2D Materials Focus Topic
Room 103B - Session 2D+MI+SA-MoM

2D Materials Characterization including Microscopy and Spectroscopy

Moderator: Matthias Batzill, University of South Florida

8:20am **2D+MI+SA-MoM1 Scanning Tunneling Microscopy and Spectroscopy of Air Exposure Effects on Molecular Beam Epitaxy Grown WSe_2 Monolayers and Bilayers**, *J.H. Park,* Univeristy of California, San Diego*; S. Vishwanath,* Cornell University*; X. Liu,* University of Notre Dame*; H. Zhou,* Cornell University*; S.M. Eichfeld,* Pennsylvania State University*; S.K. Fullerton-Shirey,* University of Pittsburgh*; J.A. Robinson,* Pennsylvania State University*; R. Feenstra,* Carnegie Mellon University*; J. Furdyna,* University of Notre Dame*; D. Jena, H.G. Xing,* Cornell University*;* ***Andrew Kummel,*** University of California, San Diego

The effect of air exposure on 2H-WSe_2/HOPG was determined *via* scanning tunneling microscopy. WSe_2 was grown by molecular beam epitaxy on highly oriented pyrolytic graphite (HOPG), and afterwards, a Se adlayer was deposited *in-situ* on WSe_2/HOPG to prevent unintentional oxidation during transferring from the growth chamber to the STM chamber. After annealing at 773 K to remove the Se adlayer, STM images show that WSe_2 layers nucleate at both step edges and terraces of the HOPG. The grain boundaries and the step edges of WSe_2 ML have a bias dependence in STM imaging, consistent with difference electronic states with the defect-free terraces. After exposure air for 1 day, although the edge of WSe_2 is partially oxidized, the grain boundaries still maintain a defective electronic structure. Exposure to air for 1 week and 9 weeks caused air-induced adsorbates to be deposited on the WSe_2 surface; however, as shown for localized electronic structure measurement using scanning tunneling spectroscopy (STS), the bandgap of the terraces remained unaffected and nearly identical to those on de-capped WSe_2. The air-induced adsorbates can be removed by annealing at 523 K. In contrast to WSe_2 terraces, air exposure caused the edges of the WSe_2 to oxidize and form protrusions, resulting in a larger STS bandgap compared to the terraces of air exposed WSe_2 monolayers. The preferential oxidation at the WSe_2 edges compared to the terraces is likely the result of dangling bonds at step edges. In the absence of air exposure, the dangling edge bonds have a smaller band gap compared to the terraces and a shift of about 0.73 eV in the Fermi level towards the valence band. However, after air exposure, the band gap of the oxidized WSe_2 edges became larger about 1.08 eV that of the WSe_2 terraces, resulting in the electronic passivation of the WSe_2.

8:40am **2D+MI+SA-MoM2 Tuning the Trion Photoluminescence Polarization in Monolayer WS_2**, ***Aubrey Hanbicki,*** *K.M. McCreary, M. Currie,* Naval Research Laboratory*; G. Kioseoglou,* University of Crete*; C.S. Hellberg, A.L. Friedman, B.T. Jonker,* Naval Research Laboratory

Monolayer transition metal dichalcogenides (TMDs) such as MoS_2 or WS_2 are semiconductors with degenerate, yet inequivalent *k*-points labeled *K* and *K'* that define the direct bandgap. The valence band maximum in each valley has only one spin state in which the spins are opposite for *K* and *K'*. Consequently, one can selectively populate each valley independently with circularly polarized light and determine the valley populations via the polarization of emitted light. Monitoring changes in emitted polarization, therefore provide insights into the fundamental processes of intervalley scattering. We prepare single-layer WS_2 films such that the photoluminescence is from either the neutral exciton or the negatively charged trion [1,2]. In most TMDs, the optical polarization is small at room temperature, and we find that the neutral exciton emission indeed has zero polarization at room temperature. However, we observe a room temperature optical polarization in excess of 40% for the trion. The trion polarization always exceeds that of the exciton and exhibits a pronounced, non-monotonic temperature dependence – the polarization nearly doubles as the temperature increases from 125 K to 175 K. The observed increase in optical polarization directly correlates with a decrease in emission intensity between 125-175 K indicating that this effect is a consequence of the onset of nonradiative processes. Because this dependence involves trion systems, one can use gate voltages to modulate the polarization or intensity emitted from TMD structures. Using an applied gate voltage, we can modulate the electron density and subsequently the polarization of WS_2 trions continuously from 20-40%. Both the polarization and the emission energy monotonically track the gate voltage with the emission energy increasing by 45 meV. We discuss the role electron capture of the trion has on suppressing the intervalley scattering process. This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

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9:00am **2D+MI+SA-MoM3 Quantum Hall Effect in Graphene Visualized through Scanning Tunneling Microscopy and Spectroscopy**, ***Adina Luican-Mayer,*** University of Ottawa, Canada **INVITED**

The ability to controllably layer atomically thin crystals into custom-made materials holds promise for realizing physical systems with distinct properties, previously inaccessible. The experimental results described in this talk seek to uncover the unique nature of the charge carriers in such few-atoms-thick materials as well as effects that interlayer coupling and disorder have on their properties. To that end we use scanning tunneling microscopy (STM) and spectroscopy (STS) experiments performed on graphene systems at low temperatures and in magnetic field. We study Landau quantization in graphene and by performing spatially resolved STM/STS we demonstrate the true discrete quantum mechanical electronic spectrum within the Landau level band near charged impurities in graphene in the quantum Hall regime.

9:40am **2D+MI+SA-MoM5 Enhancing the Electrical Conductivity of VUV-reduced Graphene Oxide by Multilayered Stacking**, ***Yudi Tu,*** *T. Utsunomiya, T. Ichii, H. Sugimura,* Kyoto University, Japan

Reducing graphene oxide (GO), a highly oxidized graphene derivatives, by utilizing light irradiation has drawn great attention, due to its flexibility to locally fabricating conductive patterns and tuning the electrical property. We have demonstrated the reduction of GO under the 172 nm vacuum-ultraviolet (VUV) irradiation under high vacuum and combined it with mask photolithography to make reduced graphene oxide (rGO) conductive pattern at sub-μm scale.[1,2] The recovery of electrical conductivity at the reduced regions was confirmed by conductive-probe atomic force microscope (CAFM). However, further researches by applying micro Raman spectroscopy (μRS), scanning tunneling microscopy (STM) and CAFM have revealed that the pristine defects induced by the harsh oxidative synthesis of GO is unable to be repaired. On purpose to enhance the electrical conductivity of rGO pattern, generating more conductive paths for the carriers' transportation is of great importance. In this presentation, we will demonstrate the enhanced electrical conductivity in multilayered rGO sheets. The nanoscale conductive sp^2 domains in rGO are connected to construct 3-dimensional conductive paths between the multilayered sheets.

The GO-coated Si substrate was irradiated by the VUV light in the high vacuum ($< 10^{-3}$ Pa) chamber. The CAFM current mapping revealed that GO and the derived rGO were heterogeneous hybrids of both conductive and insulating domains. Interestingly, besides the nanoscale domains distribution revealed by the previous μRS and STM results, the microscale domains distribution was also observed within the sheets, which was attributed to the uncertainly harsh oxidation synthesis. The CAFM current mapping showed obvious enhancement on the electrical conductivity of bi-layered rGO comparing with the single-layered rGO. A triangle approximate model was applied to estimate the lateral electrical conductivity of rGO sheets. It was found that the tip contact area showed no clear influence on the lateral electrical conductivity. By further measuring the current signals from both bi-layered and single-layered rGO sheets, it was found that the enhancement was not due to the parallel-connection of two rGO sheets but originated from the newly constructed 3-dimensional conductive paths between them.

(1) Tu, Y.; Ichii, T.; Utsunomiya, T.; Sugimura, H. *Appl. Phys. Lett.***2015**, *106*, 133105.

(2) Tu, Y.; Ichii, T.; Khatri, O. P.; Sugimura, H. *Appl. Phys. Express***2014**, *7*, 75101.

10:00am **2D+MI+SA-MoM6 Silicene-like Reconstruction via Surface Relaxation of Hexagonal-$MoSi_2$ Crystallites**, ***Cameron Volders,*** *P. Reinke, G. Ramalingam, E. Monzami,* University of Virginia

The exciting properties of 2D materials have intrigued scientists and engineers for over a decade. A new wave of 2D materials are being explored in the scientific community, specifically, Silicene has garnered much attention for its potential in device integration. The current Silicene literature has accepted a synthetic method of depositing monolayer (ML) amounts of Si atoms onto a heated Ag (111) substrate to produce the 2D layer. Alternative substrates such as Ir (111) have been explored to obtain silicene, however, the validity of these results are still being debated.

The current work will address an approach, which is a potential alternative route for growing a silicene layer, based on the observation of a Silicene-like reconstruction (SLR) on the surface of nanometer-scale hexagonal $MoSi_2$ crystallites terminated by the (0001) plane. The bulk (0001) $MoSi_2$ surface is comprised of Si hexagons with a Mo atom in the center. The honeycomb pattern exhibited by the SLR is formed via relaxation of the (0001) plane where the Si atoms decouple from the underlying h-$MoSi_2$ crystallites. Signatures of a 'graphite-like' Si structure have been reported in literature, but have not yet been pursued in 2D materials studies. We will present an extensive study of the SLR based on Scanning Tunneling Microscopy and Spectroscopy data.

Initially, this work will describe a parameter space in which the SLR can be confidently reproduced. Mo atoms are deposited onto a Si (001) surface and annealed to grow the h-$MoSi_2$ crystallites, which is where the SLR resides. Our experimental data supports an optimal growth regime of approximately 750˚C and 3-5 ML's of Mo. The focus will then switch to demonstrating the geometrical parameters of our SLR are strikingly similar with that of the current Silicene literature. Our experimental results indicate the honeycomb pattern of the SLR corresponds to a superstructure. When comparing the lattice constant and Si-Si distance in our structure with that of silicene literature, the results strongly suggest we are observing a low-buckled silicene layer. Also included, will be a statistical treatment contributing to the validity that a surface relaxation process is the pathway by which the layer is grown. Specific features are always observed, including a well-defined 'rim' structure and defect motif, when the SLR is observed.

