for elaborate substrate preparation and time-consuming growth procedures.

Epitaxial aluminum films were successfully grown by off-axis magnetron sputtering on c-plane sapphire. This study assessed the effects of varying

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both substrate preparation conditions and growth and prebake temperatures on crystallinity and smoothness. X-ray diffraction and reflectivity measurements demonstrate superior crystallinity and surface smoothness for films grown at 200°C/15mTorr Ar. An additional substrate preparation procedure which involves 1) a modified RCA procedure and 2) prebake in oxygen environment is shown by atomic force microscopy to be highly effective in reducing void density and depth.

5:40pm **QS+2D+EM+MN+NS-TuA11 2019 AVS Mid-Atlantic Student Awardee Talk: Minimizing Coulomb Oscillation Linewidth on Silicon Quantum Dots, Yanxue Hong¹, A.N. Ramanayaka, M.D. Stewart, Jr., X.Q. Wang, R.V. Kashid, P. Nambodiri, R.M. Silver, J.M. Pomeroy**, National Institute of Standards and Technology (NIST)

In quantum science research, both cryogenic temperatures and low measurement noise are required for high fidelity. For silicon quantum dot devices, an increase in either one causes broadening of Coulomb blockade peaks, which is usually referred to as a high electron temperature. Here we report on temperature-dependent (T-dependent) conductance measurements and evaluation of effective electron temperature (T_{eff}) using an STM-patterned atom-scale silicon single-electron transistor (SET). Measurements are made in various cryogenic systems over temperatures varying from 10 mK to 25 K. The effective electron temperature is extracted by fitting the experimental data using a theoretical model. We initially find that the measured peak width has a linear dependence on the bath temperature above 1 K and saturates below 1 K. In addition, a considerable mismatch (> 2 K) between the lattice (thermometer) temperature and the carrier temperature (T_{eff}) is observed. Therefore, the Coulomb resonance is not only thermally broadened by T_{eff} but also broadened by other T-independent sources such as gate noise, triboelectric noise, etc. We study the origins of the saturation at low temperature regime and analyze factors inducing high T_{eff} . We report on progress to reduce the noise and reach an effective temperature of < 300 mK. Since our silicon SETs have high charging energies and large energy level spacings, we also seek to measure the transition from classical (multilevel) regime to quantum (single-level) regime by manipulating the bath temperature.

6:00pm **QS+2D+EM+MN+NS-TuA12 Micro-magnetic Simulations of Correlated Switching in Touching Nano-magnetic Elements, Tejumade Durowade, V. Metlushko**, University of Illinois at Chicago

Nanomagnets hold significant potential for use as building blocks for room temperature quantum computers. Bistability based on stable ground magnetization states means power dissipation can be extremely low and their small size allows magnetization to be maintained for a long period time [1]. With packing density on the order of 10^{10} /cm² and switching frequency in the terahertz range, nanomagnets are a promising replacement for current state of art metal oxide semiconductor processes that are already at the limits of continued scaling. In this work, we present the results of simulations of touching nanomagnetic disks that can be used for room operable quantum computing. Like gears in a mechanical system, the chirality of the magnetization in each disk is determined through interaction with its neighbors. These simulations offer insight into the switching dynamics within the disks as current experimental techniques lack the combined temporal and spatial resolution needed to observe the formation and annihilation of the magnetic domains that facilitate the switching process. The switching of touching symmetric disks can be achieved at zero applied field as the disks settle into a remanent vortex state, meaning minimal energy loss during the process. Due to the quantum exchange force, at the point of contact between disks, the magnetization vectors rotate in the same direction giving rise to opposite chiralities in the disks. Since logic states can be represented using the chirality of the in-plane magnetization, configurations of touching disks can potentially be used to implement basic or complex logic functions. Maintaining coherence of opposite chirality in chains of disks was achieved with the introduction of a biasing element to eliminate the bidirectionality of interaction between disks.

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- [7] M. Donahue *et al.*, *OOMMF, NIST, US Depart. Commerce*

Tuesday Evening Poster Sessions, October 22, 2019

2D Materials

Room Union Station B - Session 2D-TuP

2D Poster Session

2D-TuP2 Black Phosphorus and Endohedral-Graphene Hybrids for Novel Optoelectronic Devices, *M. Min, Srishti Chugh, A.B. Kaul*, University of North Texas

Among the various two-dimensional (2D) materials, graphene is a material of immense technological importance given its ballistic transport which provides opportunities for high-speed field-effect transistors (FETs). Other mono-elemental 2D materials such as black phosphorus (BP) provide a thickness-dependent, direct band gap ranging from ~ 0.3 eV in the bulk to ~ 1.5 eV in the monolayer limit. Here, in the first part of the work, we report on the integration of zero-dimensional materials with 2D graphene membranes to enhance the optoelectronic properties of the photodetectors. Quantum dot-graphene optoelectronic devices are discussed where mechanically exfoliated graphene flakes are used in a two-terminal device configuration. The zero-dimensional materials used in this work were cluster endohedral fullerenes, $Sc_3N@C_{80}$, and monometallic endohedral fullerene, $La@C_{82}$, based on their electron-accepting and electron-donating abilities, respectively. Temperature-dependent and wavelength-dependent optoelectronic properties of the OD-2D graphene-based hybrids will be presented. In the second part of the work, we will also show the chemical exfoliation of BP to form optoelectronic devices with protecting layers to enhance the stability of the BP. Here, we present liquid exfoliation approaches to obtain BP by sonication in organic solvent such as 1-cyclohexyl-2-pyrrolidone (CHP), *N*-methyl-2-pyrrolidone (NMP) at ambient conditions. We compare the structural properties of black phosphorus through Raman Spectroscopy analysis, Photoluminescence (PL) and two-terminal electronic device measurements to demonstrate its enhanced device stability.

2D-TuP3 Nitrogen-Doped Graphene on Cu(111): Edge-Guided Doping Process and Doping-Induced Variation of Local Work Function, *J. Neilson, H. Chinkeziyan, H. Phirke, A. Osei-Twumasi*, California State University, Northridge; *Y. Li*, Peking University, China; *C. Chichiri*, California State University, Northridge; *J. Cho*, Myongji University, Korea; *K. Palotás*, Hungarian Academy of Sciences, Hungary; *L. Gan*, Peking University, China; *S.J. Garrett, K.C. Lau*, California State University, Northridge; *Li Gao*, California State University Northridge

The nitrogen-containing sole precursor azafullerene has been used for the synthesis of nitrogen-doped graphene on the Cu(111) surface. The synthesis process, doping properties, and doping-induced variation of local work function of graphene have been studied on the atomic scale by combining scanning tunneling microscopy/spectroscopy, X-ray photoelectron spectroscopy, and density functional theory calculations. Most nitrogen dopants are at the edges of graphene islands and the graphene domain boundaries with the pyridinic configuration. Graphitic nitrogen dopants arrange into curved lines within graphene islands after multiple growth cycles, which results from a doping process guided by the edges of graphene islands. The doping-induced variation of local work function of the graphene surface has been measured on the atomic scale by recording spatially resolved field emission resonances. We find that the local work function strongly depends on the atomic bonding configuration and concentration of nitrogen dopants. The local work function decreases for graphitic nitrogen doping but increases for pyridinic nitrogen doping. This work provides new atomic-scale insights into the process for incorporating nitrogen atoms into the graphene lattice as well as the correlations between the type of nitrogen doping and the variation of local work function.

2D-TuP4 Vibrational Progression of a Single Hydrocarbon Molecule on Graphene and Hexagonal Boron Nitride, *Alexander Mehler, N. Néel, J. Halle*, Technische Universität Ilmenau, Germany; *M.L. Bocquet*, École normale supérieure, PSL University, Sorbonne Université, CNRS, France; *J. Kröger*, Technische Universität Ilmenau, Germany

Probing genuine molecular properties even after adsorption on a surface requires the efficient reduction of the molecule-surface hybridization. Two-dimensional materials, such as graphene, hexagonal Boron Nitride (hBN) and stackings thereof, are promising buffer layers to this end. Scanning tunneling microscopy and spectroscopy at low temperature is used to explore molecular orbitals and vibrational quanta of the hydrocarbon molecule DBP (Dibenzotetraphenylperiflanthen) on graphene and hBN with submolecular resolution. Independent of the metal substrate, Ir(111), Pt(111) and Ru(0001), vibrational progression in both DBP frontier orbitals

is observed for graphene and hBN, albeit with different numbers of vibrational quanta involved. Density functional calculations unveil that symmetry matching of electronic and vibrational excitations supports the observation of vibrational progression. The lifetime of the vibronic levels can be tuned by the molecular environment of a single DBP as well as by using different kinds and numbers of buffer layers.

2D-TuP5 Synthesis of Layered PdS₂ Film and Homo-junction Device Fabrication, *C.-A. Jong*, TSRI/NARL, Taiwan, Republic of China; *Y. Yang*, NTNU, Taiwan, Republic of China; *M.-H. Le*, NTHU, Taiwan, Republic of China; *P.-S. Chen*, MUST, Taiwan, Republic of China; *Chien-Bao Lin, P.-K. Chiu, C.-N. Hsiao*, TIRI/NARL, Taiwan, Republic of China

Lots of TMDs materials with fantastic properties have been widely discovered for electrical and optical device application. In order to replace current Si-based device several challenges should be overcome, including the 2D synthesis and patterning technique; heterojunction control between TMDs to TMDs, TMDs to dielectric film and TMDs to metallic film, doping technique and so on. Among them, MoS₂ and WSe₂ have shown their excellent electron and hole mobility in NFET and PFET evaluation. For electronic and photonic applications, a material existing air-stable, high carrier mobility, high on/off ratio, as well as a tunable band gap is far more desirable. Recent theoretical and experimental data show some noble chalcogenides can also form layered structures with S or Se atoms, like PdS₂ and PdSe₂[1-3]. Each Pd atom can bond to four S or Se atoms, respectively. Puckered PdSe₂ exhibit a widely tunable band gap that varies from metallic (bulk) to ~ 1.3 eV (monolayer) and the field-effect transistors made from PdSe₂ reveal high electron field-effect mobility of ~ 158 cm²/Vs are presented [4]. Recently, Mahdi et al., [5] proposed a unique alternative to reduce contact resistance through the single material junction device scheme, that is, using a single material (PdS₂) in channel and S/D region. Monolayer PdS₂ was found to be semiconducting with a bandgap of 1.1 eV and became semi-metallic as bilayer. PdS₂ was also reported with a high electron mobility than MoS₂. However, not too much experimental works has been published yet in PdS₂ synthesis. To realize the reported device integration, the thickness control and sulfurization process are important. In our previous works [6-7], a possible approach in ultra-thin and uniform 2D layer film synthesis was demonstrated combined with proposed ALE and sulfurization process.

In this study, the PdS₂ film synthesis and single material junction device fabrication will be performed. Pd film was sputtered onto SiO₂/Si substrate for sulfurization. The PdS₂ film was obtained after sulfurization and the structure is verified [8]. The XRD, XPS and Raman spectrum are measured for microstructure evaluation. A lift-off process in channel and source and drain patterning was achieved. With the help of anisotropic etch in Pd film thin down, the desired thickness and wafer scale flatness was controlled. The etched thickness and surface roughness are monitored by AFM. Followed by the etch process, the etched samples were sulfurized for PdS₂ formation. After the sulfurization process the homo-junction device using a single material was fabricated and the electrical properties was characterized.

2D-TuP6 NanoESCA III: Momentum Microscopy on 2D Materials, *Marten Patt*, Scienta Omicron GmbH, Germany; *N. Weber, M. Escher, T.-J. Kuehn, M. Merkel*, FOCUS GmbH, Germany

New 2D material classes including graphene, transition metal dichalcogenides (TMDCs) or 2D heterostructures based on TMDCs or graphene are nowadays a promising candidate to be used in future electronic devices. They are chemically versatile and thus predestined to tune their electronic structure for various applications (e.g. electronic, optoelectronic and spintronic).

To examine these materials, a fast band structure mapping in combination with a high lateral resolution in real-space and live view microscopy becomes essential. The band structure mapping is used to understand the electronic structure of new material combinations, while the real-space microscopy is needed to localize the crystals on the specimen, especially if they were produced by mechanical exfoliation or intercalation techniques [1].

The NanoESCA microscope allows to easily switch between the imaging of the real- and the momentum- space of photoemission electrons and is therefore predestined to examine novel 2D materials. In the so-called momentum microscopy mode, the NanoESCA acquires the band structure from a microscopic sample region of interest, which was beforehand defined in real-space.

We will show recent band-structure measurements of several TMDCs (see e.g. [2]) acquired with the instrument and discuss the latest technical

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improvements of the momentum microscopy technique with respect to 2D material characterization.

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2D-TuP7 Shifting of Electronic States of Meso-tetrakis(pentafluorophenyl) Porphyrin Self-assembled Monolayers Due to Internal Molecular Structure, *Jose Ortiz-Garcia, M. Wolf, M. Guberman-Pfeffer, J. Gascon, D. Thuita, C. Brückner, R.C. Quardokus*, University of Connecticut

Meso-tetrakis(pentafluorophenyl) porphyrin (T^FPP) self-assembled islands were imaged on Au (111) using an ultra-high vacuum scanning tunneling microscope (LT-UHV STM). A pulse-solenoid valve was used to deposit submonolayer coverage of T^FPP porphyrins on Au(111). A range of bias voltages were used to image occupied and unoccupied electronic states of T^FPP. Density functional theory (DFT) was used to calculate the spread in energy levels of both occupied and unoccupied molecular orbitals. We found that the spacing of the energy levels of electronic states shifts depending on the presence and location of hydrogens bonded to the inner nitrogens (locants 21-24).

2D-TuP8 Reproducibility and Replicability in Science and Engineering: A Report by the National Academies, *Jennifer Heimberg*, National Academies of Sciences, Engineering, and Medicine

One of the pathways by which scientists confirm the validity of a new finding or discovery is by repeating the research that produced it. When a scientific effort fails to independently confirm the computations or results of a previous study, some argue that the observed inconsistency may be an important precursor to new discovery while others fear it may be a symptom of a lack of rigor in science. When a newly reported scientific study has far-reaching implications for science or a major, potential impact on the public, the question of its reliability takes on heightened importance. Concerns over reproducibility and replicability have been expressed in both scientific and popular media.

As these concerns increased in recent years, Congress directed the National Science Foundation to contract with the National Academies of Science, Engineering, and Medicine to undertake a study to assess reproducibility and replicability in scientific and engineering research and to provide findings and recommendations for improving rigor and transparency in research.

The committee appointed by the National Academies to carry out this task included individuals representing a wide range of expertise: methodology and statistics, philosophy of science, science communication, behavioral and social sciences, earth and life sciences, physical sciences, computational science, engineering, academic leadership, journal editors, and industry expertise in quality control. Individuals with expertise pertaining to reproducibility and replicability of research results across a variety of fields were included as well.

This poster will present the committee's approach to the task and highlights from its findings, conclusions, and recommendations related to factors that influence reproducibility, sources of replicability, strategies for supporting reproducibility and replicability, and how reproducibility and replicability fit into the broader framework of scientific quality and rigor.

2D-TuP9 Structural and Electronic Properties of Native Point Defects in MoTe₂, *Ziling Deng, S.M. Mueller, W. Windl, J.A. Gupta*, The Ohio State University

We performed density functional theory(DFT) calculation to studied the structural and electronic properties of native point defects in MoTe₂. Various kinds of defects, e.g., vacancies, antisites with different charge states will be considered. With DFT, we will predict the constitutional defects with the lowest formation energies for all systems in Mo-rich, Te-rich and stoichiometric conditions as well as their dominated charge states. Additionally, the resulting output of our theoretical atomic scale model based on DFT-calculation will be used to simulate Scanning Tunneling Microscopy

[https://en.wikipedia.org/wiki/Scanning_tunneling_microscope](STM) images to allow for comparison with experimental STM images. This study will provide an effective method to study the defects in MoTe₂ systems, with the comparison with experiments, the results will shed new light on the defect studying in MoTe₂.

MoTe₂, a two-dimensional(2D) layered material has recently attracted much attention due to its excellent electronic properties. Intrinsic defects are commonly observed in MoTe₂ growth, which would have a significant impact on the physical, optical, thermal, and electrical properties of the material. However, studying the atomic structure of intrinsic defects in this 2D materials is difficult since they damage quickly under the intense electron irradiation in TEM. To overcome this, we have performed a joint study between STM measurements and DFT calculations to identify the atomic structure and electronic nature of native point defects in MoTe₂. We constructed analytical model from DFT and studied the structural and electronic properties of those defects. In order to understand the formation of defects and their atom-scale dynamics in MoTe₂, we will use DFT to predict the constitutional defects with the lowest formation energies as well as their dominated charge states in Mo-rich, Te-rich and stoichiometric conditions to determine the necessary chemical potentials for all systems of MoTe₂. Additionally, theoretically simulated STM images generated by density functional theory were used to compare with experimental STM data to enable us to assign structure of a number of defects observed during experiments.

This study provides an effective method to study the defects in MoTe₂ systems by presenting results for the energetics of native point defects in MoTe₂. Base on our calculation, the formation energies and charged states of the vacancies and antisites will be determined, moreover, the simulated simulated STM images allow for the identification of structural defects of MoTe₂ observed in the experiment.

2D-TuP10 A Role of Au Atoms on Oxidized Black Phosphorus; Study using Scanning Photoelectron Microscopy, *D. Kim, H. Choi, Jaeyoon Baik*, Pohang Accelerator Laboratory, Republic of Korea

We investigated oxygen reduction of black phosphorus(BP) using scanning photoemission electron spectroscopy. In spite of many effort of realizing ultra-thin film transistor of 2-dimensional atomic material of BP, inherent limitation in the transfer method such as oxidation, has not allowed application in real devices. Therefore, it is necessary to study the development of methods to prevent oxidation or reduction through the post-processing. However, such studies are very important to observe chemical composition changes using XPS, but there are other limitations in investigating based on flakes of the BP in um-size using general XPS. In this work, we observed Au atom, which deposited on BP, could play a role of catalyst reducing the oxidation on the top layers of BP. Using SPEM analysis method with 200nm spatial resolution, we verified the reduction mechanism of the um-size flake BP. As a result, we could observe that oxygen in the BP oxide disappeared through the Au atoms. Therefore, this can be applied to BP's Oxide Removal and Thickness Control technology and is expected to provide useful information for future application of the element.

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2D-TuP11 Growth and Electrical, Nano-Optical Characterization of semiconducting MoS₂/WS₂ in-plane Heterostructures, *Sourav Garg, P.K. Kung, S.M. Kim*, The University of Alabama; *A. Krayev*, Horiba Scientific, Novato

In-plane heterojunctions of atomic-thick (2D) semiconductors (MoS₂/WS₂) are novel structures that can potentially pave the way for efficient ultrathin and flexible optoelectronics, such as light sources and photovoltaics. Such heterostructures (HS) are very rare and not much is known about their characteristics. They can only be achieved through a synthetic growth process such as chemical vapor deposition (CVD). This is unlike vertical heterostructures, for which the materials can be mechanically stacked one layer on top of the other. The CVD growth of in-plane heterostructure is a thermodynamically driven process and presents a number of challenges to control the vapor pressure of the precursors. Additionally, new analytical tools need to be developed in order to gain access to and understand the physical properties of these HS.

Here, we report a one-step CVD growth of monolayer (1 nm) thick MoS₂/WS₂ in-plane heterostructures. We have characterized their morphological and optical properties using micro-Raman and photoluminescence spectroscopy. Kelvin probe force microscope was used to extract the surface potential profile across the MoS₂/WS₂ heterojunction boundary, which was then used to gain access to fundamental semiconductor heterostructure parameters such as depletion layer width

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and built-in field across the MoS₂-WS₂ interface. In-addition more rigorous study of heterostructures interface by tip enhanced PL (TEPL) had been performed.

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 IrSi₃ 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), ZrB₂(0001) and Au(110) substrates. Here, we present a new method to grow silicene via high temperature surface reconstruction of hexagonal IrSi₃ nanocrystals. The h-IrSi₃ 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 IrSi₃ 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 FeTe_{1-x}Sex (x = 0, 0.5) films grown on prototypical Bi-based bulk topological insulators. We observe fully developed U-shaped superconducting gaps in FeTe_{0.5}Se_{0.5} layers of one unit cell (UC) thickness with a transition temperature (T_c) of ~11 K, close to the one of the corresponding bulk system (T_c ~ 14.5 K) [1]. Surprisingly, we also find clear evidence for superconductivity up to T_c ~ 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 bicollinear AFM order. By using 3D-vector-resolved SP-STM techniques [3] we find an unusual reorientation of the diagonal double-stripe spin structure at Fe_{1+y}Te 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".

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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 defects³. 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 bonds⁴ 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

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9:40am 2D+AS+MI+NS-WeM6 Atomic Manipulation of Defects in the Layered Semiconductor 2H-MoTe₂, *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, MoTe₂ by scanning tunneling microscopy (STM). Bulk MoTe₂ was cleaved at room temperature in ultrahigh vacuum and imaged with a cut PtIr tip at 9K. Native defects in the MoTe₂ 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-MoTe₂.

11:00am 2D+AS+MI+NS-WeM10 Scanning Tunneling Microscopy and Spectroscopy of a Heterotriangulene-based 2D Polymer, *Zachery Enderon, 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 dimethylmethylen-bridged triphenylamine (DTPA) COF is an excellent example of the unique systems one can fabricate with these techniques¹. 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.

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11:20am 2D+AS+MI+NS-WeM11 Scanning Tunneling Microscopy Investigations of Molecules Adsorbed on Semiconducting Graphene Nanoribbons, *Sineth Premaratna, K.Z. Latt, S.-W. Hla*, Ohio University

Unlike graphene, semiconducting graphene nanoribbons possess 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 nanoribbons 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, the vibration spectroscopy measurements of the molecules further provide a strong vibration mode associated with the C=C ring stretching of the molecules. This work provides 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.

Acknowledgement: This work is supported by the DOE-BES, DE-FG02-02ER46012 grant.

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 sexiphenyl 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.

Acknowledgement: This work is supported by the DOE-BES, DE-FG02-02ER46012 grant.

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, M.A. 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.