The final stage of this presentation will focus on addressing the electronic structure of the SLR based on STS data. A few studies have provided STS measurements indicating the observation of a Dirac-point (DP) near 0.5 eV. Our experimental results contain an intriguing feature in the same region, which will be discussed.

10:40am **2D+MI+SA-MoM8 Electron Dynamics in Two-Dimensional Materials*, Philip Hofmann,*** Aarhus University, Denmark **INVITED**

Changing the dimensionality of a material results in significant modifications of its electronic properties. This is even the case if the parent material already has a layered structure with little interaction between the layers, as in the case of graphene, bilayer graphene and single-layer transition metal chalcogenides.

While the static electronic properties of novel two-dimensional materials can be studied by standard angle-resolved photoemission spectroscopy (ARPES), investigations of the ultrafast carrier dynamics require both time- and angular resolution and thus time-resolved (TR)-ARPES. There is, moreover, the technical requirement of high photon energies since the interesting part of the aforementioned materials' electronic structure (i.e. the (gapped) Dirac cone) is placed at the two-dimensional Brillouin zone boundary. Recently, it has become possible to probe states at such high k by TR-ARPES, thanks to the arrival of ultrafast high harmonic laser sources.

Here we characterize the dynamic processes around the Dirac point in epitaxial graphene [1,2], as well as around the band gap of single layer MoS_2 [3,4] using TR-ARPES. In the graphene, we can determine and control the timescales of hot carrier scattering processes. For single layer MoS_2, we can directly measure the size of the direct band gap by pumping electrons into the conduction band minimum. We find that this band gap can be strongly renormalized, both by a static interaction with the substrate and by a dynamic screening due to a high density of excited free carriers.

References

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[3] J. Miwa et al., Physical Review Letters 114, 046802 (2015).

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11:20am **2D+MI+SA-MoM10 Novel Characterization Techniques for 2D Materials: Visualizing Inherent and External Defects*, Rudresh Ghosh,*** *S.K. Banerjee, D. Akinwande,* University of Texas at Austin

Over the last decade, since the demonstration of exceptional physical, chemical and electrical properties of graphene, there has been a lot of interest in two-dimensional materials. Of these new materials significant effort has been focused on transition metal dichalcogenides (TMDs) due to their various possible applications. Initial work on TMDs, similar to that of graphene, has depended on exfoliated samples. In this work we present controlled large-area synthesis of highly crystalline few to monolayers of various TMDs (MoS2, WS2, WSe2) using both solid and gas precursors. Characterization of the TMDs are done using a combination of conventional techniques such as Raman and Photoluminescence spectroscopy, Atomic force microscopy, scanning and transmission electron microscopy. Shifts in Raman and PL spectra as a function of strain shows obvious differences between exfoliated and CVD grown material. New characterization tools with the capability of localized dielectric mapping (Microwave impedance microscopy) also show us a way to analyze defects that are inherent during CVD growth processes. Elemental identification of individual layers and their interfaces (using Time of Flight SIMS) are demonstrated as extremely useful for studying these 2d heterostructuress. Electrical device characterization and paths of optimization are also presented. Electrical characterization of the devices on various substrates is also presented.

11:40am **2D+MI+SA-MoM11 Anomalous Dynamical Behavior of Freestanding Graphene*, Paul Thibado,*** *M. Ackerman, P. Kumar, S. Singh,* University of Arkansas*; M. Neek-Amal, F. Peeters,* University of Antwerp, Belgium

Local, long-time evolution measurements of the height fluctuations of a 2D membrane allows examination of the fundamental foundations of statistical mechanics in soft condensed matter. However, such measurements have proved elusive, thereby forcing critical theoretical assumptions in our best models. We report sub-nanometer, high-bandwidth height measurements of freestanding graphene using constant-current, point-mode scanning tunneling microscopy, as a follow-up to our previous related works [1-2]. By tracking atoms directly, the ability to measure dynamic events is increased by a factor of 1000 over the present state-of-the-art membrane imaging technology. Surprisingly, the membrane velocities follow the Cauchy-Lorentz distribution consistent with a Lévy process, rather than the expected Maxwell-Boltzmann distribution. We also present molecular dynamics simulations, which illustrate spontaneous mirror buckling events that give rise to the long excursions.

Acknowledgements:

This work was supported in part by Office of Naval Research (USA) under Grant No. N00014-10-1-0181 and National Science Foundation (USA) under Grant No. DMR- 0855358.

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Magnetic Interfaces and Nanostructures
Room 101C - Session MI+2D+AC-MoM

Chiral Magnetism (8:20-10:20 am)/Magnetism and Spin Orbit Effects at Interfaces and Surfaces: Recent Experimental and Theoretical Advances (10:40 am - 12:00 pm)

Moderators: Markus Donath, Westfälische Wilhelms-Universität Münster, Germany, Hendrik Ohldag, SLAC National Accelerator Laboratory

8:20am **MI+2D+AC-MoM1 Manipulation of Magnetic Skyrmions with STM*, Kirsten von Bergmann,*** University of Hamburg, Germany **INVITED**

Magnetic skyrmions are topologically distinct from their ferromagnetic environment. They may form in an inversion asymmetric environment and are induced by a competition between magnetic exchange, Dzyaloshinsky-Moriya interaction, and typically the Zeeman energy. Scanning tunneling microscopy (STM) is a valuable tool to study the properties of nanometer-scale skyrmions [1]. In addition to measurements with spin-polarized STM tips skyrmions can also be detected with unpolarized electrodes due to spin-mixing effects in the non-collinear spin texture. We employ spatially resolved magnetic field dependent tunneling spectroscopy to identify this effect of non-collinear magnetoresistance and find that it scales with the angle between nearest neighbors [2]. With a non-magnetic STM tip it is also possible to locally switch the topology of a thin magnetic layer via the sign of the electric field between tip and sample [3]. The combination of these two phenomena –electrical detection and electric field switching of topologically distinct states– could lead to a robust non-magnetic read- and write-head for future skyrmion racetracktype devices.

[1] K. von Bergmann et al., *J. Phys.: Cond. Mat.* **26**, 394002 (2014).

[2] C. Hanneken et al., *Nature Nanotechn.* **10**, 1039 (2015).

[3] P.-J. Hsu et al., arXiv:1601.02935.

9:00am **MI+2D+AC-MoM3 Skyrmion Hall Effect***, W. Jiang,* Argonne National Laboratory*; X. Zhang,* The University of Hong Kong, Hong Kong Special Administrative Region of China*; G. Yu,* University of California Los Angeles*; M.B. Jungfleisch, J.E. Pearson, O. Heinonen,* Argonne National Laboratory*; K.L. Wang,* University of California Los Angeles*; Y. Zhou,* The University of Hong Kong, Hong Kong Special Administrative Region of China*; S.G.E. te Velthuis,* ***Axel Hoffmann,*** Argonne National Laboratory

Magnetic skyrmions are a perfect example for the ensuing complexity of mesoscale magnetism stemming from competitions between interactions crossing many lengthscales [1]. The interplay between applied magnetic fields, magnetic anisotropies, as well as symmetric and antisymmetric exchange interactions, can stabilize topologically distinct spin textures known as magnetic skyrmions. Due to their topology magnetic skyrmions can be stable with quasi-particle like behavior, and can be manipulated with very low electric currents. This makes them interesting for extreme low-power information technologies [2,3], where data is envisioned to be encoded in topological charges, instead of electronic charges as in conventional semiconducting devices. Recently, we demonstrated the ability of generating and stabilizing magnetic skyrmions at room temperature in Ta/CoFeB/TaOx trilayers, where the broken inversion symmetry gives rise to a net chiral exchange interaction [4,5]. Using spin Hall effects [6] from the Ta layer it is possible to efficiently move these skyrmions with electric currents. Theoretically it is expected that the motion of the skyrmions have a significant transverse component, the skyrmion Hall effect, which is directly related to the topological charge resulting in a net gyrotropic force. Here we demonstrate the direct observation of this transverse motion [7] using magneto-optic Kerr effect imaging. We observe that the skyrmion Hall angle varies continuously from zero just above the depinning threshold until 15º for current densities up to 107 A/cm2. This gradual variation of the skyrmion Hall angle indicates the changing competition between pinning and gyrotropic forces as the skyrmion motion transitions from the creep to the flow regime. The maximum observed Hall angle is in good agreement with theoretical expectations.

This work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Lithographic patterning was carried out at the Center for Nanoscale Materials, which is supported by DOE, Office of Science, BES (#DE-AC02-06CH11357).

References

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9:20am **MI+2D+AC-MoM4 Microscopic Magnetic Structures in Dy/Y Superlattices Measured by Polarized Neutron Reflectometry with Off-specular Scattering***,* ***Gary Mankey****, J. Yu, P. LeClair,* University of Alabama*; R. Fishman, J.L. Robertson, H. Ambaye, V. Lauter, H. Lauter,* Oak Ridge National Laboratory

Epitaxial Dy/Y superlattices with vertically-oriented c-axes, nanometer-scale layer thicknesses and 8-80 repeats were fabricated by magnetron sputtering on a-sapphire substrates with Nb buffer layers. The samples are designed to study how helical magnetic structures in Dy are modified by coupling through non-magnetic Y layers. X-ray characterization was used to evaluate the crystallographic orientations and interface widths of the superlattices. The macroscopic magnetic properties were characterized by low-temperature magnetometery that shows cooling in a 1 T in-plane field results in significant ferromagnetically-aligned moments below magnetic transition temperatures of approximately 150 K. The microscopic magnetic structures were investigated by polarized neutron reflectometry with off-specular scattering (PNROS) with variable magnetic fields in a temperature range from 300K down to 5K. PNROS confirms the magnetic transition and shows how the microscopic magnetic structures of the multilayered samples change with temperature. The ordering of the helical modulation is sensitive to the interfacial roughness of the multilayers as well as the magnetic and temperature history of the samples. The turn angles of the helical magnetic moment can be extracted from fitting the data. When the samples are cooled from room temperature to 5 K in a 10 mT in-plane applied magnetic field, the helical magnetic structures appear to decompose into lateral domains of opposite chirality, as evidenced by strong off-specular Bragg sheets. The Bragg sheets originate from the magnetic peaks associated with the helical magnetic ordering. The strength of the scattering from these sheets varies from sample to sample, suggesting that some samples may have a preferred chirality, due to differences in the microscopic film structure.