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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 $\alpha\text{-In}_2\text{Se}_3$ for Non-Volatile Memory Applications, *M. Si, Peide Ye*, Purdue University

$\alpha\text{-In}_2\text{Se}_3$ 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 $\mu\text{A}/\mu\text{m}$, low supply voltage with scaled gate insulator and the potential to exceed the existing Fe-FETs for non-volatile memory applications.

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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_2As_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. David**, 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 $(\text{CH}_3(\text{CH}_2)_n\text{NH}_3)(\text{CH}_3\text{-NH}_3)_{n-1}\text{Pb}_{n+1}\text{I}_{3n+1}$ 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 $[\text{PbI}_6]^{4-}$ 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. For 2D 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 $[\text{PbI}_6]^{4-}$ 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

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- [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-NbSe₂, 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 NbSe₂ doesn't exist in nature, here we show that single layer 1T

NbSe₂ 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 NbSe₂ is also a Mott insulator, similar to that of bulk 1T TaS₂. 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-NbSe₂ 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.

Supported by NSF-DMR 1508325, and Ohio Supercomputer Center .

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.

Work done in collaboration with S. K. Banerjee, L. F. Register, B. J. LeRoy, A. H. MacDonald, T. Taniguchi, and K. Watanabe.

- [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).
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Wednesday Morning, October 23, 2019

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 $1 \text{ W m}^{-1} \text{ K}^{-1}$ 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 move¹ 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 $3 \times 10^5 \text{ V/cm}$ 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 ($150 \text{ V}/5 \mu\text{m}$). 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 tunneling² 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.

FG, MH, and LJB gratefully acknowledge support from AFOSR Grant No. FA9550-18-1-0066 (A. Sayir). HVW and MG acknowledge Deutsche Forschungsgemeinschaft (Gr 1011/26-1).

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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. Warmington*, 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 $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ complex structures. We studied $\text{Si}_{1-x}\text{Ge}_x/\text{Si}/\text{Si}_{1-x}\text{Ge}_x/\text{Si}/\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ 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 $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ 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 $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ 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_2O_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_2O_5) has attracted considerable interest for its potential use as a cathode for solid state lithium ion batteries. While researchers have studied the V_2O_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_2O_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 $\text{Li}_x\text{V}_2\text{O}_5$ 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_2O_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

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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.

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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).

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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 (RXK, HZX).

12:00pm **EM+2D+AS+MI+MN+NS+TF-WeM13 Reference Materials for Localization Microscopy**, *C.R. Copeland, R.G. Dixon, 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.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+2D+SS-WeM

Exotic Nanostructured Surfaces for Heterogeneously-Catalyzed Reactions

Moderators: Ashleigh Baber, James Madison University, Erin Iski, University of Tulsa

8:20am **HC+2D+SS-WeM2 Selective Alkane Chemistry on IrO₂(110) Surfaces, Aravind Asthagiri, M. Kim, The Ohio State University; J.F. Weaver, University of Florida**

Selective conversion of alkanes to higher value species using heterogeneous catalysts is of great interest with the increasing availability of light alkanes from shale fracking. We have used a combination of temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) to demonstrate that the stoichiometric terminated IrO₂(110) surface can activate methane and ethane below room temperatures, and furthermore, that this surface can be selective towards ethane dehydrogenation to ethylene. For ethane, DFT shows that adsorption and initial C-H bond cleavage to surface bound C₂H₄* is facile and the selectivity step occurs between further C-H bond breaking leading to complete oxidation versus ethylene desorption. The reactivity of this surface is mediated by the presence of undercoordinated Ir (Ir_{cus}) and adjacent bridge O atoms (O_{br}). Using the combination of TPRS and DFT we find that pre-hydrogenating the IrO₂(110) surface results in the formation of HO_{br} sites that increases the selectivity towards ethylene by increasing the barrier to C-H bond cleavage for C₂H₄* and decreasing the desorption energy of C₂H₄*. We will discuss efforts to use DFT and microkinetic modeling to explore doping strategies of both the Ir_{cus} and O_{br} sites to promote selectivity towards ethylene formation.

8:40am **HC+2D+SS-WeM3 Design of Nanostructured Catalysts for Better Performance, Francisco Zaera, University of California, Riverside INVITED**

One of the major challenges in heterogeneous catalysis is the preparation of highly selective and robust catalysts. The goal is to be able to synthesize solids with stable surfaces containing a large number of specific surface sites designed for the promotion of a particular reaction. New synergies between surface-science studies and novel nanosynthesis methodology promise to afford new ways to design such highly selective catalysts in a controlled way. In this presentation we will provide a progress report on a couple of projects ongoing in our laboratory based on this approach. Platinum-based catalysts have been prepared for the selective trans-to-cis conversion of olefins, with a design based on early surface-science work with model surfaces and quantum mechanical calculations that indicated a particular preference for (111) facets in promoting the formation of the cis isomers. We are currently extending this research by using the concept of "single-site catalysis" with Pt-Cu bimetallics for the selective hydrogenation of unsaturated aldehydes. In a second example, new metal@TiO₂ yolk-shell nanomaterials conceived for both regular and photo-induced catalytic applications have been used to promote CO oxidation at cryogenic temperatures and to suggest that in photocatalysis the role of the metal may not be to scavenge the excited electrons produced in the semiconductor upon absorption of light, as commonly believed, but rather to promote the recombination of the adsorbed atomic hydrogen initially produced by reduction of H⁺ on the surface of that semiconductor. New mixed-oxide surfaces are being designed using atomic layer deposition (ALD) as well.

9:20am **HC+2D+SS-WeM5 Characterization of a Pd/Ag(111) Single Atom Alloy Surface Using CO as a Probing Molecule for H₂ Dissociation, Mark Muir, M. Trenary, University of Illinois at Chicago**

Tuning catalysts for selective hydrogenation reactions is ultimately determined by the nature of the active site for H₂ dissociation and the adsorption of atomic hydrogen on the surface. Several single atom alloys (SAAs) consisting of small amounts of Pd deposited onto surfaces of metals that do not activate H₂ dissociation, such as Cu(111) and Au(111), have been previously studied. In the present study, we characterize Pd/Ag(111), a possible new single atom alloy surface using reflection absorption infrared spectroscopy (RAIRS) of adsorbed CO as a probe. From 0.01 to 0.04 ML Pd/Ag(111), a ν(CO) stretching peak was seen at 2050 cm⁻¹ corresponding to CO adsorbed on palladium atoms at the on-top site,

indicating a single atom alloy surface. By increasing the palladium coverage to approximately 0.05 ML and above, a second ν(CO) stretching peak was seen at 1950 cm⁻¹ corresponding to CO adsorbed on a palladium bridge site, indicating palladium dimer formation. The surface palladium coverage was determined using temperature programmed desorption (TPD) of CO and Auger electron spectroscopy (AES). By annealing these surfaces to 500 K, the palladium atoms diffuse into the subsurface, and a ν(CO) stretching peak at 2150 cm⁻¹ (CO adsorbed on silver atoms) is greatly enhanced in intensity due to subsurface palladium. The subsurface to surface palladium ratios on the single atom alloy surfaces were varied from capped Ag/Pd/Ag(111), to a 50:50 ratio, to approximately a 60:40 ratio. The ability of subsurface palladium on the Pd/Ag(111) SAA surfaces to facilitate hydrogen dissociation was explored using H₂ and D₂ TPD.

9:40am **HC+2D+SS-WeM6 Propyne Hydrogenation over a Pd/Cu(111) Single Atom Alloy Catalyst Studied with Infrared Spectroscopy, Mohammed Abdel-Rahman, M. Trenary, University of Illinois at Chicago**

The hydrogenation of propyne (C₃H₄) to propylene (C₃H₆) using a Pd/Cu(111) single atom alloy (SAA) has been studied using polarization dependent-reflection absorption infrared spectroscopy. This method allows for simultaneous monitoring of reactants and products in the gas-phase and species adsorbed on the surface during the reaction. The results were compared with the hydrogenation of propyne using Pd-free Cu(111) as well as previous studies on Pd/Cu SAA alumina-supported metal catalysts. Propylene production first occurs at 383 K as indicated by the presence of an infrared peak at 912 cm⁻¹, which is a uniquely characteristic of gas-phase propylene. The presence of propyne oligomers on the surface is indicated by a dramatic increase in the peak intensity at 2968 cm⁻¹ at temperatures above 400 K. The progression of the peaks at 912 and 3322 cm⁻¹ was used to calculate the rate of production of propylene and the rate of consumption of propyne, respectively. This reaction rate was used to determine a turnover frequency (TOF) for the reaction on the Pd/Cu SAA catalyst.

11:00am **HC+2D+SS-WeM10 "Single-Atom" Catalysis: How Structure Influences Reactivity, Gareth S. Parkinson, TU Wien, Austria INVITED**

The field of „single-atom“ catalysis (SAC) [1-2] emerged as the ultimate limit of attempts to minimize the amount of precious metal used in heterogeneous catalysis. Over time, it has become clear that metal adatoms behave differently to supported nanoparticles [3-4], primarily because they form chemical bonds with the support and become charged. In this sense, SAC systems resemble the mononuclear coordination complexes used in homogeneous catalysis, and there is much excitement that SAC could achieve similar levels of selectivity, and even heterogenize problematic reactions currently performed in solution. It is important to note, however, that homogeneous catalysts are designed for purpose based on well-understood structure-function relationships, but the complexity of real SAC systems means that the structure of the active site is difficult to determine, never mind design. In this talk, I will describe how we are using precisely-defined model supports [5] to unravel the fundamentals of SAC. I will show a selection of our latest results in this area, including scanning probe microscopy, x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) data to show how the local structure of Ir₁/Fe₃O₄(001) and Rh₁/Fe₃O₄(001) single atom catalysts changes based on preparation and adsorption of reactants, and how the structures obtained can be rationalised by analogy to Ir(I) and Ir(IV) complexes, respectively. If time permits, I will also show that CO oxidation activity in the Pt₁/Fe₃O₄(001) system is promoted by water.

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[2] Liu, J., Catalysis by supported single metal atoms. *ACS Catalysis* **7** (2016) 34-59.

[3] Gates, B.C., et al., Atomically dispersed supported metal catalysts: perspectives and suggestions for future research. *Catalysis Science & Technology* **7** (2017) 4259-4275.

[4] Parkinson GS, *Catalysis Letters* **149** (2019), 1137-1146

[5] Bliem, R., et al., Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science*, **346** (2014) 1215-8.

11:40am **HC+2D+SS-WeM12 Oxidation Reactions on Rh(111), Marie Turano, G. Hildebrandt, Loyola University Chicago; R.G. Farber, The University of Chicago; D.R. Killelea, Loyola University Chicago**

The uptake and subsequent surface structures of oxygen on transition metal surfaces reveal much about the reactivity of the metal catalyst. On clean Rh(111) at room temperatures in ultra high vacuum (UHV), oxygen

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molecules (O_2) readily dissociate into two adsorbed oxygen atoms, asymptotically approaching a saturation coverage of 0.5 monolayers (ML, $1 \text{ ML} = 1.5 \times 10^{15} \text{ O atoms cm}^{-2}$). However, exposing Rh(111) to gas-phase oxygen atoms (atomic oxygen, AO) generated by thermally cracking molecular oxygen over a hot Ir filament, allows for higher oxygen coverages. In addition, oxygen not only adsorbs to the surface, but it may also penetrate into the subsurface region of the crystal. After atomic oxygen exposures at elevated temperatures, the Rh(111) surface is covered in a combination of oxides, adsorbed surface oxygen, and subsurface oxygen (O_{sub}). The coexistence of a variety of structures allows for the determination of which species is reactive to the oxidation of carbon monoxide (CO) on highly oxidized Rh(111) surfaces. Using scanning tunneling microscopy (STM), we have determined that CO oxidation occurs mainly at the interface between the metallic and oxidic surface phases on Rh(111) where the O_{sub} , upon emergence from the bulk, replenishes the surface oxygen. Once O_{sub} is depleted, CO consumes the oxide and the surface quickly degrades into the $(2 \times 2)\text{-O} + \text{CO}$ adlayer.

12:00pm HC+2D+SS-WeM13 Adsorption and Motion of Atomic Oxygen on the Surface and Subsurface of Ag(111) and Ag(110), S.B. Isbill, C.J. Mize, L.D. Crosby, Sharani Roy, University of Tennessee Knoxville

Silver surfaces act as important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards understanding the mechanism of heterogeneous catalytic oxidation by silver, the role of subsurface oxygen in such catalysis has yet to be elucidated. Subsurface oxygen is adsorbed just beneath the surface of the metal and is believed to play an important role in surface reconstruction and oxidation catalysis. In the present study, density functional theory (DFT) was used to study the interactions of atomic oxygen with the surface and subsurface of the Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption of atomic oxygen at different coverages and examine its effects on the structural and catalytic properties of silver. Our study of O/Ag(111) showed that adsorption of atomic oxygen was strong at low coverage but became weaker with an increase in coverage, much more so for surface oxygen than for subsurface oxygen. Therefore, at higher and industrially relevant oxygen coverages, oxygen preferred to bind to the subsurface than to the surface. In contrast, atomic oxygen bound more strongly to the surface than to the subsurface at all studied coverages. Based on the results from DFT, we constructed analytic models for adsorption in O/Ag(111) and O/Ag(110) as well as performed kinetic Monte Carlo simulations to explain the differences in coverage dependence of surface adsorption versus subsurface adsorption on the two surfaces. The results provide qualitative insight on why surface and subsurface oxygen might have qualitatively different effects on the electronic, geometric, and catalytic properties of silver.

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. Datzler, 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 $\text{Ba}(\text{Fe}_{1-x}\text{T}_x)_2\text{As}_2$, 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 ($\text{Ni}_{0.04}$ and $\text{Co}_{0.08}$) and hole ($\text{Cr}_{0.04}$) 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 $(\text{LuFeO}_3)_m(\text{LuFe}_2\text{O}_4)_n$, 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 $(\text{LuFeO}_3)_m(\text{LuFe}_2\text{O}_4)_n$ 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 $(\text{LuFeO}_3)_m(\text{LuFe}_2\text{O}_4)_n$ 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.

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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 probing 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 (MoS₂, PtSe₂, and LaOBiSe₂, 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 interactions 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 extent of the magnetic d -orbitals. The Bethe-Slater curve guides 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 KC¹, 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 spintronic devices, a single-phase microstructure with promising half-metallic character is recently reported in a bulk Co_{1.5}Ti_{0.5}FeGe Heusler alloy¹. This alloy has Ti substitution for Co atoms in the parent Co₂FeTiGe alloy, where the parent alloy does not exhibit half-metallic behavior². 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 MgAl₂O₄(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 L2₁ 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 MgAl₂O₄(100) are atomically smooth with a rms roughness of 0.2 nm. Magnetic measurements of films grown at 800°C 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 Co₂FeGe, *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/Fe₂₀Ni₈₀ bilayers as a function of NiO and Fe₂₀Ni₈₀ thickness. We present results using a different approach to determine the spin diffusion length, using trilayers of Fe₂₀Ni₈₀/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 Fe₂₀Ni₈₀ and strongly increases the effective damping parameter. With NiO between the Pt spin sink and the ferromagnetic Fe₂₀Ni₈₀, 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 Y₃Fe₅O₁₂/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).

Materials and Processes for Quantum Information, Computing and Science Focus Topic

Room B231-232 - Session QS+2D+EM+MN+NS+VT-WeM

Material Systems and Applications for Quantum Sciences

Moderators: Mena Gadalla, Harvard University, Kai Xiao, Oak Ridge National Laboratory

8:00am QS+2D+EM+MN+NS+VT-WeM1 Quantum Information at the Molecular Foundry - An Overview of New Toolsets for QIS Research, Adam Schwartzberg, S. Cabrini, D.F. Ogletree, A. Weber-Bargioni, Lawrence Berkeley National Laboratory (LBNL)

The fundamental unit of quantum computation and sensing is the qubit, and many physical systems have been investigated for practical realization. These include superconducting Josephson junction circuits, color centers, and isolated cold atoms or ions. Superconducting qubit circuits (SCQBs) being one of the most promising avenues to quantum computation.

¹ Falicov Student Award Finalist

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However, there are limitations to their practical application due to noise sources which shorten their functional lifetime.

In this talk I will introduce a suite of integrated, high-fidelity fabrication instrumentation that will allow new communities of users to investigate the fundamental limits of state-of-the-art quantum systems at the Molecular Foundry. We will enable users to understand existing systems and design new ones by creating a quantum fabrication toolset for directed growth of conventional and novel materials, advanced lithography and pattern transfer paired with in- and ex-situ surface characterization.

Three key QIS fabrication capabilities at the Molecular Foundry:

A robotic fabrication cluster system with materials deposition, including atomic layer and physical vapor depositions, plasma etching, and analytical characterization instrumentation, all automated by and contained within a vacuum sample handling robot.

A high resolution electron beam writing system will allow quantum device patterning with complete flexibility in feature shape, density and size, enabling nanoscale feature control.

A low temperature transport measurement system will allow for the investigation of novel materials for superconductors and dielectrics and “close the loop” between design and fabrication, proxy measurements such as interface characterization, and actual performance of quantum computation and sensing elements.

This instrumentation suite will enable the elucidation of chemical composition, structure, location, and size of microscopic noise sources in a superconducting quantum system, understanding the fabrication steps that introduced such noise sources, and developing fabrication approaches that minimize their presence.

I will also discuss ongoing and new research directions at the Molecular Foundry through internal staff and external user research.

8:20am QS+2D+EM+MN+NS+VT-WeM2 Quantum Vacuum Metrology to Advance Quantum Science Capabilities, Jay Hendricks, J.E. Ricker, K.O. Douglass, National Institute of Standards and Technology (NIST); J.A. Fedchak, J. Scherschligt, National Institute of Standards and Technology (NIST)

NIST is developing a series of next generation pressure and vacuum standards that will serve as a basis for key vacuum technology platforms required for emerging quantum science applications. The production of quantum sensors and devices is anticipated to require extremely demanding process control with exact knowledge of background residual gas, process chamber pressure, and accurate measurement of gas pressure feedstocks.

In 2019, National Metrology Institutes around the world worked to redefine the international system of units, the SI, such that the base units are now based on fundamental constants.

Moving forward, the next generation of pressure and standards will provide a new route of SI traceability for the pascal. By taking advantage of both the properties of light interacting with a gas and that the pressure dependent refractive index of helium can be precisely predicted from fundamental, first-principles quantum-chemistry calculations, a new route of realizing the pascal has been demonstrated. This talk will briefly cover the classical methods of realizing pressure that have served the metrology community well for the past 375 years. And then will take a deeper dive into the next generation of light-based pressure standards that will enable the elimination of mercury manometers, replacing them with a smaller, lighter, faster, and higher precision standards. From a metrology standpoint, the new quantum-based SI pascal will move us from the classical force/area definition, to an energy density (joules per unit volume) definition. Should the technique be further miniaturized, it will lead to a revolution in pressure metrology, enabling a photonics-based device that serves both a gas pressure sensor and a portable gas pressure standard all in one.

NOTE: this topic is appropriate for VT sessions as well but thought it would be interesting to the broader audience that is interested in emerging quantum-based technologies that are needed to advance the field of quantum science.

8:40am QS+2D+EM+MN+NS+VT-WeM3 Quantum Control of Spins in Silicon Carbide with Photons and Phonons, D. Awschalom, S.J. Whiteley, G. Wolfowicz, K.C. Miao, Christopher Anderson, University of Chicago INVITED

There are numerous efforts to embrace solid-state defects and construct quantum systems to enable new information technologies based on the quantum nature of the electron. Current studies include semiconductors with incorporated point defects, whose quantum mechanical spin properties allow a fundamentally different means to process information. In particular, interfacing solid-state defect electron spins to other quantum systems is an ongoing challenge. Here we demonstrate electrically driven coherent quantum interference in the optical transition of single divacancies, enabling new control of the spin-photon interface [1]. By applying microwave frequency electric fields, we coherently drive the excited-state orbitals and induce Landau-Zener-Stückelberg interference fringes in the resonant optical absorption spectrum. Furthermore, we develop a stroboscopic X-ray diffraction imaging technique that provides direct imaging and quantitative measurement of local strain at the nanometer scale. In conjunction with the fabrication of surface acoustic wave resonators, we mechanically drive coherent Rabi oscillations between arbitrary ground-state spin levels, including magnetically forbidden spin transitions, allowing for acoustic quantum control of local spins in silicon carbide and the exploration of spin-phonon coupling in the solid state [2]. These properties establish divacancies as strong candidates for quantum communication and hybrid system applications, where simultaneous control over optical and spin degrees of freedom is paramount.

[1] K. C. Miao *et al.*, arxiv: 1905.12780

[2] S. J. Whiteley *et al.*, Nature Phys. **15**, 490 (2019)

9:20am QS+2D+EM+MN+NS+VT-WeM5 Tunable Control over InSb(110) Surface Conductance Utilizing Charged Defects, Robert Walko, S.M. Mueller, S. Gant, J.J. Repicky, S.J. Tjung, E. Lang, E. Fuller, K. Werner, The Ohio State University; F. Bergmann, Bergmann Messgeraete Entwicklung; E. Chowdhury, J.A. Gupta, The Ohio State University

In this work we present a scanning tunneling microscopy (STM) study of tip-induced switching of charge states in individual indium adatoms on the InSb(110) surface. These adatoms are deposited onto the surface by controlled voltage pulses between the STM tip and the surface. We observe them in two distinct charge states: positive and neutral. Adatom-induced band bending from the positively charged state has been observed to induce a tenfold increase in surface conductance relative to the charge neutral state, the effect of which can be observed >100nm away from the indium adatom. When the STM tip is brought sufficiently close to the defect, electrons can tunnel from the tip to the defect and cause the charge state to switch from positive to neutral. During imaging, this switching leads to a “crater” feature around the defect due to the lower conductance of the charge neutral state. The spatial extent of the crater can be tuned via the applied bias voltage, the tunneling set-point current, and photoillumination of the surface. We explain this phenomenon using a model of competing rates between the filling and emptying of the defect state, similar to dangling bonds on the Si(111) surface.

This work acknowledges funding from the DOE (# DE-SC0016379)

9:40am QS+2D+EM+MN+NS+VT-WeM6 Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform, Matthew R. Rosenberger, U.S. Naval Research Laboratory; C.K. Dass, Air Force Research Laboratory; H.-J. Chuang, S.V. Sivaram, K.M. McCreary, U.S. Naval Research Laboratory; J.R. Hendrickson, Air Force Research Laboratory; B.T. Jonker, U.S. Naval Research Laboratory

We present a paradigm for encoding strain into two dimensional materials (2DM) to create and deterministically place single photon emitters (SPEs) in arbitrary locations with nanometer-scale precision. Our material platform consists of a 2DM placed on top of a deformable polymer film. Upon application of sufficient mechanical stress using an atomic force microscope tip, the 2DM/polymer composite deforms, resulting in formation of highly localized strain fields with excellent control and repeatability. We show that SPEs are created and localized at these nanoindentations, and exhibit single photon emission up to 60K. This **quantum calligraphy** allows deterministic placement and real time design of arbitrary patterns of SPEs for facile coupling with photonic waveguides, cavities and plasmonic structures. In addition to enabling versatile placement of SPEs, these results present a general methodology for imparting strain into 2DM with nanometer-scale precision, providing an invaluable tool for further investigations and future applications of strain engineering of 2DM and 2DM devices.

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Reference: Rosenberger et al., "Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform," *ACS Nano*, 2019, <https://pubs.acs.org/doi/10.1021/acsnano.8b08730>

11:00am **QS+2D+EM+MN+NS+VT-WeM10 Challenges in Topological and Quantum Materials, *David Alan Tennant***, Oak Ridge National Laboratory
INVITED

Quantum materials are rapidly advancing but still present great challenges. Topological quantum

materials in particular are receiving great attention as they provide potentially robust routes to

quantum information processing that are protected against decoherence processes. Among key

challenges are the prediction and realization of magnetic materials in the form of magnetic Weyl

semimetals and quantum spin liquids as ways of realizing exotic quasiparticles such as Majorana fermions

that can be used for application. These materials present new experimental challenges in terms of identifying their

quasiparticles and demonstrating quantum coherence in their ground states states. Here I will

show how we are using the integrated application of machine learning along with experiment and synthesis

to advance the discovery and understanding of these materials.

11:40am **QS+2D+EM+MN+NS+VT-WeM12 Rare Earth Silicon Photonics Engineering for Quantum Applications, *Arindam Nandi*, *X. Jiang*, *D. Pak***, Purdue University; *D.N. Perry*, *E.S. Bielejec*, Sandia National Laboratories; *Y. Xuan*, *M. Hosseini*, Purdue University

Controlling intermodal coupling between multiple excitations within a photonic material may enable the design of novel quantum photonic metamaterials exhibiting anomalous effects. Understanding the complex mode dynamics towards the engineering of system Hamiltonian has been the subject of intensive research in recent years. Here, we design an atomic lattice composed of nearly 1000 rare earth ion segments deterministically engineered in silicon photonic structures to modify the emission properties of erbium in silicon. We observe anomalous photon emission at the telecommunication wavelength from atoms geometrically arranged to reduce the propagation loss. Moreover, we map asymmetric emission lineshapes led by intermodal Fano-type interference of the atomic and photonic resonance modes. Our observation paves the way for designing active metamaterials and novel topological photonics with engineered linear and nonlinear interactions for broad applications in quantum information. Moreover, I will result for direct integration of rare earth crystals with silicon photonic chip for implementation of quantum optical memories. The approach can impact the fields of quantum communication and computation through, for example, developing superradiant single photon sources, the study of non-equilibrium many-body quantum dynamics, and engineering quantum transport in a scalable solid-state platform.

Wednesday Afternoon, October 23, 2019

2D Materials

Room A216 - Session 2D+EM+MN+NS-WeA

2D Device Physics and Applications

Moderator: Ivan Oleynik, University of South Florida

2:20pm **2D+EM+MN+NS-WeA1 Monolayer Electronics and Optoelectronics - Advances, Opportunities and Challenges, Ali Javey, University of California at Berkeley** **INVITED**

Two-dimensional semiconductors exhibit excellent device characteristics, as well as novel optical, electrical, and optoelectronic characteristics. In this talk, I will present our recent advancements in surface passivation, contact engineering, surface charge transfer doping, and heterostructure devices of layered chalcogenides. We have developed a passivation technique that allows for observation of near-unity photoluminescence quantum yield in monolayer semiconductors. I will discuss the mechanism by which non-radiative recombination can be fully removed in monolayers. The work presents the first demonstration of an optoelectronically perfect monolayer, and highlights one of their unique properties. Finally, I will discuss an AC carrier injection mechanism to enable bright light emitting devices using monolayers, overcoming the problem of Schottky contacts.

3:00pm **2D+EM+MN+NS-WeA3 Investigation on Graphene Band-gap Engineering for Graphene Transistors Applications, Benfdila Arezki, University M. Mammeri Tizi-Ouzou, Algeria**

Graphene transistors are considered to be the successor's basic element for the next generation of advanced integrated circuits. However, graphene material suffers from the absence of bandgap to behave as semiconductor. The present paper deals with the investigation on the bandgap engineering approach aiming an increase of the switching characteristics of the graphene transistors.

The main obstacle for graphene transistor is the material zero bandgap that worsens the switching characteristics of the GFETs. Several techniques have been proposed to open a bandgap in graphene, among these engineering techniques, we can cite the Substrate induced bandgap, Bandgap engineering using h-BN/Ni (111). It is known that in theory a maximum of 0.50 to 0.53 eV can be obtained. Such bandgaps are observed on Graphene Bi-Layer (GBL) sheets grown on silicon carbide (SiC).

Other methods are the substitutional doping (SD), Nitrogen doping (NB). In any case graphene engineering should be considered in chemistry and physics view points. A high selective hydrogenation of graphene grown by lithography under the form of nanoruban showed a very interesting result of 0.7 eV. This process is part of selective chemical graphene functionalization techniques (SCGF).

In this paper we will deal with the graphene nanoruban and the opening of a bandgap capable of inducing an appreciable switching current ratio of at least $I_{ON}/I_{OFF} > 10^6$.

The Graphene Nano Ribbon (GNR) structure used in the form of GNRFET for logic circuits and RF devices combines the high field, high mobility and the possibility of opening a bandgap. The higher carrier mobility of graphene is the basis of all electrical characteristics of graphene transistors.

In this paper we have used a semi-classical device model including the band to band tunneling that is described in Ref⁶ to emphasize on the bandgap engineering. Device performances are studied based on the current-voltage characteristics with respective bandgap width variations. I_{OFF} current estimated and the performance ratio deduced.

3:20pm **2D+EM+MN+NS-WeA4 Fully Inkjet Printed, High Photo-responsive, 2D WSe₂-Graphene Based Flexible Photodetector, R.F. Hossain, A.B. Kaul, Avra Bandyopadhyay, University of North Texas**

Tungsten di-selenide (WSe₂), a classic representative of two dimensional (2D) layered materials has recently drawn much attention due to its unique optoelectronic properties, offering a potential platform to construct hetero-structure photodetector (PD) for ultrafast optoelectronic devices on low-cost, flexible substrates [1,2]. As WSe₂ exhibits a weak van der Waals interlayer bonding, one of the approaches to obtain 2D WSe₂ is through top-down liquid phase exfoliation (LPE), where the bulk crystal is dispersed in a solvent through appropriate sonication and centrifugation conditions [1]. In this work, we report on the synthesis of WSe₂ via LPE and the first-ever assembly of an all inkjet printed WSe₂-graphene hetero-structure PD on flexible polyimide film, where the WSe₂ acted as a photo-active semiconductor and graphene was the carrier collector. The inkjet printed PD was photo-responsive to broadband incoming radiation in the visible regime, and exhibited a high photoresponsivity $R \sim 0.70$ A/W, and

detectivity $D \sim 3 \times 10^{10}$ Jones. The strain-dependent measurements were conducted with bending for different curvatures, indicating the feasibility of such devices for large format arrays printed on flexible substrates. The capacitance-frequency ($C-f$) measurements were performed to investigate the trap states. In conclusion, this unique all inkjet printed 2D hetero-junction photodetector formed on flexible and conformable substrate was successfully shown to be highly photo-responsive to a wide range of light intensities and strain levels, making it a promising prospect for scalable flexible electronic and optoelectronic devices and circuitry.

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4:20pm **2D+EM+MN+NS-WeA7 Chemical Vapor Sensing with Transition Metal Dichalcogenides via Photoluminescence Modulation, Aubrey T. Hanbicki, P.M. Campbell, S.V. Sivaram, U.S. Naval Research Laboratory; A.J. Kusterbeck, Nova Research, Inc.; V.K. Nguyen, R.A. McGill, K.M. McCreary, B.T. Jonker, E.D. Cobas, F.K. Perkins, U.S. Naval Research Laboratory; A.L. Friedman, Laboratory for Physical Sciences**

Two-dimensional transition metal dichalcogenides (TMDs) such as MoS₂ and MoSe₂ are promising materials for chemical vapor sensing applications. Their potential includes straightforward fabrication, readily available materials, and good selectivity, sensitivity, and speed of response. We previously showed [1] that monolayer TMDs are sensitive to and selective for vapors of strong electron donors and/or strong electron acceptors in concentrations as low as 1 part per million (ppm). Another attractive aspect is that TMDs have been shown to detect chemical vapors and gases in several ways, for instance via changes in electrical conductance or photoluminescence (PL) [2]. Sensors commonly have been fabricated based on the chemiresistive device properties, but here we will discuss our recent studies implementing TMD sensors using the PL as the core element of the sensor. We show that the PL intensity of monolayer CVD-grown WS₂ can rapidly (<< 1sec) detect triethylamine (TEA), a decomposition byproduct of the VX series of nerve agents, in concentrations <<1 ppm. The optical response is similar to the electrical response of other TMDs previously shown [1]. We shall discuss the mechanisms determining the size and shape of the optical responses. We envision suites of different TMDs using both optical and conductance sensing to rapidly and selectively detect chemical agents.

This research was performed while S.V.S held a National Research Council fellowship at NRL. This work was supported by core programs at NRL.

References

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4:40pm **2D+EM+MN+NS-WeA8 Effective and Robust Graphene Immunological Sensors Functionalized through Non-covalent Ninding of Antibody-Conjugated Tripodal Compound, A. Hugo, CEA-LETI, France; C. Sun, Northwestern University; M. Kumar, CEA-LETI, France; R. Othmen, J. Renard, V. Bouchiat, CNRS-Institut Néel, France; J. Mann, Northwestern University; J.M. Parpia, H.G. Craighead, Cornell University; P. Mailley, CEA-LETI, France; W.R. Dichtel, Northwestern University; T. ALAVA, Sebastian Hentz, CEA-LETI, France**

Electrical detection is a very robust technique to transduce the adsorption of charged protein to a biological selective layer (i.e. biosensing). Electrolyte gated field effect transistors (EGFET) integrating graphene monolayers as the transducing element have shown outstanding electrical sensitivity in liquid compared to silicon and diamond based EGFET. In order to build graphene EGFET as effective biosensing unit it is important to attach at its surface a functional layers of biological molecules that will carry the task of enforcing specific detection of compound. Protein are widely used as specific bioreceptor for sensor biological functionalization yet it has been shown that protein lose their function when simply adsorbed on graphene. Covalent binding being out of the way for 2D dimensional crystals such as graphene (for the inherent deterioration of mechanical and electrical properties) we have shown that custom made tripodal compound attaching the graphene basal plane through Pi-stacking of aromatic moieties could be used to attach specific biomolecules to graphene while maintaining their biological function hence their specificity.

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In this report we present an optimized fabrication process for graphene EGFET that includes patterning and passivation of electrical contact. The devices reproducibly show state of the art electrical performances. We demonstrate that the process can be simply transferred to different host substrates to integrate graphene EGFET ubiquitously on Silicon, glass or printed circuit board with similar performances. Finally, we implemented biological functionalization of the sensors by attaching streptavidin to the sensor thanks to the non-covalent tripodal compound. We report consistent changes in the Dirac peak of graphene due to the adsorption of tripodal compound and streptavidin as well as the binding of biotin, specifically bound to streptavidin. We show the detection to be specific and reproducible.

5:00pm **2D+EM+MN+NS-WeA9 Electronic Properties of Ultra-Thin Na₃Bi: A Platform for a Topological Transistor, Mark Edmonds, Monash University, Australia** INVITED

Na₃Bi in bulk form represents a zero-bandgap topological Dirac semimetal (TDS), but when confined to few-layers is predicted to be a quantum spin Hall insulator with bulk bandgap of 300 meV.¹ Furthermore, application of an electric field to few-layer Na₃Bi has been predicted to induce a topological phase transition from conventional to topological insulator.²

I will discuss our efforts to grow epitaxial few-layer Na₃Bi via molecular beam epitaxy, and probe its electronic structure and response to an electric field using scanning probe microscopy/spectroscopy and angle-resolved photoelectron spectroscopy. We demonstrate that monolayer and bilayer Na₃Bi are wide bandgap quantum spin Hall insulators ($E_g > 300$ meV) that can be tuned with an electric field to semi-metallic, and at higher electric fields re-opened as a conventional insulator.³ This is the first experimental demonstration of such an electric field tuned topological phase transition in any material. Finally, I will discuss our most recent efforts to perform transport measurements on few-layer Na₃Bi at doping levels corresponding to bulk conduction and edge conduction, with and without an applied magnetic field.

References

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6:00pm **2D+EM+MN+NS-WeA12 Negative Fermi-level Pinning Effect Induced by Graphene Interlayer in Metal/Graphene/Semiconductor Junction, H.H. Yoon, W. Song, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea; S. Jung, SK Hynix, Republic of Korea; J. Kim, Ulsan National Institute of Science and Technology (UNIST); K. Mo, G. Choi, H.Y. Jeong, J.H. Lee, Kibog Park, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea**

We report the direct observation revealing that the electric dipole layer originating from the off-centric distribution of interacting electrons at metal/graphene interface can induce the negative Fermi-level pinning effect in metal/graphene/semiconductor junction made on a semiconductor substrate containing regions with low interface-trap density. The graphene interlayer takes a role of diffusion barrier preventing the atomic intermixing at interface and preserving the low interface-trap density region. The change of electrostatic potential across the metal/graphene interface due to the interaction dipole layer and the doping of graphene is found to cause the negative Fermi-level pinning effect, supported by the Schottky barrier decreasing as metal work-function increasing. In case of metal/graphene/GaAs junction, the local small patches with very thin or no native oxide layer are considered to be responsible for the negative Fermi-level pinning. In the prevailing region with normal native oxides surrounding the small patches, the Fermi-level pinning appears to be strong. Meanwhile, the negative Fermi-level pinning is found to occur globally in metal/graphene/SiC junction where the SiC substrate is known to produce a low density of interface traps. This work provides an experimental method to form Schottky and Ohmic-like contacts simultaneously on a semiconductor substrate covered partially with graphene by using identical metal electrodes.

**Electronic Materials and Photonics Division
Room A214 - Session EM+2D+NS+TF-WeA**

THEME Session: Electronics and Photonics for a Low-Carbon Future

Moderators: Michael A. Filler, Georgia Institute of Technology, Stephen McDonnell, University of Virginia

2:20pm **EM+2D+NS+TF-WeA1 Uncovering the Materials Paradigm for Solar Absorbers through In situ Imaging and Characterization, Mariana Bertoni, Arizona State University** INVITED

The behavior of solar cells is very often limited by inhomogeneously distributed nanoscale defects. This is the case throughout the entire lifecycle of the solar cell, from the distribution of elements and defects during solar cell growth as well as the charge-collection and recombination during operation, to degradation and failure mechanisms due to impurity diffusion, crack formation, and irradiation- and heat-induced cell damage. This has been known for a while in the field of crystalline silicon, but inhomogeneities are far more abundant in polycrystalline materials, and are the limiting factor in thin-film solar cells where grain sizes are often on the order of the diffusion length.

We will show that the high penetration of hard X-rays combined with the high sensitivity to elemental distribution, structure, and spatial resolution offers a unique avenue for highly correlative studies at the nanoscale. We will present results on CdTe and Cu(In,Ga)Se₂ where carrier collection is directly correlated to the compositional and structural properties of the material under a large variety of synthesis and operating conditions. The segregation of copper at the grain boundaries of both solar absorbers will be discussed in detail as well as the defects impact to carrier collection efficiency. Furthermore, the kinetics of copper segregation during growth and processing will be presented.

3:00pm **EM+2D+NS+TF-WeA3 Atomic Layer Deposition's Potential in Sustainability, Karen Buechler, ALD NanoSolutions** INVITED

Atomic layer deposition (ALD) is an exciting thin film deposition technique which holds the promise to permit enormous material innovations. These material innovations are currently enabling advanced catalysts, high capacity energy storage, advanced manufacturing technologies and many other products. Many of these products work towards reducing energy needs. This talk will highlight several examples of advanced material development through ALD which lead to advanced products which in turn are reducing the carbon footprint of consumers and manufacturers.

4:20pm **EM+2D+NS+TF-WeA7 Challenges in Materials and Processing to Implementation of Energy Efficient SiC Technology, Mei-Chien Lu, Monte Rosa Technology**

Energy and sustainability have been the main driving forces for the implementation of silicon carbide technology for efficient energy conversion in recent applications in electrical vehicles, hybrid electrical vehicles, data center power management, and photovoltaic and wind power. The decades-long research and development efforts are attributed to the complexity of polytypes of crystal structures of silicon carbide. Reducing these inherent defects from crystal growth and epitaxial layer growth are crucial and continuing tasks. Device architectures are found to be more efficient along selected crystal planes. Innovative processing technologies have to be developed to make these devices built by compound semiconductors with strong covalent bonding manufacturable. Fundamental challenges in materials, devices, and processing technologies will first be briefed. A patent landscape analysis is then conducted herein to reveal the past trends to pave the paths for future research and development. Implementations of silicon carbide devices are in its infancy with some full SiC inverter adopted by a commercial electrical vehicle manufacturer. Market shares and momentum of silicon carbide power electronics as well as the expectations from perspectives of department of energy and industry major players will be discussed. The continuous efforts to address the challenges in materials and processing are encouraged to support the full scale implementation of energy efficient silicon carbide technology.

4:40pm **EM+2D+NS+TF-WeA8 High Efficiency of Hot Electron Transfer at a Metal-Insulator-Semiconductor to Electrolyte Interface, Hyun Uk Chae, R. Ahsan, Q. Lin, R. Kapadia, University of Southern California**

Hot electrons generated from metal has drawn considerable interest in recent years due to the potential for lowering the high-barrier chemical reactions. The majority of hot electron controlling strategy at present have been plasmonic devices using localized surface plasmon resonance (LSPR).

Several works have been done using plasmons to induce the hot electron generation to use as catalysts for chemical reactions like hydrogen evolution reaction (HER). However, the efficiency of those devices is extremely low and the mechanism behind it is quite complicated and remain unclear until now. To take advantage of hot electrons efficiently, properly and simply designed devices are required. Here, we demonstrate the different mechanisms of hot electron transfer in a thin gold film in an Au-Al₂O₃-Si metal-insulator-semiconductor (MIS) junction by modulating Au film thickness, the applied voltage between Au-Si junction. Hot electron injection contributes to modifying the electron distribution inside the Au electrode, which enables HER to be driven more at same overpotential in solution. This work present that the injection of non-equilibrium electrons can shift the onset voltage of HER by ~0.6 V on the gold film in a 0.5 M H₂SO₄ solution. The efficiency of hot electron density efficiency shows ~85% at 2V of MIS junction bias and solution bias of -1.5 V vs Ag/AgCl is also presented. In addition to experimental results, we carried out the 2-D Monte Carlo simulation to track the injected hot electrons to study for the detail behaviors of thermalization mechanism inside the Au region which indicates the rate of HER. Since electrons quickly lose their energy within femtosecond by electron-electron or electron-phonon scattering, it is significant to see how they behave inside the injected medium to understand the reactions more precisely. The high-efficiency of hot electron usage reported here can be an opening towards the creation of practical hot-electron devices, which could be widely applied to the various fields.

5:00pm **EM+2D+NS+TF-WeA9 Integrated Photocathodes for Solar Driven Conversion of Carbon Dioxide to value-added Products**, J.W. Ager, Lawrence Berkeley Lab, University of California, Berkeley; **Guru Gurudayal**, PPG **INVITED**

If renewable power sources such as solar and wind could be used to produce chemical precursors and/or fuels, it would provide an alternative to mankind's unsustainable use of fossil fuels and slow the rate of CO₂ emission into the atmosphere [1,2]. Solar to chemical energy conversion by photoelectrochemical processes is a promising approach to address this challenge. Analogous to photovoltaics [3], driving the uphill redox reactions required for net solar to chemical energy conversion necessitates directional charge transport [4]. Additionally, in order to convert carbon dioxide to hydrocarbons, one must manage multi-electron transfer reactions (e.g. 12 in the case of ethylene and ethanol), and minimize potential losses in all parts of the system [5].

Charge selective contacts can be used to steer direct photo-generated carriers to catalytic sites that perform CO₂ reduction in an integrated photocathode. In contrast to conventional photocathode designs which employ p-type absorbers, we used a back illumination geometry with an n-type Si absorber to permit the use of absorbing metallic catalysts which would otherwise block the light. Back and front interfaces were configured by ion implantation and by surface passivation to achieve carrier selectivity. Surface texturing of the Si was used to optimize light absorption on the illuminated side and increase the surface area available for catalysis on the electrolyte side. Selectivity to C-C coupled products was achieved by using hierarchical Au-Ag-Cu nanostructures as electrocatalysts [6].

The photovoltage, 550-600 mV under simulated 1-sun illumination, confirms the carrier selectivity and passivation of the front and back interfaces. Compared to planar controls, textured photocathodes generate higher current densities, exceeding 30 mA cm⁻². Under simulated diurnal illumination conditions, over 60% faradaic efficiency to C₂₊ hydrocarbon and oxygenate products (mainly ethylene, ethanol, propanol) is maintained for several days. By coupling photocathodes to series-connected semi-transparent halide perovskite solar cells, we demonstrated stand-alone, CO₂ reduction with a 1.5% conversion efficiency to hydrocarbons and oxygenates [7].