The authors gratefully acknowledge financial support from DOE award DE-FG02-08ER46499. A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

9:40am **MI+2D+AC-MoM5 Chirality Effects in Rare Earth based Thin Films and Multilayers***,* ***Dieter Lott,*** Helmholtz Zentrum Geesthacht, Germany*; K. Chen,* Universität Köln, Germany*; V. Tarnavich,* Petersburg Nuclear Physics Institute, Russian Federation **INVITED**

Films consisting of rare-earth elements became recently in the focus of attention due there rich variety of magnetic effects owed to the complex interplay between their spin and orbital magnetic moments. On the search of novel types of magnetic sensors and other spintronic devices they offer a path for creating complex magnetic spin structures that have the potential for being used in future applications in the field of information technology. In this presentation the focus is on the phenomena of magnetic chirality that was lately found in Rare-Earth multilayers. In the first part the chirality effects will be discussed for Dy/Y and Ho/Y multilayer where the symmetry of left- and right handed helical spirals formed by the RKKY interaction can be broken by the application of a magnetic field leading to a chiral state [1-3]. Here, different theoretical models are applied to explain the observed phenomena and will be discussed here. In the second part it will be shown how chirality in a thin film system consisting of alloys of rare-earth elements and 3d transition metals may be utilized for creating an exchange bias effect that differs fundamental from the one formed by conventional antiferromagnetic/ferromagnetic film systems. Furthermore, an outlook on the highly promising rare-earth elements / 3d transition metals alloys will be given [4]. For the exploration of the chirality effects in the here given examples, the application of polarized neutrons were essential enabling one to identify the magnetic states of the samples and the investigation of the intriguing phenomena of chirality.

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10:40am **MI+2D+AC-MoM8 Is the High Tc Superconductivity in Cuprates an Interface Problem?***,* ***Qi-Kun Xue,*** Tsinghua University, China **INVITED**

We investigate the pairing mechanism of high Tc superconductivity in cuprates by using state-of-the-art molecular beam epitaxy (MBE)-scanning tunneling microscopy (STM) in ultra-high vacuum conditions. By two different approaches in sample preparation, namely Ar$^+$ ion bombardment and ozone-assisted MBE growth, we are able to study the gap structure of superconducting copper oxide planes in unprecedented way. We show that the Cooper pairing in cuprates is rather conventional and the unique interfacial structure plays a crucial role in the high temperature superconductivity.

11:20am **MI+2D+AC-MoM10 How to do Depth-Dependent Measurements on Magnetic or Magnetoelectric Thin Films***,* ***Mikel Holcomb,*** *R. Trappen, J. Zhou, C-Y. Huang, G. Cabrera,* West Virginia University*; S. Dong,* Southeast University*; Y-H. Chu,* National Chiao Tung University, Taiwan

Analysis of depth-dependent measurements can provide useful information on how material properties change near surfaces or interfaces with other materials. For example, this deviation commonly occurs in magnetic thin films and the variation of these properties can strongly influence how different materials couple with one another. We have recently utilized a combined approach of bulk and surface sensitive x-ray absorption techniques to nondestructively map out depth-dependent atomic valence and magnetization across magnetic $La_{0.7}Sr_{0.3}MnO_3$ and magnetoelectric $La_{0.7}Sr_{0.3}MnO_3/PbZr_{0.2}Ti_{0.8}O_3$ thin films. We have combined measurements on multiple sample thicknesses with theoretical approaches to map out the layer-by-layer atomic valences and how they vary with film thickness. Such efforts may play a critical role in understanding how to build future generations of devices that rely on enhanced surface and interface properties.

11:40am **MI+2D+AC-MoM11 Nano-Pico-Mikro - Dynamic Soft X-ray Microscopy of Magnetic Materials with High Sensitivity*, Hendrik Ohldag,*** SLAC National Accelerator Laboratory

Understanding magnetic properties at ultrafast timescales is crucial for the development of new magnetic devices. Such devices will employ the spin torque or spin Hall effect, whose manifestation at the nanoscale is not yet sufficiently understood, The samples of interest are often thin film magnetic multilayers with thicknesses in the range of a atomic layers. This fact alone presents a sensitivity challenge in STXM microscopy, which is more suited toward studying thicker samples. In addition the relevant time scale is of the order of 10 ps, which is well below the typical x-ray pulse length of 50 – 100 ps. The SSRL STXM is equipped with a single photon counting electronics that effectively allows using a double lock-in detection at 476MHz (the x-ray pulse frequency) and 1.28MHz (the synchrotron revelation frequency). The pulsed or continuous sample excitation source is synchronized with the synchrotron source with a few picosecond drift over 24 hours.

In the first year of operation the excellent spatial resolution, temporal stability and sensitivity of the detection electronics of this microscope has enabled researchers to acquire time resolved images of standing as well as traveling spin waves in a spin torque oscillator in real space as well as detect the real time spin accumulation in a non-metal in contact with a ferromagnet.

2D Materials Focus Topic
Room 103B - Session 2D+MI-MoA
Dopants, Defects and Interfaces in 2D Materials

Moderators: Philip Hofmann, Aarhus University, Denmark, Adina Lucian-Mayer, University of Ottawa, Canada

1:40pm **2D+MI-MoA1 High-k Dielectrics on WSe_2 by Ozone-based Atomic Layer Deposition: An In-situ XPS Study*, Angelica Azcatl,*** *R.M. Wallace,* The University of Texas at Dallas

Two-dimensional tungsten diselenide (WSe_2) is a layered material that have shown a promising performance when implemented in field effect transistors, exhibiting a hole mobility up to 250 cm^2/V·s. [1] Furthermore, WSe_2 possess hole and electron effective masses smaller than those of MoS_2, another widely studied transition metal dichalcogenide, making WSe_2 a promising candidate channel material for tunnel field effect transistor applications (TFETs). For the realization of WSe_2 based TFETs, a high quality ultra-thin high-k dielectric film is a key requirement. However, the integration of high-k dielectrics by a conventional atomic layer deposition (ALD) process results challenging due to the dearth of nucleation sites at the WSe_2 surfaces. Previous studies have shown that the deposition of high-k dielectrics by water-based ALD on WSe_2 leads to non-uniform dielectric films. [2]

In this work, we explore the use of an alternative ALD approach to obtain uniform dielectric films on WSe_2 through the use of ozone as oxidant precursor. The surface chemistry of WSe_2 upon ozone exposure was studied by in-situ X-ray photoelectron spectroscopy to understand the reactivity between ozone and the WSe_2 surface. Then, the ozone-based ALD process was studied for the deposition of Al_2O_3 and HfO_2 on WSe_2. It was found that the interfacial chemistry and the nucleation of the dielectric have a dependence on the deposition temperature. Based on these results, a temperature window was identified at which interfacial oxide formation is avoided while a uniform dielectric film is obtained. Furthermore, the differences in reactivity and growth rate between HfO_2 and Al2O$_3$ will be discussed. This study helps to elucidate the reaction mechanism of the ozone based ALD process on WSe_2 and facilitates the implementation of the ozone based ALD approach to obtain uniform and thin dielectric films on WSe_2 for TFETs applications.

This work is supported in part the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST.

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2:00pm **2D+MI-MoA2 A Two-step Atomic Layer Etching on MoS_2 Realized by Remote O_2 Plasma*, Hui Zhu,*** *X. Qin, L. Cheng, A. Azcatl, J. Kim, R.M. Wallace,* University of Texas at Dallas

Molybdenum disulfide (MoS_2), a representative layered transition metal dichalcogenide, has obtained considerable research interest in recent years, due to its promising mechanical, electronic, and photonic properties.[1,2] The mechanical exfoliation of MoS_2 has led to an intensive research on thin film field-effect transistors made with MoS_2 flakes.[3,4] However, the scalable layer engineering of MoS_2 flakes is still a challenge for device fabrication. In this work, a novel MoS_2 functionalization and layer thinning process is presented by combining the surface oxidation of MoS_2 with a remote O_2 plasma to form an amorphous MoO_x layer and subsequent annealing to selectively desorb the MoO_x surface layer. Exfoliated MoS_2 is shown to chemically oxidize in a layered manner upon exposure to the remote O_2 plasma. X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and atomic force microscopy (AFM) are employed to characterize the surface chemistry, structure and topography of the oxidation process, and indicates that the oxidation mainly occurs on the topmost layer without altering the chemical composition of underlying layer. After the desorption of MoO_x by the annealing at 500 °C, a clean, flat and chemically undisturbed MoS_2 surface as evidenced from XPS, LEED, AFM and scanning tunneling microscopy (STM) characterization. This work renders promising atomic scale fabrication applications such as surface functionalization, charging engineering and atomic layer etching.

This work was supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA, and the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765.

Reference

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[4] S. Kim, A. Konar, W.-S. Hwang, J.H. Lee, J. Lee, J. Yang, C. Jung, H. Kim, J.-B. Yoo, J.-Y. Choi, Y.W. Jin, S.Y. Lee, D. Jena, W. Choi, and K. Kim, Nat. Commun. **3**, 1011 (2012).

2:20pm **2D+MI-MoA3 Engineering the Atomic Structure of 2D Transition Metal Dichalcogenides using Electron Beam: Experiments and Simulations*, Arkady Krasheninnikov,*** Helmholtz Zentrum Dresden-Rossendorf, Germany **INVITED**

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN sheets and transition metal dichalcogenides (TMD) were manufactured. Among them, TMD sheets have received particular attention, as these materials exhibit intriguing electronic and optical properties. Moreover, the properties can further be tuned by introduction of defects and impurities. Specifically, as many in-situ transmission electron microscopy experiments indicate, electron beam irradiation can give rise to phase transitions in 2D TMDs (e.g., from H to T phase), development of line defects and domains with mirror symmetry, and other structural transformations. In my talk, I will present the results [1] of our first-principles theoretical studies of the response of 2D TMDs to electron irradiation, and dwell on the characteristics of irradiation-induced defects, their evolution and agglomeration. I will also touch upon beam-mediated phase transitions in 2D TMDs. The theoretical results to be presented were obtained in close collaboration with several experimental groups, so that a detailed comparison of the theoretical data and experimental results will be given. Finally, I will further discuss defect- and impurity-mediated engineering of the electronic structure of 2D TMDs.

[1] Nature Comm. 6 (2015) 6736; ACS Nano 9 (2015) 3274; ACS Nano (2015) ACS Nano 9 (2015) 11249; Phys. Rev. B 91 (2015) 125304; Adv. Mater. 26 (2014) 2857; Phys. Rev. X 4 (2014) 031044; see http://users.aalto.fi/~ark/publist.html for complete list of publications.

3:00pm **2D+MI-MoA5 New Computational Tool for Electron Localization: Application to Low-dimensional Monolayers of h-BN and MoS_2*, Chinedu Ekuma,*** NRC/NRL Postdoctoral Fellow*; V. Dobrosavljevic,* Florida State University*; D. Gunlycke,* Naval Research Laboratory

Low-dimensional monolayer materials such as graphene, MoS2, and hexagonal BN (h-BN) exhibit electronic degrees of freedom that produce exotic properties, which can be fine-tuned to engineer new functionalities for diverse applications. However, the performance of device applications depends strongly on the defect morphology and the quality of the sample. Herein, we explore the role of vacancy and/or Hubbard-type interactions for a spin-1/2 system in monolayer MoS2 and h-BN. We utilize a first-principles many-body typical medium dynamical cluster formalism, which is an effective medium approach with an intrinsic order parameter for characterizing disordered and/or interacting electron systems even in the regime of insulator-metal quantum transition (IMQT). The focus is mainly on the distribution of the local density of states, which is a key fingerprint of the optoelectronic properties of disordered systems. Within our formalism, we predict an IMQT in both systems and show that IMQT in h-BN is due to a combination of electron interactions and defects. A sulfur vacancy concentration as low as 0.01% in MoS2 is shown to lead to an IMQT in agreement with experiments.

3:20pm **2D+MI-MoA6 Effects of helium-ion beam irradiation on opto-electrical properties of multi-layers WSe2*, Anna Hoffman,*** *P.R. Pudasaini, M.G. Stanford, P.D. Rack, D.G. Mandrus, N. Cross, J.H. Noh, M. Koehler, G. Duscher,* The University of Tennessee Knoxville*; A. Belianinov, A.J. Rondinone,* Oak Ridge National Laboratory*; I. Ivanov, T.Z. Ward,* Oak Ridge National Lab

Transition metal dichalcogenides (TMD) possess interesting properties that render them attractive for opto-electronic applications. Tuning optical and electrical properties of mono and few layer TMDs, such as tungsten diselenide (WSe_2), by inducing defects is an intriguing opportunity to fabricate the next generation opto-electronic devices. Here we report the effects of helium ion beam irradiation on optical and electrical properties of few layer WSe_2. By controlling the ion dose irradiation**,** we can tune the concentration of point defects present on few layer WSe_2, thereby locally tuning the electrical resistivity of the material. Semiconductor-insulator-metal like transitions have been observed with exposure to increasing helium ion beam dose, resulting in more than a seven order change in electrical resistivity. Furthermore, by selectively exposing the ion beams at the metal-WSe_2 contact area, we demonstrate reduced contact resistance of the described device, thereby reducing the Schottky barrier height. This could be particularly interesting for single layer TMD devices as the Schottky contacts, formed at metal/semiconductor interfaces, have a huge influence on the TMD device's performance.

4:00pm **2D+MI-MoA8 CO_2 Adsorption Kinetics on Nitrogen Doped Graphene and Graphite***,* ***Takahiro Kondo****, R. Shibuya, D. Guo, J. Nakamura,* University of Tsukuba, Japan

Nitrogen doped carbon materials are known to have CO_2 adsorption property at room temperature under atmospheric pressure. Recently, we have clarified that the CO_2 adsorption property is created by the one of the specific type of nitrogen dopants, pyridinic-N, which has two N-C bonds based on the temperature programmed desorption (TPD) measurements of CO_2 from nitrogen-doped graphene nanosheets (N-GNS) and nitrogen-doped model graphite (N-HOPG) catalysts [1]. According to our scanning tunneling microscopy and spectroscopy (STM/STS) measurements of N-HOPG, the CO_2 adsorption sites are suggested as the carbon atoms next to the pyridinic-N, where the distinct localized states are formed at near the Fermi level in the occupied region as non-bonding p_z orbital of carbon which plays a role of Lewis base site [2]. Furthermore, based on the X-ray photoelectron/absorption spectroscopy, we found that the adsorbed CO_2 is lying flat on the N-HOPG surface [3]. In this work, we reports the kinetics of CO_2 adsorption on both N-GNS and N-HOPG. From the measurements of CO_2-TPD, the desorption temperatures of CO_2 have been found to be 373 K in both N-GNS and N-HOPG, indicating that the same Lewis base sites are formed on N-GNS and N-HOPG. The adsorption energy can be roughly estimated as 100 kJ/mol from the desorption temperature. The relatively small adsorption energy can be attributed to the larger activation barrier and/or small pre-exponential (frequency) factor for CO_2 adsorption. The adsorption probability of CO_2 at 300 K has been estimated to be as 1/100 for N-HOPG. The detail kinetics as well as the selectivity for the CO_2 adsorption among many type of mixture gas will be presented.

[1] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science 351 (2016) 361.

[2] T. Kondo, S. Casolo, J. Nakamura et al., Phys. Rev. B 86 (2012) 035436.

[3] H. Kiuchi, R. Shibuya, T. Kondo, J. Nakamura,et al.,Nano. Res. Lett. 11 (2016) 127.

4:20pm **2D+MI-MoA9 Electronic Structure of Metallic Twin Grain Boundaries in Monolayer $MoSe_2$***,* ***Matthias Batzill****,* University of South Florida

Monolayers of $MoSe_2$ grown by molecular beam epitaxy on van der Waals substrates (HOPG or MoS_2), may exhibit twin grain boundaries. These Se-deficient line defects have been predicted by DFT to be metallic with dispersing bands. We examine their structural and electronic properties by scanning tunneling microscopy (STM) and angle resolved photoemission spectroscopy (ARPES). A dispersing parabolic band is observed that intersects the Fermi-level indicating the metallic property of this defect. Below 235 K the line defect undergoes a Peierls, or charge density wave (CDW), transition. STM indicates a periodicity of 3 lattice constants of the CDW consistent with the Fermi-wavevector determined in ARPES. In addition, we determine that the defect behaves like an ideal one-dimensional metal. More specifically we show evidence of Tomonaga Luttinger liquid suppression of the density of states at the Fermi-level and the splitting of the band in a 'spinon' and 'holon' band, also known as spin-charge separation.

Magnetic Interfaces and Nanostructures
Room 101C - Session MI+2D+AC-MoA

Magnetism and Spin Orbit Effects at Interfaces and Surfaces: Recent Experimental and Theoretical Advances

Moderator: Valeria Lauter, Oak Ridge National Laboratory

1:40pm **MI+2D+AC-MoA1 $Bi_{-1}Te_1$: A New Dual Topological Insulator***,* ***Lukasz Plucinski****, M. Eschbach, M. Lanius, C. Niu, E. Mlynczak, P. Gospodaric,* FZ Jülich GmbH, Germany*; J. Kellner,* RWTH Aachen University, Germany*; P. Schüffelgen, M. Gehlmann, S. Döring, E. Neumann, M. Luysberg, B. Holländer, G. Mussler,* FZ Jülich GmbH, Germany*; M. Morgenstern,* RWTH Aachen University, Germany*; D. Grützmacher, G. Bihlmayer, S. Blügel, Schneider,* FZ Jülich GmbH, Germany

We present, a combined theoretical and experimental study on the prediction and verification of the dual topological insulating character of the stoichiometric natural superlattice phase $Bi_1Te_1 = [Bi_2]_1[Bi_2Te_3]_2$ [1]. We identify Bi_1Te_1 by density functional theory to exhibit a non-trivial time-reversal symmetry-driven character of $Z_2 = (0; 001)$ and additionally a mirror-symmetry induced mirror Chern number of $v_{M-} = -2$, which indicates that Bi_1Te_1 is both a weak topological insulator (WTI) and a topological crystalline insulator (TCI). The coexistence of the two phenomena preordain distinct crystal planes to host topological surface states that are protected by the respective symmetries. From the analysis of time-reversal invariant momenta (TRIM-points) the surface perpendicular to the stacking direction, for instance, is found as the time-reversal symmetry *dark* surface, while hosting mirror-symmetry protected non-TRIM surface states along the surface-Gamma-M direction. We confirm the stacking sequence of our MBE-grown Bi_1Te_1 thin films by X-ray diffraction and transmission electron microscopy (STEM), and find clear indications of the TCI and WTI character in the surface electronic spin structure by spin- and angle-resolved photoemission spectroscopy.

[1] M. Eschbach et al., arXiv:1604.08886 (2016).

2:00pm **MI+2D+AC-MoA2 Spin-Polarized Scanning Tunneling Microscopy of a Two-Dimensional Ferromagnetic Semiconductor at Room-Temperature***,* ***Yingqiao Ma****, A.R. Smith,* Ohio University*; A. Barral, V. Ferrari,* Centro At´omico Constituyentes, GIyA, CNEA, Argentina

Ferromagnetic semiconductors are very promising materials for the spintronic applications, as they are good spin-polarized carrier sources and easy to be integrated into semiconductor devices. The search for ferromagnetic semiconductors with Curie temperature above the room-temperature has been a long-standing goal, since the Curie temperature *Tc* of most ferromagnetic semiconductors are at the cryogenic level with little possibility of improvement, which hinders their future practical spintronic applications.

Here, we observed the ferromagnetic domain structure at room-temperature on a GaN-based two-dimensional MnGaN semiconducting surface alloy, using spin-polarized scanning tunneling microscopy/spectroscopy which is sensitive to the surface magnetic nanostructures and can completely rule out the extrinsic origin of the ferromagnetism such as magnetic elements segregation by its ultimate spatial resolution. In contrast to the randomly doped dilute magnetic semiconductors, the two-dimensional surface structure has a unique and well-ordered hexagonal-like Mn √3 x √3 - R30° symmetry. The total density of states of the Mn √3 x √3 - R30° structure calculated by the density functional theory agree well with our normalized differential tunneling *dI/dV* spectroscopy, which clearly reveal the spin-polarized and spin-split Mn surface density of states peaks and prove the semiconducting nature of the surface as the normalized *dI/dV* goes to zero at the Fermi level. By applying a small magnetic field to the sample, the magnetic hysteresis is mapped out, which further proves its ferromagnetic nature. In conclusion, we demonstrated the room-temperature ferromagnetic nature of the two-dimensional Mn √3 x √3 - R30° structure, which makes it a promising material for future realistic magnetic storage, field-controlled, and quantum computing nano spintronic devices.