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5:40pm **EM+2D+NS+TF-WeA11 Modeling of Optical Scattering in White Beetle Scales**, Seung Ho Lee, S.M. Han, S.E. Han, University of New Mexico
Keywords: Light Scattering; Diffusion Approximation

Abstract: Extremely thin “super-white” coatings that reject solar spectrum but radiate through the transparent atmospheric window in mid-infrared have broad implications in heat management and energy savings for diverse sectors, including building construction, ship manufacturing, and space vehicle operation. In our previous work, we were able to create paint-format “super-white” coatings from microsphere-based materials.^{1,2} In this work, however, we borrow our inspiration from white beetles in nature that reveal structural ingenuity at the nanometer scale to achieve such white film. White beetle scales display exceptionally strong light scattering power from a thin anisotropic random biopolymer network. While previous studies have revealed that the anisotropy plays an important role in strong light scattering, the physics of anisotropic light propagation remains less than fully understood. In particular, the studies have shown that light scattering in anisotropic random media may deviate significantly from the anisotropic diffusion approximation. This uncertainty in diffusion approximation led to a study interrogating the scale structures by fully solving Maxwell's equations. These calculations yet left questions on their accuracy, as the structural dimensions in perpendicular direction to the incident light were significantly greater than optical wavelengths. In this work, we systematically reduce the structural size in our simulations, using Fourier analysis of the white beetle scale structures. The size reduction enables fast, accurate calculations of light scattering in the biological structures. From these simulations, we find that the diffusion approximation is valid in describing light propagation in the white beetle scales. Further, we derive a light diffusion equation for anisotropic media from the radiative transfer equation and show that the equation for anisotropic diffusion derived in the past studies is inaccurate. We discuss how our newly derived equation can be used for accurate numerical calculations of light scattering and characterizing anisotropic light diffusion.

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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 a 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.

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3:00pm **MI+2D-WeA3 Emergence and Dynamics of Magnetic Order in Metamagnetic Nanostructures**, *Vojtech Uhlik*, 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.

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4:20pm **MI+2D-WeA7 Time Dependence in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ 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

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ 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 Magnetoreflexivity 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 magnetoreflexivity 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 $\text{MAPbBr}_3/\text{Co}$ sample during the neutron magnetoreflexivity measurement. This observation provides an evidence to show optically induced magnetization on the perovskite surface in contact with Co surface. Furthermore, the $\text{MAPbBr}_3/\text{Co}$ 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

Magnetolectric 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 ($\text{Fe}_{81}\text{Ga}_{19}$ 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_2O_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.

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[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. Ullaa*, Ohio University

We explore proximity-induced ferromagnetism (FM) and antiferromagnetism (AFM) on transition metal dichalcogenide (TMD), focusing on molybdenum ditelluride (MoTe_2) 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 MoTe_2 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 MoTe_2/FM -substrate and/or MoTe_2/AFM -substrate configuration can serve as building blocks for spintronic devices and

provide versatile platforms to further understand proximity effects in diverse materials systems.

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N.C. acknowledges support from Conicyt grant 21160844, DGIP and the hospitality of Ohio University. L.R. and P.A.O. acknowledge FONDECYT grant 1180914 and DGIP USM internal grant. S. E. U. and O. A.-O. acknowledge support from NSF DMR-1508325.

6:00pm **MI+2D-WeA12 Magnetocaloric Properties of Thin Film $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$: Magnetic Field Dependence and Effects of Superparamagnetism**, *Navid Mottaghi¹, 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

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (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. Azizliha, A. Haertter, M.B. Johnson, M.S. Seehra, and M.B. Holcomb, J. Phys. Condens. Matter **30**, 405804 (2018).

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Nanometer-scale Science and Technology Division

Room A222 - Session NS+2D+AS-WeA

Probing and Modifying Surface and Interfacial Chemistry at the Nanoscale

Moderators: Phillip First, Georgia Institute of Technology, Adina Luican-Mayer, University of Ottawa, Canada

2:20pm **NS+2D+AS-WeA1 Bitumen's Microstructures are Correlated with its Bulk Thermal and Rheological Properties**, *x. Yu, Worcester Polytechnic Institute; S. Granados-Focil, Clark University; M. Tao, Nancy Burnham, Worcester Polytechnic Institute*

Understanding of how the chemistry of asphalt binders (i.e., bitumens) affects their bulk properties is critical for development of structure-related mechanical models and performance-based specifications for asphalt binders, including mitigation of potholes and improved recycling of this non-renewable material. However, establishing the chemical-mechanical relationships that govern asphalt binders' properties remains a challenge due to binders' complex chemical makeup [1] and the intriguing dynamic molecular interactions among binders' various chemical constituents. [2] Here, we investigate the effect of chemical composition on binders' microstructure and thermal and rheological behavior. Two virgin binders from different crude oil origins were chosen and a series of derivative binders was made by remixing different weight ratios of the asphaltenes and the maltenes obtained from the two source binders. Thermal and

rheological properties of all binders were measured using modulated differential scanning calorimetry and dynamic shear rheometry, respectively. Binders' microscopic characteristics (e.g., nano- and microstructures and their contrast in phase images) were evaluated using atomic force microscopy. In bitumens with more miscibility between the asphaltenes and maltenes, the samples appear to undergo a sol-gel transition as the asphaltene concentration increases above 25%. In less miscible bitumens, micro-scale phase segregation is readily apparent at the surface. Our results show that bitumens' characteristic microstructures, as a result of the complex molecular interactions among their various chemical components, are correlated with their bulk thermal and mechanical properties. Notably, the asphaltene/maltene ratio alone cannot predict a bitumen's bulk properties. Instead, a bitumen's distinctive microstructures and its colloidal miscibility index provide meaningful insights into the effect of chemical composition on glass transition, phase stability, and rheological properties of the bitumen, which may in turn help improve the sustainability and design of roads. [3]

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2. X. Yu et al., Energy & Fuels **32**, 67-80 (2018).

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2:40pm **NS+2D+AS-WeA2 Energetics and Statistical Mechanical Analysis of Complexation on Metal Surfaces**, *J. Lee, J.W. Evans, T.L. Windus, P.A. Thiel, Da-Jiang Liu*, Ames Laboratory and Iowa State University

Stabilities of metal-ligand complexes on surfaces are crucial for the process of self assembly of 2D structures. We provide a comprehensive theoretical assessment at the level of Density Functional Theory (DFT) of the stability of various coinage metal-sulfur complexes, M_mS_n , with $M = \text{Cu, Ag, and Au}$, both in the gas-phase and also for these complexes adsorbed on the (111) and (100) surfaces of the same coinage metal. An early influential theoretical study on S/Cu(111) proposed that the Cu_2S_3 complex being the most stable copper containing species. Later combined low temperature STM and DFT studies suggest that a heart-shaped Cu_2S_3 and its concatenations being more stable. Larger and even more complex Ag-S complexes have been observed for S/Ag(111). No complexation have been observed for S/Cu(100) and S/Ag(100). On the other hand, a Au_4S_5 complex and its fragmentations have been observed for S/Au(100), but no complexation is observed for S/Au(111) at low S coverage. We select a set of nine types of complexes, chosen for their proposed existences, intrinsic stabilities, and affinities for adsorption on metal surfaces. For the adsorbed species, we calculate various aspects of their energetics including their formation energy from sulfur adsorbed on terraces and from metal atoms that are in thermal equilibrium with the substrate. From this perspective, our DFT analysis shows that Ag_2S_3 , Ag_3S_3 and many larger complexes on Ag(111) are strongly stable, Cu_2S_3 is stable and some larger complexes are marginally stable on Cu(111), but only Au- s_4 on Au(111) is stable. In contrast, no complex is stable on Cu(100) and Ag(100), but a group of complex is stable on Au(100), with Au_4S_5 . DFT results are consistent with experiments with the apparent exception of Au(111). This comprehensive assessment of energetics provides key input for statistical mechanical analysis of S adlayer ordering in the absence of complexation, and of the kinetics of complex formation and associated enhanced mass transport and surface dynamics.

3:00pm **NS+2D+AS-WeA3 Adding the Chemical Dimension to Lithography at All Scales: Enabling Cellular Therapies & Other Adventures in Biology and Medicine**, *Paul S. Weiss²*, University of California, Los Angeles **INVITED**

By controlling the exposed chemical functionality of materials from the submolecular through the centimeter scales, we have enabled new capabilities in biology, medicine, and other areas. I will discuss current and upcoming advances and will pose the challenges that lie ahead in creating, developing, and applying new tools using these capabilities. These advances include using biomolecular recognition in sensor arrays to probe dynamic chemistry in the brain and microbiome systems. In other areas, we introduce biomolecular payloads into cells for gene editing at high throughput for off-the-shelf solutions targeting hemoglobinopathies, immune diseases, and cancers. These methods use specific chemical functionalization and control of surface contact and adhesion in microfluidic channels.

¹ Falicov Student Award Finalist

² NSTD Recognition Award

Wednesday Afternoon, October 23, 2019

4:20pm **NS+2D+AS-WeA7 STM Directed Synthesis of Armchair Graphene Nanoribbons and Their Oxidation**, C. Ma, Oak Ridge National Laboratory; Z. Xiao, North Carolina State University; A.A. Puzos, Arthur Baddorf, Oak Ridge National Laboratory; W. Lu, North Carolina State University; K. Hong, Oak Ridge National Laboratory; J. Bernholc, North Carolina State University; A.-P. Li, Oak Ridge National Laboratory

Highly controlled synthesis of graphene nanoribbons (GNRs) can be performed on a surface by polymerization of a selected precursor. Typically, this polymerization involves surface-assisted cyclodehydrogenations during thermal activation on catalytic metal surfaces. We have shown that armchair edge GNRs can be synthesized with 7, 14, and 21 carbon atom widths by absorbing 10,10'-dibromo-9,9'-bianthryl (DBBA) precursor molecules on Au(111).¹ Synthesis follows a two-step process of which the first step is polymerization at 470 K. The second step, cyclodehydrogenation, can be promoted globally by annealing to 670 K, or locally following hole injection using a scanning tunneling microscope (STM) tip.² Wider 14 or 21-AGNRs were formed when two or three 7-wide GNRs were conjugated side-by-side via inter-ribbon cyclodehydrogenation at the edge sites. Scanning Tunneling Spectroscopy (STS) reveals an electronic band gap dependent on the ribbon width. Bandgaps of ~2.6, ~0.3, and ~0.7 eV are measured for 7, 14, and 21 GNRs respectively, consistent with expectations of simple models.

For practical applications, understanding the stability of GNRs to oxidation is important. We have examined the thermal stability of 7-AGNRs after exposure to air.² Combining STM, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the armchair GNRs are found to oxidize first at the zigzag ends while the edges remain stable. Oxygen attaches to the zigzag ends at temperatures as low as 180°C. Armchair edges are stable up to 430°C and become oxidized only above 520°C. Two oxygen species are identified, one a hydroxyl (OH) and the second atomic oxygen bridging two carbons, both of which are common in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV in the vicinity of the hydroxyl and to 1.9 eV near bridging O. These results suggest that the oxidation will significantly affect the transport properties of GNRs and provide parameters useful for maintaining integrity of GNRs during processing for devices.

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

1. C. Ma, et al., *Nano Letters* 17, 6241 (2017).
2. C. Ma, et al., *Nature Communications* 8, 14815 (2017).
3. C. Ma, et al., *Physical Review Materials* 2, 014006 (2018).

4:40pm **NS+2D+AS-WeA8 Carbon-based Two-dimensional Materials from Surface-catalyzed Reactions of Small Molecules**, M. Wolf, C.R. Gerber, Rebecca Quardokus, University of Connecticut

Aryl halides undergo an Ullmann-like coupling reaction on surfaces to yield a carbon-based two-dimensional material. 1,2-dibromobenzene couples to Au(111) lifting the gold herringbone reconstruction. The reaction intermediates and coupled gold atoms are mobile on the surface at 4 K. The FCC and HCP sections of the underlying gold substrate shift to new positions. Annealing the dibromobenzene on Au(111) decouples the intermediates from the gold. The gold herringbone reconstruction returns and a covalently-bonded carbon-based network forms on the Au(111) surface.

5:00pm **NS+2D+AS-WeA9 Bottom-up Fabrication of 2D Molecular Networks via On-surface Reactions**, Sabine Maier, University of Erlangen-Nürnberg, Germany

INVITED

On-surface synthesis has attracted significant attention in recent years due to its potential to fabricate novel low-dimensional nanomaterials with atomic precision. In order to understand and control the synthesis of high-quality low-dimensional nanostructures, many efforts have been made to steer the reaction pathway by the design of smart precursors and by applying templating effects from the substrate. One of the challenges is the fabrication of long-range ordered two-dimensional covalently-linked networks via on-surface reactions. In contrast to molecular self-assemblies that are constructed by non-covalent bonds, the irreversible nature of the covalent bonds limits the structural control, which results in small domains and defects.

In my presentation, I will focus on recent high-resolution scanning probe microscopy experiments in combination with density-functional theory about the bottom-up fabrication and electronic properties of atomically precise one- and two-dimensional molecular nanostructures on metals.^[1-4] Thereby, the effect of the flexibility, the symmetry, and chirality of the

precursor molecules on the structure formation of covalently-linked molecular structures will be discussed. In particular, I will outline how well-ordered nanoporous 1D and 2D covalent molecular structures can be fabricated by use of debromination coupling reactions. We demonstrate the narrowing of the electronic band gap by increasing the π -system in covalently-linked structures and also show delocalized electronic states in surface-supported organometallic networks. Finally, I will conclude with a comparison of the structure formation of molecular nanostructures on bulk insulators and metal surfaces.

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- [2] M. Ammon, T. Sander, S. Maier, *J. Am. Chem. Soc.*, **2017** 139 (37), 12976–12984.
- [3] Z. Yang et al. *Nanoscale*, **2018**, 10, 3769–3776.
- [4] X. Zhang et al., *ACS Nano*, **2019**, 13 (2), 1385–1393.

5:40pm **NS+2D+AS-WeA11 Determining the Jahn-Teller Stabilization Energy of Surface Vacancies on Si(111)- $\sqrt{3} \times \sqrt{3}$ -R**, Daejin Eom, Korea Research Institute of Standards and Science, Republic of Korea; C.-Y. Moon, Korea Research Institute of Standards and Science; J.-Y. Koo, Korea Research Institute of Standards and Science, Republic of Korea

The vacancy defect on the Si surface becomes increasingly important with the device scaling because it works as the charge trapping and scattering center with varying ionization states. Yet its characteristics have not been addressed as comprehensively as the bulk vacancy in Si. In fact, its behavior would be affected by the gap state evolution and the Fermi level pinning on the Si surface. On the other hand, the (111)-surfaces of Si come to have the $\sqrt{3} \times \sqrt{3}$ reconstruction instead of the 7×7 one when they are heavily B-doped [1,2]. This $\sqrt{3} \times \sqrt{3}$ surface does not evolve any energy state within the band gap, being contrary to the 7×7 one [2]. Also, the Fermi level is shifted to the valence band maximum on the $\sqrt{3} \times \sqrt{3}$ surface whereas it is pinned in the middle of the gap on the 7×7 surface [2]. Hence the vacancy defects on the two surfaces may have dissimilar characteristics from each other. Here, we generate the vacancy defects on the $\sqrt{3} \times \sqrt{3}$ surface via the atom manipulation technique and measure their structural and electronic properties by using the scanning tunneling microscopy and spectroscopy. We find that, unlike the 7×7 surface, the vacancy defects on the $\sqrt{3} \times \sqrt{3}$ surface are Jahn-Teller distorted in the ground state, but undergo the symmetry-restoring transition when gated by the external bias. We also determine the energy gain or stabilization energy of the Jahn-Teller transition quantitatively. These findings would extend our knowledge on the surface vacancies on Si and eventually contribute to the fabrication of better-performing nanometer-scale devices.

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6:00pm **NS+2D+AS-WeA12 Influence of the Substrate on Self-Assembly: Terphenyl Monolayers investigated by NC-AFM and FM-KPFM**, Niklas Biere¹, Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany; S. Koch, P. Stohmann, Y. Yang, A. Götzhäuser, Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Germany; D. Anselmetti, Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany

Carbon Nano Membranes (CNM) are mechanically stable and homogeneous quasi-2D systems, which are formed by electron radiation induced, cross-linked self-assembled monolayers (SAM). Contrary to graphene, the CNM structural and functional properties can be tailored by the selection of precursors for the SAM formation [1]. CNMs show the capability to act as a molecular sieve to filter e.g. water molecules from impurities with extraordinary efficiency [2]. While this result promises remarkable applications, the actual process of CNM formation as well as their structure and the mechanism for water permeation is still in the focus of our investigations. Furthermore, the choice of substrate influences the self-assembly of our precursor molecules more than previously expected, even with isoelectronic surfaces like gold and silver. In this work, we will present data acquired by noncontact-AFM combined with FM-KPFM under ultra-high vacuum conditions to investigate and compare the morphology of in-situ prepared SAMs and CNMs of terphenylthiols on Au(111) and Ag(111).

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- [2] Y. Yang et al., *ACS Nano* **12** (2018) 4695–4701.

¹ NSTD Graduate 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].

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

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

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[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. Ekanayaka¹, 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 Mn³⁺ 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 d⁰ 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 (N₂) atmosphere leads to PL decline, while subsequent exposure to oxygen (O₂) 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 O₂ concentration. Combining the two sets of information, we are able to quantitatively evaluate the interaction between a single surface defect and a single O₂ molecule using a kinetic model. This model provides fundamental insights that could help reconcile the contradicting views on the interactions of molecular O₂ 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 1/2 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 Bi₂Se₃ 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

Tl 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 Bi₂Se₃ 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 Bi₂Se₃ 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 Bi₂Se₃. 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 Bi₂Se₃ to pristine Bi₂Se₃. In the case of pure Mn metal on Bi₂Se₃, 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 Bi₂ bilayers near the surface. Depositing a monolayer of MnSe_x produces very different results than the pure metal case. Bi₂Se₃ 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-MnSe₂ 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/Tl interface. This work is supported by NSF MRSEC under award number DMR-1420451.

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11:20am **2D+EM+MI+NS+QS+SS-ThM11 Atomically Resolved Electronic Properties of Defects in the in-plane Anisotropic Lattice of ReS₂**, *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 ReS₂ 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 ReS₂, 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.

Chemical Analysis and Imaging Interfaces Focus Topic

Room A120-121 - Session CA+2D+AS+BI+NS-ThM

Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces II

Moderators: Utkur Mirsaidov, National University of Singapore, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am **CA+2D+AS+BI+NS-ThM1 From Surfaces to Solid-Gas and Solid-liquid Interfaces: Ambient Pressure XPS and Beyond**, *Miquel B. Salmeron*, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

The rapidly increasing field of surfaces under ambient conditions of temperature and pressure, in gas and liquid environments, reflects the importance of understanding surface properties in conditions closer to practical situations. A lot of progress has been made in the last two decades, enabled by the emergence of a number of new techniques, both spectroscopy and microscopy, that can deliver atomic scale information with the required surface/interface sensitivity. I will present recent advances with examples that illustrate the novel understanding derived from the use of new techniques. One in the gas-solid interface where two important barriers have been bridged: the pressure gap, and the temperature gap. These gaps are very important when dealing with weakly bound molecules, where only in the presence of gas at a suitable pressure, or at low temperatures, a non-negligible coverage of adsorbed molecules can be achieved. The temperature gap manifests also in the removal of kinetic barriers. By bridging these two gaps a host of new interface structures have been unveiled that bring new understanding to catalytic phenomena. This will be illustrated with the examples of Cu and CuCo alloys in the presence of CO. In the case of solid-liquid interfaces, the introduction of new methods using well established x-ray spectroscopies is opening the way to the study of the important electrical double layer structure as a function of applied bias, as I will illustrate with the application of X-Ray absorption and IR to sulfuric acid-Pt and Ammonium Sulfate-graphene interfaces.

8:40am **CA+2D+AS+BI+NS-ThM3 Probing Solid-liquid Interfaces with Tender X-rays**, *Zbynek Novotny, N. Comini, B. Tobler*, University of Zuerich, Switzerland; *D. Aegerter, E. Fabbri*, Paul Scherrer Institute, Switzerland; *U. Maier*, Ferrovac GmbH, Switzerland; *L. Artiglia, J. Raabe, T. Huthwelker*, Paul Scherrer Institute, Switzerland; *J. Osterwalder*, University of Zuerich, Switzerland

Many important chemical and biological processes occur at the interface between a solid and a liquid, which is difficult to access for chemical analysis. The large inelastic scattering cross section of electrons in the condensed matter makes X-ray photoelectron spectroscopy (XPS) highly surface sensitive but less sensitive to buried interfaces. This limitation can be overcome by stabilizing an ultrathin layer of liquid with a thickness in the order of a few tens of nanometres and by employing tender X-rays (photon energy ranging between 2-8 keV) that can be used to probe the buried solid-liquid interface. We have recently built and commissioned a new instrument at the Swiss Light Source that combines ambient-pressure XPS with in-situ electrochemistry. With this new setup, we can stabilize a thin liquid layer on a solid surface by a dip&pull method [1], and by using tender X-rays (2-8 keV) from the Phoenix beamline, we can probe the properties and chemistry at the solid-liquid and liquid-gas interface while having a potential control over the ultrathin electrolyte film. The capabilities of this new instrument were demonstrated during the first commissioning beamtime, where we stabilized a thin electrolyte layer (0.1 M KOH) over the Ir(001) electrode. The dip&pull technique was used for the first time using well-defined single-crystalline surfaces (see Supplementary document). Core-level binding energy shifts following the applied potential were observed for species located within the electrolyte film. This included the oxygen 1s level from liquid water, potassium, and, interestingly, also an adventitious carbon species, while the interface was carbon-free. We will present the results from the first commissioning beamtime and outline the future directions we are going to pursue using this new instrument.

[1] S. Axnanda, E. J. Crumlin et al., *Sci. Rep.* 5, 09788 (2014).