2:20pm **MI+2D+AC-MoA3 Spin-Orbit Induced Surface States of Rashba Systems and Topological Insulators***,* ***Peter Krüger****, T. Förster, M. Rohlfing, P. Eickholt, A.B. Schmidt, M. Donath,* Westfälische Wilhelms-Universität Münster, Germany **INVITED**

The generation of spin-polarized electrons on the basis of spin-orbit coupling at the surfaces of nonmagnetic solids has attracted considerable interest in recent years. Adlayers of heavy atoms, in particular, give rise to an interesting physics of spin-split surface states going far beyond the simple Rashba model. However, only very few studies have been reported that address unoccupied states of these systems, despite their relevance for potential applications. In the first part of this contribution, we present results from ab-initio calculations as well as spin- and angle-resolved inverse photoemission (IPE) for systems showing empty bands with a giant spin splitting and a unique structure of the spin polarization. For Tl/Si(111) and Tl/Ge(111), we identify spin-split states whose polarization vector rotates from the Rashba direction to an out-of-plane polarization when going from Gamma to K. Surprisingly, the spin splitting of the bands on Tl/Ge(111) is much smaller than on Tl/Si(111) despite the stronger surface localization and the heavier substrate. Our detailed analysis of the electronic structure shows that a remarkable interplay between spin-orbit coupling and hybridization is responsible for this unexpected result. Furthermore, we notice a distinct spin asymmetry in the intensity of the measured spectra at M, a time-invariant k-point. Our simulations of the IPE process unravel this puzzling behavior.

In the case of topological insulators, spin-orbit coupling gives rise to topologically protected surface states. We identify problems of the widely used density-functional theory (DFT) with a proper description of these states and demonstrate that they can be overcome by employing the GW self-energy operator within ab initio many-body perturbation theory. In particular we have investigated thin films of Bi2Se3, Bi2Te3, and Sb2Te3 with thicknesses from one to six quintuple layers. The quasiparticle band structures show highly improved agreement with experiments compared to DFT. In addition to a correction of the band gaps, the energetic positions and dispersions of the surface states change significantly around the Dirac point. As the wave functions are updated in our approach, the two-dimensional topological phases (quantum spin Hall or trivial) in GW can be different from the DFT result. We find the nontrivial quantum spin Hall phase, together with a sizable band gap 0.13 eV for a Bi2Te3 slab of 2 QL thickness.

[1] P. Eickholt et al., Phys. Rev. B 93, 085412 (2016)

[2] T. Förster et al., Phy. Rev. B 92, 291404 (R) (2015)

3:00pm **MI+2D+AC-MoA5 Spin-Resolved Momentum Microscopy of Strongly Correlated Electron Systems and Topological Insulators*, Christian Tusche,*** Forschungszentrum Jülich, Germany **INVITED**

One of the fundamental concepts in solid state physics is the description of the degrees of freedom of the electrons in the solid by the relation of the energy E vs. the crystal momentum k in a band structure of quasi particles. Of particular importance is the spin of the electron that leads to phenomena like ferromagnetism, spin-polarized surface- and interface-states, and recently, the discovery of new material classes like topological insulators. The latter attracted wide interest by the unusual relations of electron-spin and -momentum. In addition, strong spin-orbit coupling also leads to a rich band-structure of highly polarized states beyond the well known "Dirac cone" surface state. A direct conclusion on the ground state polarization in these systems is rather complicated by the peculiar interplay between spin- and light-polarization, as directly observed in spin-resolved photoemission maps over the full surface Brillouin zone .

On the experimental side, the novel concept of momentum microscopy evolved to provide an intuitive and comprehensive insight to these band structures. A momentum microscope captures the complete 2π solid angle of emitted photoelectrons into a high resolution image of electronic states in reciprocal space [1]. With the introduction of imaging spin analyzers, the efficiency of spin-resolved measurements experienced a tremendous boost [2]. Together with modern synchrotron radiation sources, delivering photon energies from UV to soft X-rays as well as a flexible timing structure, the electron spin now becomes routinely accessible in photoemission experiments. In particular, new developments like time-of-flight momentum microscopy now provide comprehensive three-dimensional data sets of the complete valence band region within a single measurement [3]. Here, we discuss examples and prospects of spin resolved momentum microscopy, ranging from tomographic imaging of the spin-resolved Fermi surface of ferromagnets to the rapid band-structure mapping of novel materials.

[1] C. Tusche, A. Krasyuk, J. Kirschner: Ultramicroscopy 159, p. 520 (2015),

[2] C. Tusche, M. Ellguth, A. A. Ünal, C.-T. Chiang, A. Winkelmann, A. Krasyuk, M. Hahn, G. Schönhense, J. Kirschner: Appl. Phys. Lett. 99, 032505 (2011)

[3] C. Tusche, P. Goslawski, D. Kutnyakhov, M. Ellguth, K. Medjanik, H. J. Elmers, S. Chernov, R. Wallauer, D. Engel, A. Jankowiak, G. Schönhense: Appl. Phys. Lett., in press (2016)

4:00pm **MI+2D+AC-MoA8 Spin-orbit-Induced Effects in the Electronic Structure of W(110) and Ta(110): Similarities and Differences*, Markus Donath,*** *K. Miyamoto, H. Wortelen, B. Engelkamp,* Muenster University, Germany*; H. Mirhosseini,* Max Planck Institute for Microstructure Physics, Germany*; T. Okuda,* Hiroshima Synchrotron Radiation Center, Japan*; A. Kimura,* Hiroshima University, Japan*; A.B. Schmidt,* Muenster University, Germany*; J. Henk,* Martin Luther University Halle-Wittenberg, Germany

Tungsten and tantalum are direct neighbors in the periodic table and exhibit, at first glance, a very similar electronic structure. Only the bands of tantalum are less occupied due to the lack of one electron. For W(110), an exceptional surface state was discovered [1]: Resembling a topological surface state (TSS), it exhibits a linear dispersion with a helical spin texture in reciprocal space, often called Dirac-cone-like behavior. Interestingly and again reminiscent of the TSS behavior, photoemission calculations predict a spin reversal upon changing the light polarization used for excitation from *p* to *s* [2]. We verified this orbital-symmetry-selective spin texture by spin-resolved photoemission [3]. This result unveils, in which way spin-orbit interaction entangles spin and orbital degrees of freedom. “Spin control” is not restricted to topological insulators but a much more general phenomenon.

A surface state, similar to the Dirac-cone-like state on W(110), may be expected for Ta(110), yet above the Fermi level. Surprisingly, our spin-resolved inverse-photoemission results do not show this state. Instead, spin-polarized unoccupied surface bands [4] and an occupied d_{z^2}surface state with Rashba-like spin texture [5] were identified, which have no equivalents on W(110). These findings are explained by subtle differences in the energetic positions of the surface states relative to the bulk states for W(110) and Ta(110), which critically depend on the values for the lattice constant and the surface relaxation.

[1] K. Miyamoto *et al.*, Phys. Rev. Lett. **108**, 066808 (2012); Phys. Rev. B **86**, 161411(R) (2012); J. Electron Spectrosc. Relat. Phenom. **201**, 53 (2015).

[2] H. Mirhosseini *et al.*, New J. Phys. **15**, 033019 (2013).

[3] K. Miyamoto *et al.*, Phys. Rev. B **93**, 161403(R) (2016).

[4] B. Engelkamp *et al.*, Phys. Rev B **92**, 085401 (2015).

[5] H. Wortelen *et al.*, Phys. Rev. B **92**, 161408(R) (2015).

4:20pm **MI+2D+AC-MoA9 Formation of a 2D Interface by Low Energy Proton Implantation in ZnO Microwires*, Israel Lorite,*** *Y. Kumar,* Universität Leipzig, Germany*; B. Straube, S. Perez,* Universidad Nacional de Tucumán, Argentina*; C. Rodriguez,* Universidad Nacional de La Plata, Argentina*; P. Esquinazi,* Universität Leipzig, Germany

Recently we showed the possibility of obtaining room temperature magnetic order by implanting protons (H+) at low energies (300 V) into Li-doped ZnO microwires [1]. The low energy implantation is enough to produce Zn vacancies (V_{Zn}) within 10 nm from the surface, without creating too much disorder in the ZnO lattice. The formation of a stable density of defects in the 10 nm depth region is possible since Li doping reduces the energy of stabilization of V_{Zn}. Thus, the concentration of V_{Zn} will be approximately the one of the Li doping. Along with the observation of magnetic order at room temperature, the ZnO microwires present an anomalous temperature dependence of the negative magnetoresistance. Such a behavior can be related to the formation of an interface at the boundary between the magnetic and non-magnetic structure produced by the implantation. In this contribution we show the observation of a photo-galvanic effect related to the Rashba effect. This effect is due to the formation of a 2D electron gas at the interface of the magnetic/non-magnetic structure. In addition, an increase of this effect is observed by the application of a small external magnetic field, related to the existence of a 10 nm magnetic region produced during the proton irradiation.

[1] I.Lorite, et al; Advances in methods to obtain and characterize room temperature magnetic, Appl. Phys. Lett. 106, 082406 (2015)

4:40pm **MI+2D+AC-MoA10 Density Functional Studies of Magnetic and Spintronic Materials, *Ruqian Wu,*** University of California Irvine **INVITED**

Magnetism, one of the oldest branches of physics, is having its renaissance in recent years due to the interest in developing various nanomagnets, molecular magnets and magnetic nanojunctions for the development of innovative devices. Magnetization of surfaces and nanostructures is sensitive to the change of environment and hence the availability of ultrahigh vacuum is crucial for the exploration of various magnetic systems. Equally important is the rapid advance of density functional theory (DFT) approaches, which now can reliably predict large amount physical properties of real materials in either their ground states or excited states. In this talk, I will discuss several our recent theoretical progresses in spin-related physics, including 1) the search for giant magnetic anisotropy energy in nanostructures; 2) the design to imprint large spin orbit coupling into graphene and other two-dimensional materials for the realization of quantum spin Hall effect and quantum anomalous Hall effect; 3) the photo-spin-voltaic effect; and 4) the generation of spin-polarized two-dimensional electron gas at oxide interfaces. Most of our DFT studies are performed in close collaboration with experimental groups so some experimental results will also be discussed.

Work at UCI was supported by DOE-BES (Grant No. DE-FG02-05ER46237) and NERSC.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+2D+AS+NS+SS-MoA

Probing Topological States And Superconductivity

Moderators: An-Ping Li, Oak Ridge National Laboratory, Chuanxu Ma, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Tuning Dirac States by Strain in Topological Insulators*, Lian Li,*** University of Wisconsin-Milwaukee **INVITED**

Topological insulators (TIs) are distinguished by their metallic boundary states populated by massless Dirac fermions and bulk topological Z_2 index. Changes in the band topology induced by external variables such as strain, electrical field, and composition thus provide a means to tune the boundary states. As a large spin-orbit coupling is necessary to produce an inverted band gap, most TIs discovered to date are narrow gap semiconductors consisting of heavy elements. These materials typically exhibit layered crystal structure with anisotropic bonding characteristic: strong covalent bonding in-plane and weak van der Waals (vdW) bonding out-of-plane, which has been predicted to facilitate effective strain engineering of their bulk band topology.

In this talk, I will first give an overview of the opportunities and challenges in the epitaxial growth of layered TIs. Using the prototypical 3D TI Bi_2Se_3 as an example, I will show that the characteristic anisotropic bonding facilitates a spiral growth mode on virtually any substrates by molecular beam epitaxy. The coalescence of these spirals results in a high density of grain boundaries that consist of alternating edge dislocation pairs, leading to periodic in-plane stretching and compression. Using scanning tunneling spectroscopy, I will show that this local strain field strongly modifies the Dirac surface states, where in-plane compression expands the vdW gap and destroys the Dirac states.

Next, I will show our recent work on the strain engineering of Dirac edge states of epitaxial Bi bilayer films grown on three different substrates: the (111) surface of 3D TIs Bi_2Se_3, Sb_2Te_3, and Bi_2Te_3. Using scanning tunneling microscopy/spectroscopy, I will show that for moderately strained (<6%) single Bi bilayer on Sb_2Te_3 and Bi_2Te_3, edge states are observed; while on highly compressed single Bi bilayer on Bi_2Se_3 (>8%), edge states are suppressed. These findings, supported by density functional theory calculations, demonstrate the uniform control of edge states in 2D topological insulators by strain.

2:20pm **SP+2D+AS+NS+SS-MoA3 Detection of Current Induced Spin Polarization in Topological Insulators via Four-Probe Spectroscopy*, Saban Hus,*** Oak Ridge National Laboratory*; Y. Chen,* Purdue University*; A.-P. Li,* Oak Ridge National Laboratory

Charge currents carried by the nontrivial surface states of topological insulators (TIs) exhibit a net spin polarization due to spin-momentum locking. Electrical detection of such a spin polarization is crucial for technological applications. However, in 3D TI materials the existence of a bulk conduction channel makes it difficult to quantify the density and the spin polarization of the current carried by the surface states. Here we report in-situ, spin sensitive four-probe spectroscopy measurements on Bi_2Te_2Se single crystals. A ferromagnetic probe detects the net spin accumulation on the surface states while a set of four-probe spectroscopy measurement is used for a quantitative separation of 2D and 3D conduction. We also examine the effect of surface doping by residual gas molecules on the current induced spin polarization. Even though, the additional carriers by dopants enhance the 2D conductance in TIs they reduce the net spin polarization of current carried by topological surface states.

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

2:40pm **SP+2D+AS+NS+SS-MoA4 Switching Handedness of Chiral Solitons Under Z_4 Topology*, Tae-Hwan Kim,*** Pohang University of Science and Technology, Republic of Korea*; S. Cheon, H.W. Yeom,* Institute for Basic Science (IBS), Republic of Korea

Chirality is a ubiquitous and interesting property of asymmetry in many fields ranging from biology, chemistry to physics. Because of its topologically distinct nature, such chiral objects in condensed matter are often topologically excited states, which are protected by system's topology and can be used to carry information robustly against external perturbations. For instance, nanoscale magnetic skyrmions, spatially localized chiral spin texture with particle-like properties in ferromagnets, have been investigated intensively as topological information carriers for next generation spintronic devices. However, logic operations using topological excitations such as skyrmions are only conceptually proposed. On the other hand, chiral solitons are recently discovered as the topologically protected edge states of one-dimensional Z_4 topological insulators [1,2], which can be exploited as topological information carriers in electronic system. In this talk, I show experimentally and directly that switching between solitons with different chirality is possible by merging them with achiral solitons [3]. I will also show that this chiral switching corresponds to the realization of topological addition of the Z_4 topological number or chirality. With their distinct topologically protected chirality, chiral solitons could uniquely be applied for robust multilevel information storage and logic operation by storing, carrying, and switching three differently topological bits of information.

[1] T.-H. Kim and H. W. Yeom, Phys. Rev. Lett. **109**, 246802 (2012).

[2] S. Cheon, T.-H. Kim, S.-H. Lee, and H. W. Yeom, Science **350**, 182 (2015).

[3] T.-H. Kim, S. Cheon, and H. W. Yeom, submitted (2016).

3:00pm **SP+2D+AS+NS+SS-MoA5 Spectroscopic-imaging STM Studies on Dirac-Landau Levels in the Topological Surface State*, Tetsuo Hanaguri,*** RIKEN Center for Emergent Matter Science, Japan **INVITED**

We show that spectroscopic-imaging scanning tunneling microscopy (SI-STM) is a powerful tool to investigate unique electronic features of massless Dirac electrons in a magnetic field.

In contrast to the conventional massive electron that is described by a single-component wave function, the massless counterpart demands the two-component wave function. In the case of the surface state of topological insulators, these two components are associated with the spin degrees of freedom, thereby governing the magnetic properties. Thus, it is highly desirable for spintronics applications to elucidate where and how the two-component nature emerges. We found that the two-component nature manifests itself in the internal structures of Landau orbits. We visualized the local density-of-states (LDOS) distributions associated with the Landau orbits in the topological surface state of Bi_2Se_3 using SI-STM. In the presence of the potential variation, Landau orbits drift along the equipotential lines, forming ring-like patterns in the LDOS images. The observed internal structures of the rings are qualitatively different from those of conventional massive electrons but are well reproduced by the calculation based on a two-component model Dirac Hamiltonian. Our model further predicts non-trivial energy-dependent spin-magnetization textures around the potential minimum. This is originated from the interplay between the two components and may provide a clue to manipulate spins in the topological surface state.

In addition to the Landau orbits, we succeeded in observing the Zeeman shift of the lowest Landau level from which precise g factor of the massless Dirac electron can be estimated. We performed experiments on two topological insulators, Bi_2Se_3 and Sb_2Te_2Se, and determined the surface g factors of them to be 18 and -6, respectively. Such remarkable material dependence suggests that the Zeeman effect is tunable by controlling the chemical composition, providing a new knob in manipulating the spins in the topological surface state.

4:00pm **SP+2D+AS+NS+SS-MoA8 The Rashba and Quantum Size Effects in Ultrathin Bi films*, Toru Hirahara,*** Tokyo Institue of Technology, Japan **INVITED**

Precise characterization of physical properties in nanometer-scale materials is interesting not only in terms of low-dimensional physics but also in application to devices. Due to the reduced dimensionality and symmetry, these systems possess various interesting properties that cannot be found in the bulk. In this presentation, focusing on epitaxial ultrathin bismuth films formed on a silicon substrate, we introduce an intriguing interplay of the quantum size and Rashba effects in reciprocal space. Utilizing spin- and angle-resolved photoemission spectroscopy, we observed clear Rashba-split nature of the surface-state bands in these Bi films. However, the band dispersion did not follow the simple Rashba picture and the spin-splitting was lost where they overlapped with the bulk projection. From first-principles calculations, this was explained as a change in the nature of the band-splitting into an even-odd splitting induced by the quantum size effect [1]. Furthermore, we show that the interplay of the quantum size effect and the presence of the surface state induces a complicated change in the Fermi level position of the bulk states in bismuth, which is critical in discussing the surface-state contribution in the film properties [2,3].

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4:40pm **SP+2D+AS+NS+SS-MoA10 Understanding the Microscopic Effects of Annealing in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ Superconductor**, ***Qiang Zou***, *Z. Wu, Q. Zheng, S. Rajputł, D.S. Parker, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

By hole or electron doping of the parent iron-based BaFe$_2$As$_2$ compound, the high-transition temperature superconductivity emerges from the suppression of the antiferromagnetic order. [1] It was widely reported that thermal-annealing significantly improves some superconducting characteristics in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, including T_c [2] The microscopic origin of such effect is still an open question. To make a connection between the global and the microscopic behavior of the materials, we did a comparison measurement on the pair of well-characterized x, we call ' as-grown' vs 'annealed' Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ crystals, and using low temperature scanning tunneling microscopy and spectroscopy (STM/S). The superconducting gap maps deducted from the dI/dV maps were compared. The gap width distribution of the as-grown sample are obviously narrower than that of the annealed one. The coherent peak position also shifted to higher value for the annealed sample. The corresponding reduced-gaps of $2\Delta/k_bT_{c1}$ are about 2.3 and 5.4 for the as-grown and annealed crystals, respectively. The difference of the reduced-gaps indicates that the pairing strength of the annealed crystal is stronger than the as-grown one.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division . A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Reference

1. Stewart, G. R. (2011). "Superconductivity in iron compounds", *Reviews of Modern Physics*, *83*(4), 1589.

2. Gofryk, K., et al. "Effect of annealing on the specific heat of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$" *Physical Review B, 83(6), 064513*

5:00pm **SP+2D+AS+NS+SS-MoA11 Annealing Effect on the Properties of Superconducting Parent BaFe$_2$As$_2$ Crystal**, ***Shivani Rajput***, *Q. Zou, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