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9:00am **CA+2D+AS+BI+NS-ThM4 X-ray Photoelectron Spectroscopy Insight into X-ray Induced Radiolysis at Heterogeneous Liquid Electrolyte Interface**, *Christopher Arble*, National Institute of Standards and Technology (NIST); *H. Guo*, Southeast University, China; *E. Strelcov*, *B. Hoskins*, National Institute of Standards and Technology (NIST); *M. Amati*, *P. Zeller*, *L. Gregoratti*, Elettra-Sincrotrone Trieste, Italy; *A. Kolmakov*, National Institute of Standards and Technology (NIST)

Assessing chemical processes of electrolyte interfaces under operando conditions is an aspirational goal of great importance to many industrial applications¹ that remains technically challenging to investigate. XPS is a powerful characterization tool that can probe elemental and chemical information of atoms with nanoscale depth sensitivity but has traditionally been restricted to UHV conditions. There has been a concerted effort to enable quantitative in-situ measurements of gas and liquid interfaces under realistic environments.²⁻⁴ Recently, advances in 2D materials, i.e., graphene, have been utilized to probe heterogeneous interfaces through molecularly impermeable, electron transparent membranes to maintain UHV pressure in the analysis chamber.⁵

Herein we apply photoemission spectromicroscopy to study the electrochemical dynamics of an array of several thousand individual electrolyte cells encapsulated with electron transparent bilayer graphene.⁶ We monitored the chemical speciation at the electrode- aqueous CuSO₄ electrolyte interface as a function of potential. During the electrochemical experiments, the effects of irradiation upon the solution were observed to influence the system, and spectral deconvolution identified oxidized species of copper and oxygen as well as reduced states of sulfur that were connected to reaction pathways tied with radiolysis. Corresponding SEM images and subsequent EDS spectral maps display spatially confined irradiated byproducts which can be associated with the species observed in with XPS.

Observations of XPS spectroscopic regions in the system were taken at varied X-ray dosages to probe the impacts of radiolysis on the liquid solution concerning the spectroscopic observation of electrochemical deposition of Cu. This experimental methodology imparts a greater understanding of the influence of X-ray induced water radiolysis processes towards the quantification of the electrode/electrolyte interfaces and the underlying dosages necessary for artifact-free data acquisition in condensed media.

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5. Kraus, J.; et al., *Nanoscale* **2014** 6, (23), 14394-14403
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9:20am **CA+2D+AS+BI+NS-ThM5 Theoretical Investigation of Reactivity at Complex Solid-Liquid Interfaces**, *R. Rousseau*, *Manh Nguyen*, Pacific Northwest National Laboratory

INVITED

Contrary to solid/gas interfaces, in solid/liquid interfaces the molecules in the liquid can be organized such that those near the surface are appreciably different from the bulk. This can be impacted by: the composition of the liquid phase, the size shape and loading of nanoparticles and the hydro/lipophilicity of the support. In this talk we will outline the findings from our ongoing studies of both thermal and electrochemically driven hydrogenation of organic molecules. We will present both classical and ab initio molecular dynamics calculations that simulate the structure and composition within the double both at the support as well as on surface of catalytic nanoparticles. The calculations explicitly identify the different roles of entropy and binding energy on the activity and selectivity of solution phase hydrogenation. A first example [1] shows how phenol/water mixtures behave on hydrophilic and lipophilic surfaces, and provides a possible explanation as to why a higher phenol hydrogenation conversion is observed [2] on Pd catalysts on hydrophilic surfaces than on lipophilic surfaces. We show how reaction rates can be manipulated by changing the concentration of phenol adjacent to the catalysts through modification of the degree of support hydrophilicity, size and loading of nanoparticles, and temperature. In a second example [3], we simulate the speciation on a Au and graphitic carbon cathodic surface of a complex solvent mixture containing organics, salts, acids, as a function of cathode charge and temperature. Here we show that the ability to transfer an electron to the organic is governed by the amount of organic in the double layer as well as its orientation with respect to the electrode

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surface. While both examples included have been drawn from the upgrading of bio-oil ex pyrolysis, the principles shown are relevant to any application in heterogeneous catalysis with condensed reaction media.

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11:00am **CA+2D+AS+BI+NS-ThM10 In-situ/Operando Soft X-ray Spectroscopy for Interfacial Characterization of Energy Materials and Devices**, *Y.-S. Liu*, *X. Feng*, *Jinghua Guo*, Lawrence Berkeley National Laboratory

In-situ/operando soft x-ray spectroscopy offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical environment of elements and other critical information of solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando capabilities for the characterization of interfacial phenomena in energy materials and devices.

A number of the experimental studies, which revealed the catalytic and electrochemical reactions in real time, will be presented, e.g. solid (metal film)/liquid (water) electrochemical interface, Mg-ion batteries, and Li-S batteries [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectroscopy characterization provides the unique information for understanding the real reaction mechanism.

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"Revealing the Electrochemical Charging Mechanism of Nanosized Li₂S by in Situ and Operando X-ray Absorption Spectroscopy", L. Zhang, D. Sun, J. Feng, E. Cairns, J.-H. Guo, *Nano Lett.* **17**, 5084 (2017).

11:20am **CA+2D+AS+BI+NS-ThM11 The Importance of Amino Acid Adsorption on Polymer Surfaces in *P. Aeruginosa* Biofilm Formation**, *Olutoba Sanni*, University of Nottingham, UK

High throughput materials discovery screens have revealed polymers that reduce bacterial surface colonization which have progressed to currently ongoing clinical trials [Hook *et al.* *Nature Biotech* 2012]. These novel poly(meth)acrylate coatings reduced biofilm formation by *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Escherichia coli* in laboratory cultures *in vitro* and *in vivo* in a mouse foreign body infection model. These coatings are known to function by preventing biofilm formation, however why the bacterial cells respond in this way to these polymers has yet to be elucidated. The initial interaction between bacteria and surfaces has been identified as a key determining factor when bacteria decide to either irreversibly attach and colonise a surface or not.

The exposure of most materials to biological milieu is accompanied by adsorption of biomolecules. In protein containing media there is a strong relationship between the adsorbed protein layer formed on materials and mammalian cell attachment. However, in protein-free media such as used

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by Hook et al., this cannot be a contributor to early bacterial cell attachment. Consequently, here we carry out careful surface chemical analysis on two polymers known to exhibit drastically different biofilm formation in a standard protein-free, amino acid containing bacterial culture medium (RPMI).

Time of flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analysis determined that high amino acid adsorption correlates with the surface exhibiting low *P. aeruginosa* colonisation. A total of 10 peaks characteristic of specific amino acids were identified by ToF-SIMS to be adsorbed on polymer. We successfully fitted the Freundlich and Langmuir adsorption isotherm models from which we determined adsorption capacity of polymers, calculated the on/off rate of amino acid adsorption on both anti-biofilm and pro-biofilm surfaces. With XPS, the overlayer coverage of amino acids on the polymer surface was established to be approximately 0.2 nm.

The study was extended to quantify in high throughput manner the adsorption of amino acids from RPMI media onto surfaces of 288 polymer materials printed onto a microarray. Ion fragments generated from ToF-SIMS were used to produce a regression model from which we identified polymers with cyclic moieties as major promoters of amino acid adsorption.

This is the first report suggesting adsorbed amino acids or other adsorbed nutrients may correlate with the biofilm formation tendency of materials.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+2D+SS-ThM

Nanoscale Surface Structure in Heterogeneously-Catalyzed Reactions

Moderators: Rebecca Fushimi, Idaho National Laboratory, Eric High, Tufts University

8:20am **HC+2D+SS-ThM2 Low-temperature Investigation of Propylene on TiO₂/Au(111)**, *M. Gillum, M. DePonte, J. Wilke, E. Maxwell, V. Lam, D. Schlosser, Ashleigh Baber*, James Madison University

The partial oxidation of propylene creates industrially important feedstocks that are used in a multitude of chemical fields ranging from textiles to cosmetics to air sanitation. One avenue of research on propylene oxidation is being conducted using metal/oxide model catalysts, as they have shown an affinity for high selectivity oxidation reactions. To gain a comprehensive understanding of olefin intermolecular and surface interactions, temperature programmed desorption (TPD) studies were conducted using Au(111)-based model catalysts with different surface preparations. Using TPD, we were able to identify the specific adsorption sites of propylene on a TiO₂/Au(111) model catalyst, differentiating between the TiO₂ nanoparticles, the Au-TiO₂ interface, and the gold surface. Desorption kinetics propylene were studied on pristine and titania-modified Au(111) surfaces. Desorption products were monitored using quadrupole mass spectrometry and the surface morphology was analyzed using ex-situ atomic force microscopy. The presence of titania was confirmed via X-ray photoelectron spectroscopy. By understanding the characteristic behaviors with combined experimental techniques, active sites and reaction pathways for partial olefin oxidation over Au-based catalysts may be identified.

8:40am **HC+2D+SS-ThM3 Structure and Reactivity of Supported Oxide and Metal Nanoparticles**, *Geoff Thornton*, University College London, UK
INVITED

Heterogeneous catalysts typically consist of metal nanoparticles on an oxide support. Model experiments involving nanoparticle growth on single crystalline oxide have been successfully employed to understand aspects of the nucleation, structure and reactivity. This contributes to catalysis design programs. Many subtleties continue to emerge, some of which will be discussed in this talk. For instance, low temperature STM experiments have allowed direct imaging of CO overlayers formed on the Pd nanoparticles themselves supported on TiO₂. The results show that the nanoparticles grow like a carpet over substrate step-edges, giving rise to a curved top facet that changes the adsorption behavior. Au nanoparticles supported by TiO₂ have been the subject of much work since the discovery by Haruta that Au is a low temperature oxidation catalyst. Despite this earlier work there has been no definitive evidence for the binding site or the direction of charge transfer associated with gold atoms and nanoparticles on the

model substrate TiO₂(110). We show with STM that single Au atoms are in indeed bound to oxygen vacancies on the substrate, with dimers similarly anchored. Associated DFT calculations suggest electron transfer from bridging O vacancies to Au. XPEEM in conjunction with STM have also been used to probe the electronic character of Au nanoparticles as a function of particle size and coverage. Pt and related metals on CeO₂/ZrO₂ are used for CO oxidation in autocats. The accepted mechanism is that the oxide supplies oxygen to the metal to react with CO, with the oxide being directly reoxidized. In XPEEM studies of a model inverse catalyst we show that the reoxidation can also involve the metal.

9:40am **HC+2D+SS-ThM6 Structural and Chemical Effects of Cesium on the Cu(111) and Cu_xO/Cu(111) Surface**, *Rebecca Hamlyn*¹, Stony Brook University; *M. Mahapatra*, Brookhaven National Laboratory; *I. Orozco*, Stony Brook University; *M.G. White, S. Senanayake, J.A. Rodriguez*, Brookhaven National Laboratory

Surface additives, particularly those of alkali metals, are commonly used for promotion of catalytic processes. These processes include carbon oxide reactions such as the water-gas shift and methanol synthesis over Cu-based catalysts. Both reactions are known to be promoted by Cs doping. Partially oxidized Cu is also understood to have a critical role in the activity of the aforementioned processes, as strictly metallic copper will not survive under redox conditions. In an effort to better understand how small additions of alkalis such as Cs act as promoters, we have carried out model studies of cesium over a metallic and oxidized copper surface using scanning tunneling microscopy and x-ray photoelectron spectroscopy. We find that the oxide structure assists in anchoring Cs over the weaker electrostatic interactions with the bare copper surface, allowing for room temperature imaging. Furthermore, with higher coverages or elevated temperature, cesium induces formation of a new ordered structure. This work provides a molecular-scale understanding of the cesiated surface, and serves as a basis for insight toward its mechanism of action in conversion of relevant gases (H₂O, CO, CO₂).

11:00am **HC+2D+SS-ThM10 Mythbusting: From Single Crystals in UHV to Catalytic Reactors**, *R.J. Madix, Christian Reece*, Harvard University **INVITED**

For decades it has been an objective of surface science studies of chemical reactivity to make a direct connection to heterogeneous catalysis. Over these years the difficulties encountered in connecting these two areas of research gave rise to the dismissal of this possibility by the catalysis community and the invention of such shorthand terms as “pressure gap” and “materials gap” to express this view. Usually overlooked is also the fact that catalytic reactions are conducted at much higher temperatures than the related studies on single crystal surfaces, so a “temperature gap” also exists. In fact, these regimes of reactivity are directly linked by fundamental knowledge of the identity and rate constants for the operative elementary steps comprising the catalytic cycle under catalytic conditions. Further, for many catalytic materials, its state can be defined by the reaction conditions themselves in quasi-thermodynamic terms. Connection between the reactivity observed on the single crystals with that on the catalyst surface is possible by the use of a transient pressure method which is conducted over the actual catalyst material under Knudsen flow conditions. Recently we have demonstrated this historically elusive connection between UHV-based studies and catalytic performance for the catalytic oxygen-assisted synthesis of methyl formate from methanol over a nanoporous gold catalyst. The connection is entirely based on the kinetics and mechanism determined on single crystal gold surfaces. A brief history of this development will be discussed and the specifics of how this bridge was built examined.

11:40am **HC+2D+SS-ThM12 Cooperativity Between Pd and AgO_x Phases on Ag(111)**, *V. Mehar, M. Yu, Jason Weaver*, University of Florida

Metals dispersed on a reactive metal-oxide have potential to effect selective catalysis through cooperative interactions between the co-existing metal and metal-oxide phases. In this talk, I will discuss our recent investigations of the structure and reactivity of oxidized Ag(111) as well as Pd/AgO_x surfaces that are generated by depositing metallic Pd onto a single-layer AgO_x structure in ultrahigh vacuum (UHV). Scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) show that the oxidation of Ag(111) with atomic oxygen mainly produces a single-layer AgO_x phase with a p(4 × 5r3) structure as well as smaller amounts of p(4 × 4) and c(3 × 5r3) structures during the initial stages of oxidation. Surface infrared spectroscopy and temperature programmed reaction spectroscopy (TPRS) demonstrate that the single-layer AgO_x structures are

¹ Heterogeneous Catalysis Graduate Student Presentation Award Finalist

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nearly unreactive and bind CO negligibly at temperatures down to ~100 K. In contrast, we find that CO adsorbs and oxidizes efficiently on Pd islands during TPRS, even when the AgO_x phase is the only oxidant source. STM further demonstrates that the metallic Pd islands induce partial reduction of the AgO_x support structure at 300 K. We find that the Pd/AgO_x surfaces continue to exhibit high CO oxidation activity with increasing Pd coverage up to nearly 2 ML (monolayer), suggesting that oxygen transfer from the AgO_x phase occurs at both the interior and perimeter of Pd islands. Our results reveal a cooperative mechanism for CO oxidation on Pd/AgO_x surfaces wherein O-atoms from the AgO_x support phase migrate onto metallic Pd islands and react with adsorbed CO to produce CO₂. These findings illustrate that oxygen transport across metal/metal-oxide interfaces can be highly efficient when the oxygen chemical potential is lower on the initial metal phase (Pd) compared with the metal-oxide (AgO_x) support.

12:00pm **HC+2D+SS-ThM13 Migration Across Metal/Metal Oxide Interfaces: Enhancing the Reactivity of Ag Oxide with H₂ by the Presence of Pd/Pd Oxide**, *Christopher O'Connor¹, M.A. van Spronsen, E. Muramoto, T. Egle, R.J. Madix, C.M. Friend*, Harvard University

An important factor in exploiting bifunctionality in dilute alloy catalysts is surface migration across interfaces separating the dissimilar materials. Herein, we demonstrate the transfer of hydrogen atoms from islands of Pd oxide onto a surrounding O/Ag(111) surface using ambient pressure X-ray photoelectron spectroscopy (APXPS) and scanning tunneling microscopy (STM). These Pd oxide islands enhance the rate of reduction of Ag oxide by more than four orders of magnitude compared to pure oxidized Ag(111). The increase in the rate of reduction of Ag oxide by H₂ is attributed to H₂ activation on Pd/Pd oxide followed by migration (spillover) to Ag/Ag oxide and rapid reaction thereafter. The oxidation and subsequent reduction processes induce significant structural changes of the catalyst surface. We further establish that the transfer of hydrogen atoms occurs from islands of metallic Pd onto a surrounding Ag(111) surface using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed reaction spectroscopy (TPRS). For the metallic PdAg system, hydrogen spillover is shown to be a kinetically limited process that can be controlled by temperature, pressure of H₂ and surface concentration of Pd. The highest efficiency for the amount of hydrogen spillover per surface Pd occurs for a dilute concentration of Pd in Ag. This study establishes that the migration of intermediates across interfaces can occur for oxidized PdAg alloy surfaces and specifically that hydrogen atom migration has a significant effect on the catalytic activity of this type of binary material.

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 University; *F.Y. Yang, M. Randeria, J.A. Gupta*, The Ohio State University

We imaged isolated <10 nm sized skyrmions in SrIrO₃ on SrRuO₃ by spin-polarized scanning tunneling microscopy. We fabricated bilayers of 2 unit cells of SrIrO₃ atop of 10 unit cells of SrRuO₃ via off-axis sputtering. This thickness combination was selected because it showed a strong topological hall signal. We observed a granular morphology of SrIrO₃ mounds with rare patches of exposed SrRuO₃. We can distinguish SrIrO₃ from SrRuO₃ by scanning tunneling spectroscopy where, SrIrO₃ grains show a gap-like feature, while SrRuO₃ have states near the Fermi level. The height histogram of the observed granular structures is consistent with an average of 2 unit cells of SrIrO₃. The grains of the SrIrO₃ 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 SrIrO₃ 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

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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 Standards 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 Ni₈₀Fe₂₀ 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/Co₉₀Fe₁₀ and a Pt/Co₉₀Fe₁₀ 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 doses. 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, NaSn₂As₂, 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 talk 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).

Nanometer-scale Science and Technology Division Room A222 - Session NS+2D+QS-ThM

Direct Atomic Fabrication by Electron and Particle Beams & Flash Session

Moderators: Canhui Wang, National Institute of Standards and Technology (NIST), Xiaolong Liu, Northwestern University

8:00am **NS+2D+QS-ThM1 Multiprobe Scanning Tunneling Microscopy and Spectroscopy: Atomic-level Understanding of Quantum Transport in Functional Systems, Marek Kolmer¹, W. Ko, A.-P. Li**, Oak Ridge National Laboratory

Techniques based on multiprobe scanning tunneling microscopy (MP-STM) allow determination of charge and spin transport in variety of systems supported on surfaces of solid materials. In classical 2- and 4-probe methods STM tips are navigated by scanning electron microscope or high-resolution optical microscope typically in micrometer scales down to hundreds of nanometers. These MP-STM methods are currently regarded as universal tools for in-situ characterization of mesoscopic transport phenomena [1,2].

Such a mesoscopic experimental paradigm has recently been changed by downscaling of 2-probe STM experiments towards the atomic level [3,4]. In this case current source and drain probes are positioned in atomically defined locations with respect to the characterized nanosystems. Our experiments rely on fully STM-based tip positioning protocol with probe-to-probe separation distances reaching tens of nm [3,4]. Such probe-to-probe lateral positioning precision is combined with about pm vertical sensitivity in probe-to-system contacts. These two factors enable realization of two-probe scanning tunneling spectroscopy (2P-STs) experiments, where transport properties can be characterized by macroscopic probes kept in atomically defined tunneling conditions [4].

Here, we will apply 2P-STs methodology to probe quantum transport properties in functional systems: graphene nanoribbons (GNRs) epitaxially grown on the sidewalls of silicon carbide (SiC) mesa structures. These GNRs display ballistic transport channels with exceptionally long mean free paths and spin-polarized transport properties as proven by mesoscopic multiprobe transport experiments [5-7]. Interestingly, the nature of these ballistic channels remains an open question. We will show that 2P-STs experiments give new insight into quantum origin of the transport behaviors.

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[4] Kolmer M. et al., *Nat. Commun.*, **10**, 1573 (2019)

[5] Baringhaus J., *Nature*, **506**, 349-354 (2014)

[6] Aprojanz J. et al., *Nat. Commun.*, **9**, 4426 (2018)

[7] Miettinen A.L. et al., submitted, arXiv:1903.05185 (2019)

This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

8:20am **NS+2D+QS-ThM2 Light and Heavy Ions from New Non-classical Liquid Metal Ion Sources for Advanced Nanofabrication, Paul Mazarov**, RAITH GmbH, Germany; *T. Richter, L. Bruchhaus, R. Jede*, Raith GmbH; *Y. Yu, J.E. Sanabia*, Raith America; *L. Bischoff*, Helmholtz Zentrum Dresden-Rossendorf, Germany; *J. Gierak*, CNRS—Université Paris-Sud, France **INVITED**

Nanofabrication requirements for FIB technologies are specifically demanding in terms of patterning resolution, stability and the support of new processing techniques. Moreover the type of ion defines the nature of the interaction mechanism with the sample and thus has significant consequences on the resulting nanostructures [1]. Therefore, we have extended the technology towards the stable delivery of multiple ion

¹ NSTD Early Career Award Finalist

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species selectable into a nanometer scale focused ion beam by employing a liquid metal alloy ion source (LMAIS) [2]. This provides single and multiple charged species of different masses, resulting in significantly different interaction mechanisms. Nearly half of the elements of the periodic table are made available in the FIB technology as a result of continuous research in this area [3]. This range of ion species with different mass or charge can be beneficial for various nanofabrication applications. Recent developments could make these sources an alternative technology feasible for nanopatterning challenges. In this contribution the operation principle, the preparation and testing process as well as prospective domains for modern FIB applications will be presented. As example we will introduce a GaBiLi LMAIS [4]. It enables high resolution imaging with light Li ions and sample modification with Ga or heavy polyatomic Bi clusters, all coming from one ion source. For sub-10 nm focused ion beam nanofabrication and microscopy, the GaBiLi-FIB or the AuSiGe-FIB could benefit of providing additional ion species in a mass separated FIB without changing the ion source.