Understanding of electronic interactions in a parent phase of a superconducting crystal is crucial in determining the mechanism behind high Tc superconductivity. Bulk measurements show that annealing of parent BaFe$_2$As$_2$ crystal at 700 ^{0}C for 30 days causes a 5 K shift in magnetic transition temperature (T_N) compared to as grown crystal. To understand the effect of annealing and details of magnetic phase transition, we investigate as-grown and annealed BaFe$_2$As$_2$ crystals at atomic scale using a variable temperature scanning tunneling microscopy/ spectroscopy at various temperature points across T_N. Tunneling spectroscopy exhibit a ~ 0.53 eV gap type feature above T_N, while V-shape dI/dV spectra below T_N. The dI/dV mapping measurements show that as-grown BaFe$_2$As$_2$ crystals are electronically inhomogeneous, and averaging the differential conductance spectra over a large area does not truly represent the electronic properties of the sample at local scale, whereas annealed sample is comparatively electronically homogeneous.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

2D Materials Focus Topic
Room 103B - Session 2D+MI-TuM
Novel 2D Materials

Moderators: Daniel Gunlycke, Naval Research Laboratory, Yuanbo Zhang, Fudan University, China

8:00am **2D+MI-TuM1 Computational Design of 2D Materials and Layered Heterostructures for Opto-electronics***, Kristian Thygesen,* Technical University of Denmark **INVITED**

The class of 2D materials is rapidly expanding and now includes semiconductors, insulators, metals, and superconductors. Many of these novel materials exhibit unique properties that are easily tuneable due to their atomically thin nature making them potential candidates for applications in a large range of technological areas. In this talk I will give a general introduction to the electronic structure of 2D materials including the characteristic features of screening and collective excitations. Concrete illustrations will be given from the Computational 2D Materials Repository (1+2) which contains high-accuracy first-principles calculations for a large number of 2D materials. The 2D materials form the basis of a much larger class of materials consisting of vertically stacked 2D layers held together by weak van der Waals forces. I will describe challenges and opportunities for the first-principles modelling of van der Waals heterostructures including our multi-scale Quantum Classical Heterostructure (QEH) model (3) that enables accurate modelling of plasmons, excitons and band structures of general incommensurable heterostructures containing hundreds of layers. Examples of computational designed heterostructures will be given.

(1) Computational Materials Repository, https://cmr.fysik.dtu.dk/

(2) Computational 2D Materials Database: Electronic structure of transition metal dichalcogenides and oxides, F. A. Rasmussen and K. S. Thygesen, J. Phys. Chem. C 119, 13169 (2015)

(3) The Dielectric Genome of van der Waals Heterostructures, K. Andersen, S. Latini, and K. S. Thygesen, Nano Letters 15, 4616 (2015)

8:40am **2D+MI-TuM3 Mo_2Ga_2C: Structural Determination of a New Nanolaminated Carbide and its 2D Modification by Selective Etching***, **Chung-Chuan Lai**, R. Meshkian, M. Dahlqvist, J. Lu, L.-Å. Näslund,* Linköping University, Sweden*; O. Rivin, E.N. Caspi,* Nuclear Research Center-Negev, Israel*; O. Ozeri,* Nuclear Research Center-Soreq, Israel*; L. Hultman, P. Eklund,* Linköping University, Sweden*; M.W. Barsoum,* Drexel University*; J. Rosen,* Linköping University, Sweden

Studies of molybdenum carbides are motivated by, for example, the electric and the catalysis properties, including the recently predicted high Seebeck coefficient of 2D Mo_2C [1]. It has been reported that 2D transition metal carbides (also known as MXenes) can be made by selective etching of corresponding nanolaminated ternary carbides [2], e.g., $M_{n+1}AC_n$ phases where M is typically from group 4 – 6, A is from group 13 – 14, and n is 1 – 4 [3]. However, no suitable precursor has been available to make 2D Mo_2C until most recently, through the discovery of Mo_2Ga_2C [4]. Here, we determined the structure of Mo_2Ga_2C phase from X-ray and neutron diffraction, scanning transmission electron microscopy and X-ray photoelectron spectroscopy, and further validated the structure by ab initio calculations [5]. The structure of Mo_2Ga_2C can be described as Mo_2C layers interleaved by two Ga layers, standing head-to-head along the *c*-axis of the hexagonal lattice. The Mo_2Ga_2C phase is closely related to another known nanolaminated carbide, Mo_2GaC, in its crystal structures, evident from chemical bonding analysis. However, selective etching of Ga using hydrofluoric acid (HF) is easily attained for the new Mo_2Ga_2C phase, while being more challenging for Mo_2GaC. A reduction in Ga signal with subsequent exfoliation of Mo_2C layers upon etching is here presented for Mo_2Ga_2C, making Mo_2Ga_2C the first precursor for MXene synthesis based on A = Ga, and for MXene synthesis of 2D Mo_2C [6].

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9:00am **2D+MI-TuM4 Synthesis of Borophenes: Anisotropic, Two-Dimensional Boron Polymorphs***, **Andrew Mannix** [*] [†] , B. Kiraly,* Northwestern University/Argonne National Lab.*; J.D. Wood, M.C. Hersam,* Northwestern University*; N.P. Guisinger,* Argonne National Laboratory

As the lightest metalloid element, bulk boron exhibits great physical and chemical complexity. In contrast, atomic clusters of boron form simple planar and cage-like structures that resemble those of carbon. Theoretical studies suggest that nanostructured boron allotropes (e.g., nanotubes and sheets) should exhibit structures similar to atomic boron clusters. To date, however, boron nanostructures have been scarcely explored experimentally, partly due to difficulties in synthesis and the need for atomically pristine experimental conditions. Recently, we have reported the synthesis of two-dimensional boron sheets (i.e., borophenes) on a silver surface under ultra-high vacuum conditions [*Science***350,** 1513–1516 (2015)]. Atomic-scale scanning tunneling microscopy shows the growth of two distinct phases, both of which exhibit anisotropic, chain-like structures. We confirm that these sheets are planar, chemically distinct, and atomically thin through extensive ex situ characterization supported by first principles calculations. Furthermore, in situ scanning tunneling spectroscopy of the borophene sheets shows metallic characteristics consistent with theoretical predictions, in contrast to semiconducting bulk boron.

9:20am **2D+MI-TuM5 Atomic and Electronic Structures of Graphitic Carbon Nitride (g-C3N4) Monolayers on HOPG***, **Sangwoo Park**, HM. Kang,* Sungkyunkwan University, Republic of Korea*; J.H. Yang, J.H. Choy,* Ewha Womans University, Republic of Korea*; YJ. Song,* Sungkyunkwan University, Republic of Korea

In this work, we report atomic and electronic studies of graphitic carbon nitride (g-C3N4) monolayers on a highly-ordered pyrolytic graphite (HOPG) by using atomic force microscope (AFM), kelvin probe force microscope (KPFM) and low temperature scanning tunneling microscope (LT-STM). The g-C3N4 is the most stable allotrope of carbon-nitrides and a very promising candidate for metal-free coordination chemistry and heterogeneous catalyst. Also it is applicable photocatalytic hydrogen production and fuel cell. After successful spin-coating of the g-C3N4 monolayers on HOPG, we found the inter-molecular interactions between the flakes or the atomic registries of adsorption on the substrate. This coating mechanism and atomic/electronic properties of g-C3N4 on HOPG will be discussed in detail.

9:40am **2D+MI-TuM6 Periodic Array of Graphene Quantum Dots Embedded in a Carbon-Boron-Nitrogen Alloy***, **Jakob Jørgensen**,* Aarhus University, Denmark*; L. Camilli, A. Stoot,* Technical University of Denmark*; A. Cassidy, R. Balog,* Aarhus University, Denmark*; J. Sadowski,* Brookhaven National Laboratory*; P. Bøggild,* Technical University of Denmark*; L. Hornekær,* Aarhus University, Denmark

Two-dimensional (2D) materials have received enormous attention in the field of materials science and condensed matter physics in the last decade, with the ultimate goal being developing a new technology based on these materials [1]. A huge variety of promising 2D materials have been identified and the ability to combine these into complex structures is essential. For this reason the synthesis of 2D hetero-structures – i.e., structures resulting from the combination of two or more 2D materials – have been subject to an intense research effort over the last few years [2]. Here we report the first observation of spontaneous formation and self-assembly of graphene quantum dot superlattices embedded in a two-dimensional boron-carbon-nitrogen alloy.

By exposing a hot Ir(111) surface to carbon and boron-nitrogen precursor molecules it is found, using scanning tunnelling microscopy (STM), that the otherwise bulk-immiscible graphene and hexagonal boron nitride (hBN) materials can form a stress induced BCN alloy. Furthermore, pure-phase dislocations are found to co-exist with the alloy resulting in the bright triangular pattern of carbon enriched nanoribbons with a width of approximately 1 nm. Above a critical carbon concentration, an array of quantum dots (QD) of highly regular size and periodicity appears. Based on

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

[†] **National Student Award Finalist**

STM in combination with synchrotron x-ray photoemission spectroscopy (XPS) these QDs are determined consist of pure phase carbon, i.e. they are graphene QDs. These findings are consistent with well-established theories on elastic relaxations in ultrathin strained systems [3]. Thus our findings show a pathway to grow a highly periodic array of graphene quantum dots imbedded in a semiconducting BCN alloy.

In addition, using low energy electron microscopy (LEEM), the growth of the alloy structure is followed *in-situ* and diffraction experiments confirm the presence of the ordered quantum dot pattern even on a macroscopic level.

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11:00am **2D+MI-TuM10 Electric Field Control of 2D Materials with Electron Correlation*, Yoshi Iwasa,*** University of Tokyo, Japan **INVITED**

Scaling down materials to an atomic-layer level produces rich physical and chemical properties as exemplified in various two-dimensional (2D) crystals extending from graphene, transition metal dichalcogenidesto black phosphorous. These include Dirac physics, quantum Hall physics, and valleytronic functions, which are caused by the dramatic modification of electronic band structures, simply by thinning. In the case of transition metal dichalcogenides (TMDs), the band gap becomes direct in monolayers, and the broken inversion symmetry and the strong spin-orbit interaction causes peculiar valley-dependent spin polarization in zero-magnetic field [1], as well as peculiar opto-valleytronics [2, 3].