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9:00am **NS+2D+QS-ThM4 Visualizing the Interplay between Spatial and Magnetic Confinement in Graphene Quantum Dots**, *Joseph Stroscio*, National Institute of Standards and Technology (NIST) **INVITED**

At the heart of the wave nature of quantum mechanics is the quantization of energy due to quantum confinement, taking place when the particle's de Broglie wavelength becomes comparable to the system's length scale. In a quantum dot (QD), electrons are confined in all lateral dimensions using geometric constraints or a combination of electric and magnetic fields. Being a tunable quantum workbench, QDs have found a ubiquity of applications. Behaving as artificial atoms they have found extensive use as qubits in quantum information technologies, and tools for emulating basic models of condensed-matter physics. QDs offer an ideal platform for studying the interplay between quantum confinement, caused by spatial constraints or by large magnetic fields via cyclotron motion, and interaction effects. Recently, the ability to apply local nanometer scale gate potentials in graphene heterostructures has enabled the creation of QDs for Dirac quasiparticles. Graphene QDs are formed inside circular p-n junctions, where one has detailed control of electron orbits by means of local gate potentials and magnetic fields. We study the interplay between spatial and magnetic confinement using scanning tunneling spectroscopy measurements of the energy spectrum of graphene QDs as a function of energy, spatial position, and magnetic field. In zero field, the Dirac quasiparticles are confined by Klein scattering at large incident angle at the p-n junction boundary. The confined carriers give rise to an intricate eigenstate spectrum, effectively creating a multi-electron artificial atom. Applying a weak magnetic field results in a sudden and giant increase in energy for certain angular momentum states of the QD, creating a discontinuity in the energy spectrum as a function of magnetic field. This behavior results from a π -Berry phase associated with the topological properties of Dirac fermions in graphene, which can be turned on and off with magnetic field. With increased applied magnetic field, the QD states are observed to condense into Landau levels, providing a direct visualization of the transition from spatial to magnetic confinement in these artificial graphene atoms. With further increase in magnetic fields, an intricate interplay between Coulomb charging of compressible Landau levels separated by incompressible rings emerges, which we map as a function of energy, spatial position, and magnetic field utilizing the exceptional capabilities of scanning tunneling spectroscopy.

9:40am **NS+2D+QS-ThM6 Using Controlled Manipulation of Molecules to Trace Potential Energy Surfaces of Adsorbed Molecules**, *O.E. Dagdeviren*, C. Zhou, Yale University; *M. Todorovic*, Aalto University, Finland; *Eric Altman*, U.D. Schwarz, Yale University

The development of scanning probe microscopy techniques has enabled the manipulation of single molecules. More recently it has been demonstrated that the forces and energy barriers encountered along the manipulation path can be quantified using non-contact atomic force microscopy (AFM). To explore the practicality of using this novel approach to experimentally measure the energy barriers an adsorbed molecule encounters as it moves across a surface decorated by other molecules including potential reaction partners, we have been studying benzene molecules on Cu (100) as a model system. We first choose a specific manipulation path and then move the tip repeatedly along this path as the tip-sample distance is reduced while recording the AFM cantilever oscillation amplitude and phase. To preserve the accuracy of the recovered tip-sample interaction potentials and forces, we use oscillation amplitudes significantly larger than the decay length of the tip-sample interaction potential are used. Operating the microscopy in the tuned-oscillator mode and analyzing the resulting cantilever oscillation amplitude and phase as functions of the spatial coordinates allows recovery of the potential energy of the interaction between the tip and the sample, the force on the tip normal to the surface, and the lateral force acting on the tip along the manipulation path, all as functions of tip vertical and lateral position with 0.01 Å resolution. In over 50 distinct manipulation events, the molecules were either pushed, pulled, jumped to the tip, or did not move depending on the chemical environment surrounding the molecule and the chemical identity of the tip. For further insight, we have compared the experimentally measured energy landscapes and manipulation outcomes with computational results obtained using a Bayesian Optimization Structure Search protocol.

11:00am **NS+2D+QS-ThM10 Direct Writing of Functional Heterostructures in Atomically Precise Single Graphene Nanoribbons**, *Chuanxu Ma*, Oak Ridge National Laboratory; *Z. Xiao*, North Carolina State University; *J. Huang*, *L. Liang*, Oak Ridge National Laboratory; *W. Lu*, North Carolina State University; *K. Hong*, *B.G. Sumpter*, Oak Ridge National Laboratory; *J. Bernholc*, North Carolina State University; *A.-P. Li*, Oak Ridge National Laboratory

Precision control of interfacial structures and electronic properties is the key to the realization of functional heterostructures. Here, utilizing the scanning tunneling microscope (STM) both as a manipulation and characterization tool, we demonstrate the fabrication of a heterostructure in a single atomically precise graphene nanoribbon (GNR) and report its electronic properties¹. The heterostructure is made of a seven-carbon-wide armchair GNR (7-aGNR) and a lower band gap intermediate ribbon synthesized bottom-up from a molecular precursor on an Au substrate. The short GNR segments are directly written in the ribbon with an STM tip to form atomic precision intraribbon heterostructures. Based on STM studies combined with density functional theory calculations, we show that the heterostructure has a type-I band alignment, with manifestations of quantum confinement and orbital hybridization. We further investigate the negative differential resistance (NDR) devices using the GNR heterostructure based double-barrier models². Our computational results indicate that nanoscale engineering for NDR needs to consider atomic size effect in design and atomic precision in fabrication. This combined theoretical-experimental approach opens a new avenue for the design and fabrication of nanoscale devices with atomic precision.

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11:20am **NS+2D+QS-ThM11 Effects of Helium and Neon Processing on 2D Material Properties**, *Alex Belianinov*, Oak Ridge National Laboratory; *S. Kim*, Pusan National University, South Korea; *V. Iberi*, *S. Jesse*, *O.S. Ovchinnikova*, Oak Ridge National Laboratory

Recent advances in CVD-growth consistently yield high quality 2D materials for large(er) scale fabrication. Monolayers of molybdenum and tungsten diselenide and sulfide, graphene, and other exotic 2D materials are becoming routine in fabrication of functional electronic and optoelectronic devices. In order to attain novel functionalities, it is critical to tune and

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engineer defects in 2D materials directly with nanometer precision. Advances in ion beam-based imaging and nanofabrication techniques have offered a pathway to precisely manipulate 2D materials and offer a roadmap to create junctions, amorphized areas, and introduce dopants for new types of electronic devices. Here, we demonstrate the use of a focused helium and neon ion beams in a scanning helium ion microscope (HIM) in tailoring material functionality in MoSe₂, WSe₂, CuInP₂S₆ and graphene.

The helium ion microscope can “direct-write” capabilities, capable of both imaging and nanofabrication with Helium and Neon gases, thus making it an excellent candidate for processing a wide range of 2D, and conventional materials. We explore milling by the helium and neon ion beams of suspended and supported samples in order to control material’s electronic and mechanical properties. We validate the results with other chemical imaging techniques such as Scanning Transmission Electron Microscopy, correlated band excitation (BE) scanning probe microscopy, and photoluminescence (PL) spectroscopy.

Acknowledgement

This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy (DOE) Office of Science User Facility.

11:40am **NS+2D+QS-ThM12 Operating Molecular Propeller in Quantum Regime with Directional Control**, *Y. Zhang, Tolulope Ajayi*, Ohio University; *J.P. Calupitan*, Université de Toulouse, France; *R. Tumbleson*, Ohio University; *G. Erbland, C. kammerer*, CEMES-CNRS, France; *S. Wang*, Ohio University; *L. Curtiss, A. Ngo*, Argonne National Laboratory; *G. Rapenne*, NAIST, Japan; *S.-W. Hla*, Ohio University

Synthetic molecular machines are fascinating and have a great promise to revolutionize a large scientific and technology fields. The immense interest to this research area is evident by the 2016 Nobel Prize in Chemistry awarded for the design and synthesis of molecular machines. Unlike biological molecular machines, which typically have the sizes of a few microns, artificial machines operating at the nanometer scale are in the quantum regime. Here, we have developed a robust multi-component molecular propeller that enables unidirectional rotations on a materials surface when they are energized. Our propeller system is composed of a stator having a ratchet-shaped molecular gear designed to anchor on a gold surface and a rotator with three molecular blades. By means of scanning tunneling microscope imaging and manipulation, the rotation steps of individual molecular propellers are directly visualized, which confirms the unidirectional rotations of both left and right handed molecular propellers into clockwise and counterclockwise directions, respectively. Moreover, the mechanical manipulation of the molecular with the scanning probe tip further reveal detailed rotation mechanism, thereby opening a new research direction to investigate mechanical properties of the molecular machines with an atomic level precision.

2D Materials

Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA

Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications

Moderator: Mark Edmonds, Monash University, Australia

2:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA1 Molecular Layers on Nanoporous Gold Electrodes**, *Elizabeth Landis*, College of the Holy Cross
Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials**, *Paul Brown*, American Society for Engineering Education; *S. Fischer, J. Kotacz, C.M. Spillmann, D. Gunlycke*, U.S. Naval Research Laboratory

Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

3:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?**, *Vladimir Korolkov*, Oxford Instruments-Asylum Research; *S.C. Chulkov, M. Watkins*, University of Lincoln, UK; *P.H. Beton*, The University of Nottingham, UK

Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces^{1,2} and bulk polymers³.

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular

contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model⁴ to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

¹Korolkov et al., Nat. Chem., 2017

²Korolkov et al., Nat. Comm., 2017

³Korolkov et al., Nat. Comm., 2019

⁴Hapala et al., Phys. Rev. B 90, 085421

3:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds**, *Jangyup Son*, University of Illinois at Urbana-Champaign; *N. Buzov*, University of California at Santa Barbara; *S. Chen*, University of Illinois at Urbana-Champaign; *D. Sung*, Sejong University, Republic of Korea; *H. Ryu*, Seoul National University, Republic of Korea; *J. Kwon*, Yonsei University, Republic of Korea; *S. Kim, J. Xu*, University of Illinois at Urbana-Champaign; *S. Hong*, Sejong University, Republic of Korea; *W. King*, University of Illinois at Urbana-Champaign; *G.H. Lee*, Seoul National University, Republic of Korea; *A.M. van der Zande*, University of Illinois at Urbana-Champaign

Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF₂) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study***, *Tao Jiang, D. Le, T.S. Rahman*, University of Central Florida

Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first

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principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO₂ towards ethanol formation, in the reaction pathway of which the crucial step for forming C₂ bond, i.e. reaction of adsorbed species CH₃* and CO* to form CH₃CO*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS₂ functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH₃* and a CO* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C₂ species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya, A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS₂ activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers, Woo-Kyung Lee, J.J. Pietron, D.A. Kidwell, J.T. Robinson, C.L. McGann, S.P. Mulvaney, U.S. Naval Research Laboratory**

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is $6.2 \times 10^4 \Omega\text{-cm}$, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA). We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA9 Sensor for Breath and Skin Diagnostics, Pelagia I Gouma, The Ohio State University**

Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA10 Symmetry Controlled Adsorption of Diodobenzene on MoS₂, Zahra Hooshmand, University of Central Florida; P. Evans, P.A. Dowben, University of Nebraska - Lincoln; T.S. Rahman, University of Central Florida**

In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS₂(0001). The intensity ratio of iodine to molybdenum

measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS₂(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS₂, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS₂(0001).

* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS₂ and 2D-MoS₂ Catalysts, Mihai Vaida, University of Central Florida**

Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H₂ molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS₂ and MoS₂. Crystalline 2D-TaS₂ and 2D-MoS₂ with surface area of 1 cm² are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS₂ occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS₂, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methyldyne radical (CH), which subsequently react with other CH radical to produce acetylene (C₂H₂).

Plasma Science and Technology Division

Room B130 - Session PS+2D+EM+SS+TF-ThA

Plasma-Enhanced Atomic Layer Etching

Moderators: Steven Vitale, MIT Lincoln Laboratory, Mingmei Wang, TEL Technology Center, America, LLC

2:20pm **PS+2D+EM+SS+TF-ThA1 Atomic Layer Etch: Real World Utilization of an Idealized Solution, Peter Biolsi, TEL Technology Center, America, LLC**
INVITED

Atomic Layer Etch: Real World Utilization of an Idealized Solution

Critical dimensions (CD) continue to shrink driven by the quest for cheaper, faster and less power-consuming devices. If simple shrink was not enough, all of the back end, middle and front end of line (BEOL, MOL and MOL) also have introduced structural complexity and stringent topographic dimension, material property integrity and fundamental integration yield requirements. Atomic layer etching (ALE) has gained favor as an approach to extract more control over the fabrication of small CD complex topographic structures, atomic layer etching. The idea is that alternating steps of self-limiting processes (e.g., passivation layer formation) and desorption (e.g., the removal of a passivation layer) mitigate aspect ratio dependence effects that lead to the aforementioned problems. The problem is that not all passivation processes are self-limiting. For the etching of dielectric materials, a self-limiting precursor step is not available as etch processes relies on cyclic process (fluorocarbon deposition and ion bombardment steps). Fluorocarbon based processes are not self-limiting rendering them quasi-atomic layer etch. Without special consideration,

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quasi-ALE has the same problems that continuous processes possess with additional burden of throughput.

Even though ALE can be difficult to be utilized in real-world scenarios, the learning from ALE finds its use in many etch applications. An etch chamber which can provide wide range of radical to ion flux ratios and precise ion energy control (using pulsing techniques) is suitable for ALE or utilizing ALE learnings. Currently, new ALE techniques based on surface modification by ions (Hydrogen plasma treatment of Silicon Nitride) followed by removal of modified layer by F radicals (High pressure NF₃ or SF₆ plasma) or surface modification by NH₃/HF (to create a quasi-self-limiting diffusion barrier layer) followed by removal of modified layer by thermal means, are employed to etch critical layers where requirements are stringent. New frontier of etch technology will be the ability to achieve area selective etch without compromising etch rate of the process. Examples of such activities will be presented in this presentation.

3:00pm PS+2D+EM+SS+TF-ThA3 Mechanism of SiN Etching Rate Fluctuation in Atomic Layer Etching, Akiko Hirata, M. Fukasawa, K. Kugimiya, K. Nagaoka, Sony Semiconductor Solutions Corporation, Japan; K. Karahashi, S. Hamaguchi, Osaka University, Japan

Atomic layer etching (ALE) enables atomic-precision control of the surface reaction and low damage etching of the underlying layer for device fabrication. In this study, we investigated SiN ALE with process optimization of the surface adsorption and desorption steps, and we clarified the rate fluctuation mechanism.

A dual frequency CCP reactor (60 MHz/2 MHz) was used in this study. A SiN (50 nm) was deposited on the Si substrate by LPCVD. One etching cycle consisted of two steps. CH₃F/Ar plasma was applied to deposit the hydrofluorocarbon (HFC) polymer as the adsorption step. Then, Ar plasma was used in the desorption step. The thicknesses of SiN and the HFC polymer were measured by spectroscopic ellipsometry. The chemical bonding was analyzed by XPS.

A 1.2-nm-thick HFC polymer was deposited on SiN as the adsorption step. Next, we investigated the desorption step by using Ar plasma. The etched amount for 1 cycle was 0.58 nm. However, we found the etch-stop of SiN after 10 cycles of ALE, owing to the deposition (>6 nm) of a protective film on the surface. The etch-stop could be caused by sputtering of the Si upper electrode and/or re-deposition of the HFC film. To investigate the etch rate fluctuation, the SiN surface after ALE was analyzed. C-C and C-N bonds were detected after 1 cycle, and C-C bonds increased after 10 cycles. It was clear that the excess HFC polymer deposition suppressed the ALE reactions. Ar⁺ ion bombardment during the desorption step selectively eliminated the H and F in the HFC polymer, because the bonding energies of C-H and C-F were low. As the bonding energies of C-C (6.4 eV) and C-N (7.8 eV) are relatively high, these bonds remained after the desorption step. We speculated that excess C-rich polymer deposition after ALE started from the residual C-C bond. Residual Si-C bond is also possible reason, since the MD simulation revealed that the formation of Si-C bond was promoted in the fluorocarbon layer during SiO₂ ALE.^[1] These results clearly showed that the initial adsorption kinetics of HFC polymer was strongly affected by the residual carbon on the SiN surface. To suppress the C-rich polymer deposition, we studied stable SiN ALE using the desorption step of Ar/O plasma (0.36 nm/cycle) and the two-step sequential desorption step of Ar and O plasma (0.6 nm/cycle). Although the effect of O adsorption in SiO ALE has been studied previously,^[2] few studies have been reported for the case of SiN. Because the surface condition is able to fluctuate with the number of cycles, precise surface control is strongly required to achieve stable ALE.

[1] S. Hamaguchi et al., 2018 AVS, PS-FrM6. [2] T. Tsutsumi et al., JVST A 35 (2017) 01A103.

3:20pm PS+2D+EM+SS+TF-ThA4 Effect of Polymerization on Ar+ Bombardment Modification of SiO₂ and Si₃N₄ Substrates: Molecular Dynamics Simulation Study, Hojin Kim, Y. Shi, Y.-H. Tsai, D. Zhang, Y. Han, TEL Technology Center, America, LLC; K. Taniguchi, TEL Miyagi Limited, Japan; S. Morikita, TEL Miyagi Limited; M. Wang, A. Mosden, A. Metz, P.E. Biolsi, TEL Technology Center, America, LLC

To understand the selective removal of silicon oxide (SiO₂) against silicon nitride (Si₃N₄) with gaseous reactants for advanced etch process, we have studied the surface modification of both SiO₂ and Si₃N₄ substrates with Ar+ bombardment by using molecular dynamics (MD) simulation. The substrate samples was prepared with and without carbon (C) and hydrogen (H) polymerization to investigate the effect of polymerization on surface modification. C and H atoms were deposited with low ion energy not to disrupt the surface much. After preparation of substrate, Ar+ bombardment with various ion energy (IE) were performed. We obtained a damage depth with a wigner-seitz defect analysis as a function of IE and compared the cases with and without polymerization to check the role of the added polymer layer on surface modification. In pristine Si₃N₄ and SiO₂ case, at IE=25eV, both substrates starts to show the damage with penetration of Ar⁺ and follows with an exponential raise as the IE increases. Damage depth at Si₃N₄ is deeper than that at SiO₂. In polymerization, simulations show that H is more deposited than C on Si₃N₄ while on SiO₂, C is more deposited than H. no silicon-hydrogen bonds appear on both substrates and in Si₃N₄, nitrogen-hydrogen bond is dominated while oxygen-carbon bond is popular in SiO₂. For damage analysis, in Si₃N₄ case, CH polymerization helps to lower about 30% in the damage depth with exponential behavior. However, SiO₂ case shows the opposite effect of CH polymerization in the damage depth. Formed polymer layer leads to increase the damage depth by comparing with pristine SiO₂ and helps more clear exponential behavior as a function of IE. Finally, analyzed results using XPS and/or SIMS from blanket SiO₂ and Si₃N₄ films etched in a Capacitively Coupled Plasma (CCP) chamber are compared with the MD simulation results.

4:00pm **PS+2D+EM+SS+TF-ThA6 Advanced Cyclic Plasma Etch Approaches for Metal Patterning: Synergy and Surface Modification Effects, Nathan Marchack, IBM T.J. Watson Research Center; K. Hernandez, University of Texas at Dallas; J. Innocent-Dolor, M.J.P. Hopstaken, S.U. Engelmann, IBM T.J. Watson Research Center**

INVITED

Atomic layer etching or ALE is a burgeoning research area of plasma processing that offers critical advantages needed for future advancements in semiconductor devices, namely lower damage and enhanced selectivity, through its self-limited reaction cycles separated by purge steps.[1] ALE processes offer a significantly higher degree of tunability over traditional continuous-wave (CW) plasma etching, due to the fact that parameters such as gas flows, pressure, and bias power can be adjusted on a step-specific basis rather than as a global setting for the length of the process.

Our previous work investigated the effect of varying the purge step times in a quasi-ALE process using alternating Cl₂/H₂ exposures on the etched profiles of titanium and tantalum nitride.[2] Titanium and tantalum-based conductive films have been previously evaluated as gate materials for CMOS devices but more recently have been incorporated as top electrodes for novel technologies such as magnetoresistive RAM (MRAM) and hard masks for carbon electrodes utilized in biological sensing. As the trend of downscaling device size continues, the ability to pattern these films at tight pitches with minimal redeposition becomes highly important.

Sub-surface modification of films such as Si₃N₄ and indium-doped tin oxide (ITO) by low atomic weight (LAW) ions such as H⁺ has been discussed in literature as facilitating self-limited etch behavior.[3,4] We present new data exploring the incorporation of LAW species into cyclic etch processes, namely penetration depth into these metal nitride films and their role in surface oxide formation, the latter of which can contribute to novel pitch multiplication schemes.[5] SIMS measurements reveal that the depth of penetration of H⁺ for TaN films can be >40 nm and can occur through a native oxide layer that inhibits etching by Cl species. Pressure variation is a significant factor in tuning this effect, which can potentially modify the etch resistance of these films and enable novel integration schemes.

[1] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, R. A. Gottscho, J. Vac. Sci. Technol. A. 2015, 33, 020802.

[2] N. Marchack, J. M. Papalia, S. U. Engelmann, E. A. Joseph, J. Vac. Sci. Technol. A. 2017, 35, 05C314.

[3] S. D. Sherpa, A. Ranjan, J. Vac. Sci. Technol. A. 2017, 35, 01A102.

[4] A. Hirata, M. Fukasawa, K. Nagahata, H. Li, K. Karahashi, S. Hamaguchi, T. Tatsumi, Jpn. J. Appl. Phys. 2018, 57, 06JB02.

[5] N. Marchack, K. Hernandez, B. Walusiak, J.-I. Innocent-Dolor, S. U. Engelmann, Plasma Process Polym. 2019, e1900008.

4:40pm PS+2D+EM+SS+TF-ThA8 Surface Modification and Stability of Plasma-assisted Atomic-layer Etching (ALE) of Si based Materials; Analysis by Molecular Dynamics (MD) Simulation, Satoshi Hamaguchi, M. Isobe, E.J.C. Tinacba, S. Shigeno, Y. Okada, T. Ito, K. Karahashi, Osaka University, Japan

A plasma-assisted atomic-layer etching (ALE) process typically consists of alternating application of chemically reactive species (adsorption step) and Ar ion bombardment with low bias energy (desorption step) to the surface to be etched. In the adsorption step, a modified layer is formed on the material surface and, in the desorption step, the modified layer is removed with the original material underneath being intact. In this presentation,

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using the results of MD simulation of ALE for Si, SiO₂, and SiN, together with experimental observations, physical mechanisms of the formation and removal of surface modified layers in typical ALE processes will be discussed.

Our molecular dynamics (MD) simulation of SiO₂ ALE by fluorocarbon adsorption and Ar⁺ ion bombardment shows that preferential sputtering of oxygen takes place by Ar⁺ ion bombardment and a Si rich layer mixed with fluorine and carbon atoms is formed on the SiO₂ surface. Ideally this modified layer should be removed completely in the subsequent desorption step, but in general it is not. In such a layer, the atomic number ratio of Si to O can be as high as unity and carbon provided in the subsequent adsorption step tends to be deposited rather than removing O atoms from the surface by forming CO molecules. Therefore as the ALE cycles proceed, the adsorbed fluorocarbon layer thickens and eventually an etch stop may occur. With fine tuning of incident Ar⁺ ion energy, an etch stop may be avoided but the process window to achieve both continuous ALE cycles (by sufficiently high Ar⁺ ion energy) and ideal self-limit in each cycle (by sufficiently low Ar⁺ ion energy) may still be small or even nonexistent. The incompleteness of the modified surface removal in each ALE cycle seems universal phenomena for plasma-assisted ALE for most materials. For other plasma-assisted ALE processes that we examined by MD simulation, the surface modified layer formed during the adsorption step could not be removed completely by low-energy Ar⁺ ion bombardment, either. Indeed low-energy Ar⁺ ion bombardment contributes to the formation of a deeper modified layer by pushing down adsorbed species into the bulk, rather than simply removing it.

5:00pm **PS+2D+EM+SS+TF-ThA9 Innovative Future Etch Technology by Atomic-order Control**, *Yoshihide Kihara, T. Katsunuma, S. Kumakura, T. Hisamatsu, M. Honda*, Tokyo Electron Miyagi Ltd., Japan **INVITED**

In recent years, with the progress of device miniaturization and increased challenges in the scale of integration of semiconductor devices, ultra-high selectivity and atomic layer-level critical dimension (CD) control techniques are required in the fabrication processes.

In the conventional etching, using a fluorocarbon (FC) gas, the high selectivity is obtained by taking advantage of the difference of the FC protective film thickness due to the difference of materials.^[1] However, adopting the conventional approach to cutting-edge pattern structure becomes difficult due to the excessive FC film clogging the micro slit facet. To meet the highly complex requirements, alternative process was developed by using ion modification and chemical dry removal.^[2] We have made several improvements on this new approach and applied it to SiN and SiC etching. The improved new approach achieves ultra-high selectivity without FC protective film and we also confirmed this process has the characteristics of a self-limiting reaction based on ion depth profile as well as ALE.

In the patterning processes, lower pattern densities have a larger CD shrinking due to micro-loading. Hence, we developed the new process flow that combines atomic layer deposition (ALD) technique and etching. With this method, we achieved CD shrinking at atomic-layer level precision for various patterns, without causing CD loading.^[3]

Moreover, Quasi-ALE can etch the pattern while maintaining the mask CD for different pattern density. This is because Quasi-ALE precisely controls the surface reaction by controlling the radical flux and ion flux independently.^[3] Also, it was necessary to control oval CD size between X and Y respectively. We found that X-Y CD control can be easily performed by changing the balance of FC adsorption and Ar desorption in Quasi-ALE. However, there are concerns about mask selectivity and ion damage in this approach. To solve these problems, we introduce the Advanced Quasi-ALE technique which combines mask protection together with Quasi-ALE. The Advanced Quasi-ALE achieves wider X-Y CD control margin.

On the other hand, as aspect ratio is increased in the memory fabrication process, the occurrence of bowing profile is a serious problem. To address the issue, the new improvement technique has been developed that combines the concept of ALD and etching. With this method, we are able to etch profile more vertically in high A/R feature.

Reference

- [1] M. Matsui et al., *J. Vac. Sci. Technol. A* 19 1282 (2001)
- [2] N. Posseme et al., *Applied Physics Letters* 105 051605 (2014)
- [3] M. Honda et al., *J. Phys. D: Appl. Phys.*, Vol.50, No.23 (2017)

Surface Science Division

Room A220-221 - Session SS+2D+AP+AS+OX+SE-ThA

Dynamics at Surfaces/Reactions and Imaging of Oxide Surfaces

Moderators: Irene Groot, Leiden University, The Netherlands, William E. Kaden, University of Central Florida

2:20pm **SS+2D+AP+AS+OX+SE-ThA1 Adsorption, Reaction, and Diffusion of Energetic Reagents on Morphologically Diverse Thin Films**, *Rebecca Thompson^{1,2}, M.R. Brann, S.J. Sibener*, The University of Chicago

I present work from two studies illustrating the impact of condensed-phase film morphology on reaction kinetics and surface adsorption. To begin, I will discuss the **oxidative reactivity of condensed propene films**. This work is conducted in a state-of-the-art ultra-high vacuum chamber equipped for operation at cryogenic substrate temperatures. Time-resolved reflection absorption infrared spectroscopy (RAIRS) is used to track propene reactivity when films are exposed to a supersonic expansion of ground state oxygen atoms, O(³P). I demonstrate that propene reacts significantly on exposure, producing primarily propylene oxide and propanal. Oxide production is significant; partial oxidation products are rarely observed in gas phase studies and olefin oxides are incredibly important chemical intermediates in a variety of industrial processes. Regardless of initial film thickness, the reaction follows zero order kinetics, with a calculated activation energy of 0.5 kcal mol⁻¹. This low barrier closely matches that reported in gas phase studies, suggesting that the condensed-phase reaction is likely diffusion-limited. I also highlight that the propene deposition temperature has a substantial impact on reactivity. Films deposited below 50 K produce dramatically different RAIR spectra that correspond to a more amorphous film composition. These films are nearly unreactive with O(³P), indicating that oxygen diffusion is directly tied to the density and ordering in the more crystalline film.

This dependence on film structure is also observed in the second study, which explores **embedding in and adsorption on crystalline, non-porous amorphous, and porous-amorphous water ice films**. Using a combination of supersonic molecular beams, RAIRS and King and Wells mass spectrometry techniques, I demonstrate that direct embedding into the bulk is remarkably insensitive to film structure; the momentum barrier is identical between amorphous and porous-amorphous ice films. Below this barrier, however, sticking probabilities differ considerably between the different films, suggesting that the pore structure is more efficient at dissipating incident energy. These discoveries are critical for the accurate quantitative modeling of molecular uptake and reactivity on icy astrophysical bodies such as comets and planetesimals. When taken together, these two studies provide fundamental mechanistic insight into the sticking, diffusion, and reactivity of small molecules on complex films, with a specific emphasis on the impact of film morphology and organization.

2:40pm **SS+2D+AP+AS+OX+SE-ThA2 Oxidation of Semiconductors and Semimetals by Supersonic Beams of O₂ with Scanning Tunneling Microscopy Visualization**, *Ross Edel³, T. Grabnic, B. Wiggins, S.J. Sibener*, The University of Chicago

Our research examines the oxidation of semiconductor and semimetal surfaces using a novel, one-of-a-kind instrument that combines a supersonic molecular beam with an in-line scanning tunneling microscope (STM) in ultra-high vacuum. This new approach to surface reaction dynamics provides spatiotemporal information on surface oxidation over nanoscopic and mesoscopic length scales. We have uncovered the kinetic and morphological effects of oxidation conditions on three technologically relevant surfaces: Si(111)-7×7, highly oriented pyrolytic graphite (HOPG), and GaAs(110). A complete understanding of the oxidation mechanism of these surfaces is critical due to their technological applications and roles as model systems. Samples were exposed to O₂ with kinetic energies from 0.4-1.2 eV and impingement angles 0-45° from normal, with STM characterization between exposures. In some cases, we were able to monitor the evolution of specific features by revisiting the same nanoscopic locations. Our study of Si(111)-7×7 revealed two oxidation channels, leading to the formation of dark and bright reacted sites. The dark sites dominated the surface and exhibited almost no site selectivity while the bright sites preferred the corner sites of the 7×7 unit cell. Our

¹ Morton S. Traum Award Finalist

² National Student Award Finalist

³ National Student Award Finalist

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observations suggest that two adsorption pathways, trapping-mediated and direct chemisorption, occur simultaneously. On HOPG, we found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Finally, oxidation of GaAs(110) was found to proceed by two morphologically distinct, competing mechanisms: a homogeneous process leading to layer-by-layer oxide growth, and a heterogeneous process with oxide islands nucleating from surface defects. The rates of both mechanisms change with O₂ kinetic energy, with homogeneous oxidation dominating at lower energies (<0.7 eV) and heterogeneous oxidation with higher energies (≥1.0 eV). The results obtained in this work provide vital information about the morphological evolution and kinetics of semiconductor and semimetals, offering a comprehensive overview of the spatiotemporal correlations that govern oxidation dynamics on surfaces.

3:00pm **SS+2D+AP+AS+OX+SE-ThA3 Studying Molecule-Surface Interactions using Rotational Orientation Control of Ground-State Molecular Beams**, *Gil Alexandrowicz*, Swansea University, UK **INVITED**
Performing quantum state selective experiments of molecule-surface collisions provides unique insight into the interaction potential. One particularly tricky molecular property to control and measure is the rotational projection states, i.e. the orientation of the rotational plane of the molecule. Previous data was mostly restricted to photo-excited/paramagnetic species. In this talk, I will describe the molecular beam apparatus which allows to control and measure the rotational orientation of ground state molecules [1], present new experimental results for H₂ colliding with ionic surfaces and discuss the future of this new technique in terms of studying molecule-surface interaction-potentials and modifying the outcome of reactive molecule-surface collisions.

[1] Nature Communications, 8, 15357 (2017).

4:00pm **SS+2D+AP+AS+OX+SE-ThA6 Diffusion of (100)-epitaxially Supported 3D fcc Nanoclusters: Complex Size-dependence on the Nanoscale**, *King Chun Lai, J.W. Evans*, Iowa State University
Diffusion of supported 3D nanoclusters (NCs) followed by coalescence leads to coarsening of ensembles of supported NCs via Smoluchowski Ripening (SR) which is a key pathway for degradation of supported metal catalysts. The dependence of the NC diffusion coefficient, D_N , on size N (in atoms) is the key factor controlling SR kinetics, and traditional treatments assumed simple monotonic decrease with increasing size. We analyze a stochastic model for diffusion of (100)-epitaxially supported fcc NCs mediated by diffusion of atoms around the surface of the NC. Multiple barriers for surface diffusion across and between facets, along step edges, etc. are chosen to accurately describe Ag [Lai and Evans, *Phys. Rev. Materials* 3 (2019) 026001]. KMC simulations reveal a complex oscillatory variation of D_N with N . Local minima D_N sometimes but not always correspond to $N = N_c$ where the equilibrium Winterbottom NC structure is a closed-shell. Local maximum generally correspond to $N = N_c + 3$. The oscillatory behavior is expected to disappear for larger N above $O(10^2)$. Behavior has similarities to but also basic differences from that for 2D supported NCs [Lai et al *Phys. Rev. B* 96 (2017) 235406]. Through detailed analysis of the energetics of the 3D NC diffusion pathway (which involves dissolving and reforming facets), we can elucidate the above behavior as well as observed trends in effective diffusion barrier.

4:20pm **SS+2D+AP+AS+OX+SE-ThA7 Oxide Surface Formation on Rh Nanoparticle during O₂ Exposures Observed by Atom Probe Microscopy**, *Sten Lambeets*, Pacific Northwest National Laboratory; *T. Visart de Bocarmé*, Université Libre de Bruxelles, Belgium; *N. Kruse*, Washington State University; *D.E. Perea*, Pacific Northwest National Laboratory
Metallic surfaces may undergo a series of surface and subsurface structural and chemical transformations while exposed to reactive gases that inevitably change the surface properties. Understanding such dynamics from a fundamental science point of view is an important requirement to build rational links between chemical/structural surface properties and design new catalysts with desired performance or new materials with enhanced resistance to corrosion. The research presented here addresses the early oxide formation dynamics on a rhodium (Rh) single nanoparticle during O₂ exposures and reveals the inter-facet cooperation between Rh{012} and Rh{113} facets, as well as the important role that the subsurface plays.

Field Ion and Field Emission Microscopies (FIM and FEM) enable correlative atomic to nanoscale imaging of the surface of a very sharp Rh needle, the apex size and shape of which models that of a Rh nanoparticle. FIM is used to map, with atomic lateral resolution, the Rh surface revealing a complex network of crystallographic facets, while FEM is used to observe and record O₂ dissociative adsorption and subsequent reaction with H₂ over this same surface of Rh in real-time with nano-scale lateral resolution. Since FEM imaging relies on local work function variations, it notably can be used to follow the fate of adsorbed oxygen atoms (O(ads)) on the Rh surface. As a result, we directly observe that the O₂ dissociative adsorption is mainly active on the Rh{012} regions. The application of Atom Probe Tomography (APT) provided a means to map the fate of the adsorbed oxygen leading to bulk oxide formation through Rh{113} facets. Thus the correlative combination of FIM, FEM, and APT provides unique insight into the mechanism of bulk oxide formation starting from the dissociative oxygen absorption occurring at {012} facets and subsurface penetration of the adsorbed oxygen occurring through {113} facets. leading to a preferential accumulation of the oxygen within the bulk along the [111] direction. This work offers a unique methodology to explore the interactions between the different crystal facets of a complex surface, to explore the complex dynamics linking the surface and the bulk, and finally, offers exciting perspectives leading to a better understanding of heterogeneous catalysis and corrosion dynamics.

4:40pm **SS+2D+AP+AS+OX+SE-ThA8 Noncontact AFM on Oxide Surfaces: Challenges and Opportunities**, *Martin Setvin*, TU Wien, Austria **INVITED**
Recent development of the noncontact atomic force microscopy (nc-AFM) has opened new possibilities in different fields – imaging of organic molecules [1], controlling the charge state of adsorbed species [2], or enhanced chemical resolution of surface atoms [3]. I will focus on the emerging possibilities and opportunities in the field of oxide surfaces and their surface chemistry.

The limits of atomic resolution will be illustrated on clean and water-exposed binary oxides like TiO₂, In₂O₃ or iron oxides. The enhanced chemical resolution of nc-AFM offers a unique opportunity for approaching complex materials with ternary chemical composition. This will be demonstrated on bulk-terminated perovskites SrTiO₃ and KTaO₃. A dedicated cleaving procedure [4,5] allows preparing flat regions terminated by domains of SrO/TiO₂ (or KO/TaO₂) with a well-defined atomic structure. The surface stability, point defects, electronic structure, and chemical properties of such surfaces will be discussed and linked to the incipient-ferroelectric character of these materials.

[1] Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G., *Science* 2009, 325, 1110

[2] Gross, L.; Mohn, F.; Liljeroth, P.; Repp, J.; Giessibl, F. J.; Meyer, G., *Science* 2009, 324, 1428

[3] Sugimoto, Y.; Pou, P.; Abe, M.; Jelinek, P.; Perez, R.; Morita, S.; Custance, O., *Nature* 2007, 446, 64

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[5] M. Setvin, M. Reticcioli, F. Poelzleitner, J. Hulva, M. Schmid, L. A. Boatner, C. Franchini, U. Diebold, *Science* 359, 572-575 (2018)

5:20pm **SS+2D+AP+AS+OX+SE-ThA10 Edge-Enhanced Oxygen Evolution Reactivity at Au-Supported, Ultrathin Fe₂O₃ Electrocatalysts**, *Xingyi Deng, D. Kauffman, D.C. Sorescu*, National Energy Technology Laboratory
Transition metal oxides have been emerging as promising candidates to replace the state-of-the-art IrO₂ electrocatalysts for oxygen evolution reaction (OER) in alkaline electrolyte, but their key structure-property relationships are often shadowed by heterogeneities in the typical catalyst samples. To circumvent this challenge, we have combined ultrahigh vacuum surface science techniques, electrochemical measurements, and density functional theory (DFT) to study the structure-dependent activity of well-defined OER electrocatalysts. We present direct evidence that the population of hydroxylated Fe edge-site atoms correlates with the OER activity of ultrathin Fe₂O₃ nanostructures (~0.5 nm apparent height) grown on Au(111) substrates, and the Fe₂O₃/Au catalysts with a high density of edge sites can outperform an ultrathin IrO_x/Au OER catalyst at moderate overpotentials. DFT calculations support the experimental results, showing more favorable OER at the edge sites along the Fe₂O₃/Au interface with lower predicted overpotentials resulted from beneficial modification of intermediate binding. Our study demonstrates how the combination of surface science, electrochemistry, and computational modeling can be

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used to identify key structure-property relationships in a well-defined electrocatalytic system .

2D Materials

Room A215 - Session 2D-FrM

2D Late News Session

Moderators: Daniel Gunlycke, U.S. Naval Research Laboratory, Ivan Oleynik, University of South Florida

10:40am **2D-FrM8 Mechanistic Insights into a Modified ALD Process to Achieve Crystalline MoS₂ Thin Films**, *Nathaniel Richey, L. Zeng, M. Yasheng, J. Shi, I. Oh, S.F. Bent*, Stanford University

Stimulated by the discovery of two-dimensional (2D) graphene, 2D transition metal chalcogenides (TMDs) are attracting much attention owing to their similar layered structure and graphene-analogous properties. Numerous research efforts are under way to explore their potential applications, such as optoelectronics, electrochemical cells, and energy harvesting devices. However, challenges remain in the development of controllable growth methods for TMDs with large-scale conformality at moderate growth temperatures. There has been an increasing trend toward resolving these issues by employing atomic layer deposition (ALD) due to its promise of layer-by-layer growth.

Despite the promise brought by ALD, further effort is needed as the TMD films grown using low temperature ALD often show non-ideal stoichiometry and require high-temperature post-annealing to improve the film quality. As an example, the known ALD processes that use Mo(CO)₆ and H₂S as the precursors have shown an ALD window of 150 ~ 175 °C. However, results from both literature and our laboratory show that the S-to-Mo ratio is close to 1.5:1, relatively far from the ideal value of 2:1, with the presence of undesired MoO_x species. We performed an investigation into the mechanisms of this ALD process. Based on understanding that ligand loss is a rate limiting step in the ALD process, a new methodology was developed that produces higher-quality MoS₂ films from these same precursors. These results were achieved by using a slightly elevated growth temperature and enhancing the chemical vapor deposition component of Mo(CO)₆ for better CO removal. A series of MoS₂ films were synthesized on Si substrates by this modified process, resulting in controllable linear growth behavior, a S-to-Mo ratio of 2:1, and strong characteristic MoS₂ Raman peaks. Additional characterization tools, including grazing incident X-ray diffraction (GIXRD), X-ray reflectivity (XRR) and atomic force microscopy (AFM), were also used to examine the film crystallinity, density, and surface morphology. By characterizing the material as a function of process conditions, we are able to elucidate fundamental mechanisms and key kinetic factors behind the MoS₂ growth process using Mo(CO)₆ and H₂S. This study may help shed some light on future design of ALD processes for 2D TMDs.

11:00am **2D-FrM9 The Electronic Properties of Quasi-One-Dimensional TiS₃ and ZrS₃**, *Simeon Gilbert*, University of Nebraska-Lincoln; *H. Yi*, Synchrotron SOLEIL; *A. Lipatov, T. Komesu*, University of Nebraska-Lincoln; *A.J. Yost*, Oklahoma State University; *A. Sinitskii*, University of Nebraska-Lincoln; *J. Avila*, Synchrotron SOLEIL, France; *M.C. Asensio*, Madrid Institute of Materials Science; *P.A. Dowben*, University of Nebraska-Lincoln

The transition metal trichalcogenides (TMTs) are an emerging class of 2D materials in which 2D sheets are formed by the van der Waals-like bonding of quasi-1D chains. Here we present our work on the electronic properties of two TMTs, TiS₃ and ZrS₃, including the experimental band structure from nanospot angle resolved photoemission spectroscopy (nanoARPES). The band structures of both TMTs exhibit strong in-plane anisotropy due to their quasi-1D structure. The extracted effective hole mass for both materials is doubled along the chain direction, giving rise to a preferential charge transport direction. Additionally, high resolution nanoARPES measurements show a spin-orbit coupling splitting at the top of the valence band in TiS₃. This spin-orbit coupling splitting is expected to increase for heavier TMTs such as ZrS₃. We also show that metals such as Au and Pt can form Ohmic contacts with TMTs rather than Schottky barriers using X-ray photoemission spectroscopy at the metal-semiconductor interface. Other advantages of TMTs include clean edge termination, band gaps of ~1eV and high predicted electron mobilities. Combined with their anisotropic electron transport, strong spin-orbit coupling and Ohmic contacts, these advantages make the TMTs strong candidates for use in nanoscale electronics, optoelectronics and spintronics.

11:40am **2D-FrM11 Definition of CVD Graphene Micro Ribbons with Lithography and Oxygen Plasma Ashing**, *Fernando Cesar Rufino, A.M. Pascon*, UNICAMP, Brazil; *D.R.G. Larrudé*, Mackenzie Presbyterian University, Brazil; *L. Espindola, F.H. Cioldin, J.A. Diniz*, UNICAMP, Brazil

The excellent physical properties of graphene [1], such as transport (high electron mobility 250000 cm²/Vs), elasticity (in the order of TPa) and mechanical strength (in the order of GPa), make this 2D material a strong candidate in electronic devices development, especially in the area of radiofrequency and applications in sensors. In researches related to electronic devices, graphene can be a great ally in the development and miniaturization of Field Effect Transistors, FET. Concerns related to the miniaturization process are the equipment and the materials necessary to achieve this objective, since the repeatability and the cost of the manufacturing process are two essential variables to ensure the viability of the proposed project.

In this work, we present the union of conventional techniques in the fabrication of microdevices and the application of graphene obtained by chemical vapor deposition (CVD), in the development of Field Effect Transistors based on Graphene, GFET [2]. In the fabricated GFETs, the conduction channel is formed by parallel micro ribbons of graphene, with the smallest dimension of 250 nm of width. This dimension was obtained by Photolithography and oxygen plasma ashing. Through these two techniques we can ensure the repeatability of the fabrication process and these are low cost techniques when compared to what is commonly found in the literature, which is the definition of graphene patterns by Electron Beam Lithography (high cost and low repeatability technique). In addition, the characteristics of good quality graphene remain at the end of the fabrication process, as proven by Raman spectroscopy.

The GFETs were fabricated on two different substrates. One on Si/SiO₂ and another on glass. In both materials, the same structures with the same parameters were fabricated and were able to reach dimensions in the order of 360 nm, for comparisons we used Atomic Force Microscope (AFM) to verify the roughness and Scanning Electronics Microscope (SEM) for detection and measurement of the structures. The graphene used in the fabrication of the devices was the last material to be transferred to the sample by fishing and using PMMA [3], ensuring the least possible handling of the material and therefore possible contaminations.

References:

- [1] K. S. Novoselov et al, *Science* **306**, 666 (2004).
- [2] F. C. Rufino et al, *SBMicro* 2018.
- [3] L. Jiao et al., *Am. Chem. Soc.*, 12612 (2008).

12:00pm **2D-FrM12 Reactivity of Metal Contacts with Monolayer Tungsten Disulfide**, *Ama Agyapong, K.A. Cooley, S.E. Mohney*, The Pennsylvania State University

Using two-dimensional transition metal dichalcogenides (TMD) for electronics, optoelectronics, and catalysis often requires integration with a metal, motivating fundamental studies of metal-TMD interactions. We previously published predictions on the reactivity of metals with tungsten disulfide based on thermodynamics. [1] Our current work employs an easy approach to test these predictions on reactivity of metal contacts with monolayer (1L) WS₂ using Raman spectroscopy performed through the backside of the contact. Au, Cu, Pd, Al, and Ti were deposited by electron beam evaporation onto 1L WS₂ grown on a sapphire substrate and capped with a thin film of silica to avoid agglomeration of the metal during annealing. Samples were annealed at 100, 200, and 300 °C under Ar for 1 hour. The results from Raman spectroscopy are in excellent agreement with the predictions from thermodynamics. Au, Cu, and Pd did not react with 1L WS₂ upon deposition or annealing. Reaction of Al with 1L WS₂ occurred upon annealing, while Ti reacted upon deposition, as indicated by loss of the characteristic peaks in the Raman spectrum for WS₂. We will also describe interesting changes in the Raman spectrum for WS₂ from Au/WS₂ samples and present transmission electron microscopy of these samples.

[1] Yitian Zeng, Anna C. Domask, Suzanne E. Mohney, Condensed phase diagrams for the metal-W-S systems and their relevance for contacts to WS₂, *Materials Science and Engineering: B*, Volume 212, October 2016, Pages 78- 88: <http://dx.doi.org/10.1016/j.mseb.2016.07.005>.

The authors thank the National Science Foundation (DMR 1410334) for their support of this project. Monolayer WS₂ was provided by The Pennsylvania State University Two-Dimensional Crystal Consortium – Materials Innovation Platform (2DCC-MIP) supported by NSF cooperative agreement DMR-1539916.

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Plasma Science and Technology Division

Room B130 - Session PS+2D+SE+TF-FrM

Plasma Deposition and Plasma-Enhanced Atomic Layer Deposition

Moderators: David Boris, U.S. Naval Research Laboratory, Chenhui Qu, University of Michigan

8:20am **PS+2D+SE+TF-FrM1 Plasma-based Synthesis of 2D Materials for Devices on Flexible Substrates**, *N.R. Glavin*, Air Force Research Laboratory; **Christopher Muratore**, Department of Chemical and Materials Engineering, University of Dayton

INVITED

Synthesis of flexible two-dimensional electronic devices using low-cost, naturally abundant materials (e.g., MoS₂) directly onto inexpensive polymeric materials at economically viable scales enables use of their unique characteristics in grand challenge areas of energy, healthcare, and national security. Recently-proven approaches for low temperature, plasma-based 2D synthesis suitable for flexible substrates developed by the authors include growth of amorphous materials with subsequent photonic annealing to access crystalline domain sizes up to several microns. This approach has been demonstrated for synthesis of large area ultrathin monolithic layers as well as MoS₂/WS₂/BN multilayers with pristine interfaces, allowing interrogation of intrinsic properties of 2D materials and their heterostructures as they apply to diverse optoelectronic devices, with a current focus on molecular sensing. Advantages of plasma-based approaches will be discussed in terms of detailed kinetic studies of crystal formation and compositional evolution on the substrate surface. Correlations of structure, especially defect densities, to materials properties and device performance will be discussed in the context of diverse device applications including photodetectors and molecular sensors.

9:00am **PS+2D+SE+TF-FrM3 Homogeneous Ternary Oxides of Aluminum with Silicon, Molybdenum, and Niobium by Plasma Enhanced ALD by Sequential Precursor Pulses**, *Steven Vitale*, MIT Lincoln Laboratory

Deposition of ternary oxide films by ALD is well known. In the vast majority of cases ternary films are deposited by sequential deposition of thin layers of the constituent binary oxides, such as Al₂O₃ / SiO₂. This nanolaminate approach allows for precise control of the global film stoichiometry and is a good solution for many applications, including optical coatings where the wavelength of light is much greater than the nanolaminate thickness thus the film appears quasi-uniform. The nanolaminate approach is less desirable for electronic applications which are sensitive to surface defect sites in the material which may act as charge traps. For these applications a truly homogenous film which does not possess internal interface states is preferred. True homogenous ternary oxide growth by sequential precursor pulses before the oxidation step is much less well explored. In this work we grow homogeneous ternary oxides of Al_xSi_yO_z, Al_xNb_yO_z, Al_xMo_yO_z by plasma enhanced ALD using sequential precursor pulses. The stoichiometry of the films is measured by XPS. Using this data we propose models of how the precursors interact with the surface under competitive adsorption. It is found that trimethyl aluminum (TMA) is so strongly adsorbed to the surface at unity surface coverage that ternary oxide growth is not possible if the surface is first exposed to TMA. However if the surface is exposed to the Si, Nb, or Mo precursor first, ternary oxide growth is achieved. The growth kinetics for the three films are markedly different, however, and we explain this through models of the adsorption energy of each precursor.

9:20am **PS+2D+SE+TF-FrM4 Piezoelectric Response of ZnO Thin Films Grown by Plasma-Enhanced Atomic Layer Deposition**, *Julian Pilz*, *T. Abu Ali*, Graz University of Technology, Austria; *P. Schöffner*, *B. Stadlober*, Joanneum Research Forschungsgesellschaft mbH, Austria; *A.M. Coclite*, Graz University of Technology, Austria

ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices. Especially the utilization of piezoelectric properties of ZnO nanostructures for transforming mechanical to electrical energy has attracted much research interest. For most of these so called nanogenerators, solution based deposition methods have been applied to create the desired nanostructures, often lacking a precise control of the deposition parameters. Atomic layer deposition, on the other hand, allows conformal and uniform deposition on high aspect ratio structures with Å-level thickness control.

In this study, we investigate the piezoelectric response of ZnO thin films on flexible substrates as a starting point for piezoelectric nanostructures. The

films are grown by plasma-enhanced atomic layer deposition (PE-ALD) to thicknesses below 100 nm by adapting diethylzinc and O₂-plasma as reactants. In comparison to thermal ALD (where diethylzinc and water are used as reactants), PE-ALD allows the deposition of films with higher resistivity, an important property to minimize the leakage of piezoelectric charges. Commercially available Polyethylenterephthalat (PET) coated with Indium Tin Oxide (ITO) serves as the flexible substrate and bottom electrode, respectively. The deposition of ZnO thin films is carried out at substrate temperatures between room temperature and 100 °C, as a change in preferential crystal orientation from (100) to (002) can be observed in this temperature range. The macroscopic piezoelectric characterization is performed in a home-built stamp station, in which a defined periodic force is exerted onto the samples and the generated piezoelectric charges are measured. Out of this, the longitudinal piezoelectric coefficient d_{33} can be obtained. Preliminary results show d_{33} coefficients > 7 pC/N, which is comparable to literature results. The piezoelectric characterization is made for the different samples to understand how the d_{33} coefficient changes for films deposited at different substrate temperatures and thus having different crystal orientation. Since the [002] is the polar axis in the ZnO wurtzite crystal structure, films with preferred orientation in this direction are therefore expected to show higher d_{33} coefficients.

The work lays the basis for developing functional piezoelectric generators and sensors in thin film form. However, the concepts can be easily transferred to depositions on lithographically defined templates in order to create nanostructured ZnO, which exhibits increased piezo response.

10:00am **PS+2D+SE+TF-FrM6 Plasma-enhanced Molecular Layer Deposition of Boron Carbide from Carboranes**, *Michelle M. Paquette*, *R. Thapa*, *L. Dorsett*, *R. Bale*, *S. Malik*, *D. Bailey*, *A.N. Caruso*, University of Missouri-Kansas City; *J.D. Bielefeld*, *S.W. King*, Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecule based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are limited and typically based on the condensation of "linear" 2D or "brush-type" organic polymer chains. To this end, icosahedral carborane (C₂B₁₀H₁₂) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low- k interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, known to form close-packed monolayers and to possess labile H atoms at each of the vertices capable of cross-linking in the presence of heat, plasma, or other energy source. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, reactivity, and volatility properties not commonly encountered in traditional organic molecules. However, a challenge in developing a layer-by-layer process lies in achieving the selective coupling chemistry required, which in the case of molecular reagents requires typically exotic bis-functional derivatives. Herein we describe progress in developing a plasma-enhanced molecular layer deposition process based on carborane derivatives, where the plasma is exploited to create the surface functionalization necessary for selective coupling and to cross-link carborane layers. We investigate the deposition of several carborane derivatives on different functionalized surfaces with the application of various types of plasmas toward achieving controlled layer-by-layer growth of thin boron carbide films.

10:20am **PS+2D+SE+TF-FrM7 Gas Phase Kinetics Optimization Study for Scaling-up Atmospheric Pressure Plasma Enhanced Spatial ALD**, *Yves Creyghton*, Holst Centre / TNO, The Netherlands, Netherlands

DBD plasma sources have been successfully integrated in spatial ALD equipment for low-temperature ALD (<120 °C) of metal-oxides. Applications involving (semi)conductive substrates require remote plasma operation. Radical losses during transport from remote plasma limit substrate speeds or demand excessive plasma flow rates. Proximity remote plasma sources were developed with sufficient radical flux even at low gas flow rates. The sources were demonstrated for ALD of InZnO for high mobility thin film transistors. Further optimization asks for deeper understanding of radical kinetics. In this contribution experimental and calculated data will be presented which allow insight in the radical gain and loss processes. A reference temperature of 100 °C and gas flows in the range 2-10 slm (for a 4 cm wide source) were applied. Alumina depositions

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were carried out using TMA and 2% O₂-N₂ plasma gas. Deposited layers obtained for different relative height positions of the plasma source were analyzed. Growth per cycle (GPC) values indicate a strong decay of plasma reactivity for gaps > 0.5 mm. As O₃ should not decay over such small distance, this indicates that the process is radical based. Surprisingly the GPC also shows a peak value at 0.1 mm (Fig. 1). O₃ and NO_x were measured in the plasma exhaust gas as a function of % O₂ (Fig. 2). The 1-2% O₂ for maximum NO appears to correspond with the optimal gas composition for both high GPC values and refractive index values close to 1.58 indicating high layer quality. This result suggests NO plays a role in downstream plasma radical formation. Further understanding of the role of plasma species such as N, metastable N₂(A) and NO has been obtained by modelling. Kinetic data sets for optimization of O₃ production have been implemented in a CFD model for the transport of plasma species from the remote plasma. For the analysis of modelling results, the reaction volume has been divided in 3 parts (1) the plasma ionization zone itself, (2) the flow dominated plasma source aperture and (3) the diffusional transport dominated surface reaction zone. The dominating reactions for gain and loss of O radicals differ much between zones (Fig. 3). As the main O radical formation in zone (2) is due to metastable excited N₂(A), in zone (3) reactions between N radicals and NO are the main source of O radical generation. In both zones, the main O radical loss process is due to generation of O₃. The experimentally validated model has been used for finding improved plasma process settings (source geometry, frequency, flow) allowing the further optimization of high-throughput plasma enhanced spatial ALD of metal oxides.

10:40am **PS+2D+SE+TF-FrM8 Taking Plasma ALD to the Next Level: From Fundamental Understanding to Selective 3D Processing**, T.F. Faraz, K. Arts, Eindhoven University of Technology, The Netherlands, Netherlands; L. Martini, R. Engeln, H.C.M. Knoop, Eindhoven University of Technology, The Netherlands; **Erwin Kessels**, Eindhoven University of Technology, The Netherlands, Netherlands

INVITED

Current trends in semiconductor device manufacturing impose extremely stringent requirements on nanoscale processing techniques, both in terms of accurately controlling material properties and in terms of precisely controlling nanometer dimensions. Plasma-based processing remains key in next-generation device manufacturing with plasma-enhanced atomic layer deposition (PE-ALD or plasma ALD) being a method that has obtained a very prominent position in obtaining ultrathin films with atomic scale precision [1]. In this contribution the state-of-the-art of PE-ALD will be presented including latest insights into reaction mechanisms as well as some developments in plasma ALD equipment and emerging applications. Aspects such as the role of (energetic) ions, conformality in high aspect ratio structures, and selective processing will be discussed [2].

[1] H.C.M. Knoop, T. Faraz, K. Arts, and W.M.M. Kessels, J. Vac. Sci. Technol. A 37, 030902 (2019)

[2] T. Faraz, K. Arts, S. Karwal, H.C.M. Knoop, and W.M.M. Kessels, Plasma Sources Sci. Technol. 28, 024002 (2019).

11:20am **PS+2D+SE+TF-FrM10 Computational Investigation of Plasma Enhanced ALD of SiO₂**, C. Qu, University of Michigan; P. Agarwal, Y. Sakiyama, A. LaVoie, Lam Research Corporation; **Mark J. Kushner**, University of Michigan

Plasma enhanced atomic layer deposition (PE-ALD) of dielectric films typically consists of two steps – precursor deposition and oxidation. For example, in a SiO₂ PE-ALD process, the Si-containing precursor is often deposited in the feature without use of plasma while the oxidation step is performed by an oxygen containing plasma. In principle, the surface kinetics of both steps are self-terminating. Although the plasma step is performed using gas pressures of several to 10 Torr, in addition to O-atoms the fluxes onto the wafer contain energetic particles in the form of ions, photons, hot-neutrals and excited states. When performing PE-ALD in high aspect ratio (HAR) features, transport of these species into the feature determine the quality of the deposition. Optimizing the PE-ALD depends on control of these fluxes.

In this work, results from a computational investigation of reactor and feature scale processes in idealized PE-ALD of SiO₂ will be discussed. Reactor scale simulations of a capacitively coupled plasma sustained in Ar/O₂ mixtures were performed using the Hybrid Plasma Equipment Model (HPEM); and provided fluxes and energy distributions of radicals, ions, excited states and photons onto the wafer. Feature scale simulations were performed with the Monte Carlo Feature Profile Model (MCFPM). The idealized ALD process consists of a non-plasma first step using a Si-R (R indicates organic) precursor. The second step uses fluxes from the Ar/O₂

plasma to remove the organic and oxidize the Si site. The base-case features are moderate to high aspect ratio (AR = 7-20) vias and trenches. The metrics to evaluate the process are surface coverage of Si, O, R, stoichiometry, defect density, surface roughness and deposition rate.

In self-terminating processes, many of these metrics should scale with pt , where p is the probability of reaction and t is the step length. For example, a given surface coverage of Si-R or Si-O should depend on first order on pt . However, as deposition proceeds and a feature fills, the effective AR increases. When coupled with conductance limited transport into the feature, with increasing AR the value of pt to produce a given surface coverage increases. As the deposition proceeds and AR increases, stoichiometry and defect density begins to have a dependence on height inside the feature, as surfaces deep in the feature receive less exposure to the reactive fluxes. The consequences of ion- and photon-induced damages will also be discussed.

* Work supported by LAM Research Corp. and the DOE Office of Fusion Energy Science.

11:40am **PS+2D+SE+TF-FrM11 Analyzing Self-limiting Surface Reaction Mechanisms of Metal Alkyl Precursors and Nitrogen Plasma Species: Real-time In-situ Ellipsometric Monitoring of III-nitride Plasma-ALD Processes**, Ali Okyay, OkyayTech Inc., Turkey; A. Mohammad, D. Shukla, S. Ilhom, University of Connecticut; B. Johs, Film Sense LLC; B.G. Willis, N. Biyikli, University of Connecticut

ALD-grown films are vastly characterized via ex-situ measurements to quantify various material properties. However, gaining insight into the saturating surface reactions and growth mechanisms is only possible with real-time in-situ process monitoring of individual ALD cycles. While several in-situ measurement techniques have been employed in ALD research, in-situ ellipsometry stands out as one of the best options for real-time monitoring surface reactions. The promising potential of in-situ spectroscopic ellipsometry has already been demonstrated for a number of materials grown by remote plasma-ALD. Here, we verify that cost-effective multi-wavelength ellipsometer (MWE) can also be used effectively for real-time in-situ analysis of plasma-ALD growth cycles. We demonstrate for the first time that real-time dynamic in-situ MWE measurements convey not only accurate film deposition rate, but as well resolve single chemisorption, ligand removal, and nitrogen incorporation events with remarkable clarity. Moreover, forcing the limits for fitting the acquired in-situ MWE data, we were able to track the evolution of the optical constants of III-nitride films along the ALD cycles which indeed showed thickness-dependent behavior.

Our main motivation behind this study was twofold: (i) Analyze and compare the self-limiting growth characteristics of binary III-nitride (AlN, GaN, and InN) thin films via real-time in-situ ellipsometry and to gain insight into the ALD surface reaction mechanisms including chemical adsorption, ligand removal, and nitrogen incorporation steps. (ii) Performance evaluation of our custom designed ALD reactor featuring improved hollow-cathode plasma source by comparing our results with previous plasma-ALD grown III-nitrides.

Despite using the conventional alkyl metal precursors (trimethylaluminum, trimethyl/ethylgallium, trimethylindium) utilized also widely in MOCVD epitaxial growth, their solid-gas surface interactions with nitrogen plasma species shows notable differences, particularly with respect to substrate temperature, plasma power, plasma exposure time, and plasma gas composition. In terms of substrate temperature, AlN exhibited crystallinity at lower temperatures when compared to GaN and InN. Even at 100 °C, AlN showed crystalline behavior whereas GaN displayed amorphous character up to 200 °C. While Ar/N₂/H₂ composition is optimal for AlN, N₂/H₂ and Ar/N₂ mixtures proved to be better for GaN and InN. InN experiments revealed that the inclusion of H₂ gas led to mixed phase growth with substantial c-In₂O₃ phase. The possible surface reaction mechanisms that lead to these different growth behaviors will be discussed in detail.

12:00pm **PS+2D+SE+TF-FrM12 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN with Substrate Bias**, Mark Sowa, Veeco ALD; A.C. Kozen, University of Maryland; N.C. Strandwitz, T.F. Babuska, B.A. Krick, Lehigh University

In our previous study, we demonstrated a tertiary plasma enhanced atomic layer deposited transition metal nitride (TiVN) with exceptional wear rates and friction coefficients. We have extended that work with an investigation of another tertiary transition metal nitride system, Ti_xMo_yN_z. For films deposited at 250°C and 300W on a Veeco CNT G2 Fiji PEALD system, we have demonstrated how the ratio of TiN:MoN cycles (1:0, 2:1, 1:1, 1:2, 0:1) provides linear control of the Ti:Mo in the resulting film. Through application of an 13.56MHz RF substrate bias (0-188V) during the plasma

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step, ion bombardment energy of the substrate can be varied, providing a means for tweaking the films physical and chemical characteristics which in turn are shown to impact the resulting film's tribological properties. As PEALD metal nitrides have broader interest than wear layers and to gain insights on the interrelationships of the mechanical properties, the processing details, and other film properties, we also report on the resulting film composition/impurities, density, crystallinity, optical properties, resistivity, and morphology.

Bold page numbers indicate presenter

— A —

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- Yost, A.J.: 2D+EM+MI+NS+QS+SS-ThM3, 43; 2D-FrM9, 57
- Yousefi Sarraf, S.: MI+2D-WeA12, 41
- Yousefi, S.F.: MI+2D-WeA7, 40
- Yu, J.: 2D+EM+MI+NS-MoM10, **2**
- Yu, M.: HC+2D+SS-ThM12, 46
- Yu, S.: 2D+EM+MI+MN+NS+QS-TuM5, 14
- Yu, x.: NS+2D+AS-WeA1, 41
- Yu, Y.: 2D+AP+EM+MI+NS+PS+TF-MoA3, 7; NS+2D+QS-ThM2, 48
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- Zaera, F.: HC+2D+SS-WeM3, **32**
- Zeller, P.: CA+2D+AS+BI+NS-ThM4, 45
- Zeng, L.: 2D-FrM8, 57
- Zepeda, T.: 2D+AS+MI+NS-TuM13, 14
- Zhang, D.: PS+2D+EM+SS+TF-ThA4, 53
- Zhang, H.: 2D+EM+MI+MN+NS+QS-TuM10, **14**; 2D+EM+MI+MN+NS+QS-TuM11, 15; 2D+EM+MI+MN+NS+QS-WeM6, 29
- Zhang, W.: 2D+AP+EM+MI+NS+PS+TF-MoA3, 7
- Zhang, X.: QS+2D+EM+MN+NS-TuA8, 22
- Zhang, Y.: 2D+AS+MI+NS-WeM12, 28; NS+2D+QS-ThM12, 50
- Zhang, Z.: AP+2D+EM+PS+TF-MoM2, 2; TF+2D+AP+EL+SS-MoA5, **9**
- Zhang, Z.M.: EM+2D+AS+MI+MN+NS+TF-WeM1, 30
- Zheng, L.: MI+2D+AS+EM-ThM12, 48
- Zhou, C.: NS+2D+QS-ThM6, 49
- Zhou, T.: 2D+AP+EM+MI+MN+NS+PS+TF-MoA5, 5
- Zhu, M.: 2D+EM+MI+MN+NS+QS-TuM5, 14
- Zhu, T.: 2D+EM+MI+MN+NS+QS-TuM5, **14**; 2D+EM+MI+NS+QS+SS-ThM10, 43
- Zou, Q.: 2D+EM+MI+MN+NS+QS-TuM11, **15**; MI+2D-WeM2, 33
- Zurbuchen, M.: MI+2D-WeA10, 40
- Zutic, I.: 2D+AP+EM+MI+MN+NS+PS+TF-MoA5, 5