In reduced dimensions, on the other hand, the electron correlation effects and their consequence, electronic phase transitions, are also significantly changed from bulk systems, and thus result in new properties and functions. Here we address unique physical properties of correlated 2D electron system 1T-TaS$_2$, which was achieved simply by thinning. The ordering kinetics of the charge density wave transition was revealed to become extremely slow with reduction of thickness [4], resulting in an emergence of metastable states [5]. Furthermore, we realized the unprecedented memristive switching to multi-step non-volatile states by applying in-plane electric field.

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11:40am **2D+MI-TuM12 Graphene-based Hybrid Materials by Designer Interfaces for High-Performance Hybrid Supercapacitors*, Sanju Gupta,*** Western Kentucky University

Intense research in renewable energy is stimulated by global demand of electric energy. E lectrochemical energy storage and conversion systems namely, supercapacitors and batteries,represent the most efficient and environmentally benign technologies. Moreover, controlled nanoscaled architectures and surface chemistry of electrochemical electrode materials is enabling emergent next-generation devices approaching theoretical limit of energy and power densities and deliver electrical energy rapidly and efficiently. This talk will present our recent activities to advance design, development and deployment of composition, morphology and microstructure controlled graphene-base hybrid multilayer architectures with carbon nanotubes, conducting polymers, transition metal oxides and mesoproprous silicon wrapped with grapheme sheets as engineered electrochemical electrodes for supercapacitor cathodes and battery anodes. Experimental studies showed significant enhancement towards integrating graphene with other nanomaterials in terms of gravimetric specific capacitance, interfacial capacitance, charging-discharging rate and cyclability. We also present fundamental physical-chemical interfacial processes that govern the underlying mechanisms (surface ion adsorption versus redox reactions) in these electrodes revealed using scanning electrochemical microscopy. The findings are discussed from viewpoint of reinforcing the role played by heterogeneous ‘hybrid’ electrode surfaces composed of nanoscale graphene sheets (conducting) and other nanomaterials (semiconducting) via higher/lower probe current distribution maps. It allows us to determine ion transfer kinetics and diffusion constant, imaging electrochemical reactions and topography in a microscale at electrode/electrolyte interface.

12:00pm **2D+MI-TuM13 Realization of TaS$_2$ in the Single-Layer Limit*, Charlotte Sanders,*** *M. Dendzik,* Aarhus University, Denmark*; A.S. Ngankeu,* Aarhus University*; A. Eich,* Radboud University, Netherlands*; A. Bruix, J.A. Miwa, B. Hammer,* Aarhus University, Denmark*; A.A. Khajetoorians,* Radboud University, Netherlands*; P. Hofmann,* Aarhus University, Denmark

The electronic properties of bulk TaS$_2$ have long been a topic of significant interest, due to the fact that the material exhibits unusual charge density wave phases alongside Mott physics and superconductivity. However, little has been known about single-layer (SL) TaS$_2$. How the electronic properties of this material may change in the SL limit is of great interest, raising questions about the effects of quantum confinement and substrate interactions on exotic electronic states already seen in the bulk. Work on related materials that have been successfully fabricated as SLs points to complex consequences for the CDW and superconducting states. [1] In order to address this topic, one needs to be able to controllably fabricate high-quality, uniform samples with low defect densities for probing *in situ*. We have now succeeded in epitaxially growing high-quality SL TaS$_2$. We have characterized the SL with angle-resolved photoemission spectroscopy (ARPES), low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/S), and low-energy electron diffraction (LEED). Using the Au(111) substrate as a starting point, we find that the TaS$_2$ SL on Au(111) assumes a well-defined orientation with respect to the substrate, and a moiré superstructure; simultaneously, and counterintuitively, it adopts a “carpet flow” growth mode over substrate steps, suggesting weak interaction with the substrate. Comparing our measurements to calculations from density functional theory (DFT), we have determined that the SL assumes the trigonal prismatic (“1H”) phase. While the bulk parent material is characterized by a CDW transition temperature T_{CDW} = 75K [2], we do not observe either CDWs or superconductivity at temperatures down to 4.7K on Au(111) using STM/STS. We do, however, observe slight doping of the TaS$_2$ epilayer. While the absence of superconductivity at this temperature is not surprising, considering that the superconducting transition temperature T_C in the bulk is only 600mK [3], the absence of CDWs is of interest. This is particularly so in light of recent research on the closely related system SL-NbSe$_2$ on bilayer graphene: despite having a lower bulk CDW onset at T_{CDW} = 33K, NbSe$_2$ in the SL exhibits complete transition to the CDW state by T_{CDW} = 5K. [1]

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Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+2D+AC+AS+TF-TuM

Applications of Synchrotron-based Techniques to 2D Materials (8:00-10:00 am)/Complex Functional Materials and Heterostructures (11:00 am-12:20 pm)

Moderators: Nicholas Barrett, CEA Saclay, Giacomo Ceccone, European Commission, Joint Research Centre, IHCP, Italy

8:20am **SA+2D+AC+AS+TF-TuM2 A Versatile Method for the Fabrication of 2D-electron Systems at Functional Oxide Surfaces**, *T.C. Rödel,* Université Paris-Sud - SOLEIL, France*;* ***Patrick Le Fèvre,*** Synchrotron SOLEIL, France*; F. Fortuna, E. Frantzeskakis,* Université Paris-Sud - IN2P3, France*; F. Bertran,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France*; B. Mersey,* Université de Caen, France*; A.F. Santander-Syro,* Université Paris-Sud - IN2P3, France

A critical challenge of modern materials science is to tailor novel states of matter suitable for future applications beyond semiconductor technology. In this prospect, 2D electron systems (2DESs), analogous to those created in semiconductors heterostructures, have been observed at the LaAlO$_3$/SrTiO$_3$ interface [1] and show amazing physical properties like metal-to-insulator transitions, superconductivity or magnetism. It was then demonstrated that 2DES could also be stabilized at the surface of SrTiO$_3$ [2] or other oxides [3], although it requires the use of intense UV or X-ray synchrotron radiation to desorb oxygen from the surface and dope it with electrons. This opened the way for the use of surface sensitive techniques, like Angle-Resolved PhotoEmission spectroscopy (ARPES) which provided a clear description of the microscopic electronic structure of the quantum well states. However, 2DESs at oxygen-deficient surfaces can be only manipulated and studied in ultra-high vacuum (to preserve the O-vacancies from re-oxidation) and thus, are not suited for experiments or applications at ambient conditions. Here we demonstrate a new, versatile and cost-effective method to generate passivated 2DESs on large areas of UHV-prepared functional oxide surfaces. It consists in a simple evaporation at room temperature of an aluminum film onto the oxide surface. Aluminum acts as a reducing agent and pumps oxygen from the substrate. It oxidizes into an insulating AlO_x layer, protecting an underlying homogeneous 2DES confined in the first atomic planes of the oxide substrate. 2 Å of Al are sufficient to create a saturated 2DES on differently oriented surfaces of $SrTiO_3$, anatase-TiO_2, or $BaTiO_3$, which were all studied by ARPES to determine the band structure (effective mass, orbital order and charge carrier densities) [4].

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8:40am **SA+2D+AC+AS+TF-TuM3 Advanced Spectro-microscopy of Ion Irradiated Graphene-metal Interfaces: From Substitutional Implantation to Nanobubble Formation***, **Andrea Locatelli**, A. Sala, T.-O. Menteş,* Elettra - Sincrotrone Trieste, Italy*; G. Zamborlini,* Peter Grünberg Institute (PGI-6) Jülich*; L. Patera, C. Africh,* IOM-CNR Laboratorio TASC, Italy*; M. Imam, N. Stojić, N. Binggeli,* Abdus Salam International Centre for Theoretical Physics, Italy **INVITED**

The exploitation of graphene in the next generation electronics depends on our ability of preserving and tailoring its unique electronic and transport properties. Whereas the preservation of the free-standing characteristics of graphene demands to decouple the film from its support, their modification requires functionalization and thus chemical doping. Varied methods have been devised to implant exospecies into and under the C lattice mesh. Among them, irradiation of nitrogen ions has emerged as one of the most powerful approaches, producing enhanced physical and chemical properties rather than detrimental effects. At variance with other methods, ion irradiation enables implementation of lithographic approaches for doping graphene, a feature which is most desirable for creating arrays of devices.

The characterization of complex and laterally-heterogeneous interfaces, such as that of ion-irradiated graphene, demands advanced microscopy tools. Here, we will demonstrate the present capabilities of cathode lens spectro-microscopy. As a first example, we report a proof of principle experiment demonstrating that low energy ion irradiation through an aperture can be used to achieve local control on doping in graphene. Our study tackles the fabrication of a 2-dimensional heterojunction between *n*-doped and almost neutral single-layer graphene on Ir(111). Here, XPEEM is employed to characterize the transition region between areas with metallic and semimetal-like density of states and its thermal stability [1].

Then, we will focus on the irradiation of graphene with low energy Ar and Ne ions, reporting on the formation of nanobubbles upon annealing. The morphology and local stoichiometry of the Ar-ion irradiated interface were characterized by LEEM, XPEEM and STM, specifically addressing the thermal stability of noble gas nanobubbles. These structures display a lateral size up to tens of nanometers and height of several atomic layers. Remarkably, the Ar clusters remain trapped under graphene up to temperatures nearing 1100°C, suffering no material loss through the mesh or its edges. Ab-initio calculations demonstrate that intercalated Ar undergoes extreme pressures, up to few tens GPa. The nanobubble ripening process turns out to be driven by the minimization of the energy cost of film distortion and loss of adhesion [2]. The electronic properties of the ion irradiated interface will be also discussed.

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9:20am **SA+2D+AC+AS+TF-TuM5 Gas-source MBE Growth of 2D Materials Examined using X-ray Synchrotron Radiation***, **Hugh Bullen**, R.K. Nahm, S. Vishwanath, H.G. Xing, J.R. Engstrom,* Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. Here we report on the gas-source MBE growth of thin films of WSe_2 using $W(CO)_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $W(CO)_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence. We have examined growth for a variety of conditions: growth with coincident fluxes of $W(CO)_6$ and Se, and growth in which one of the two reactant fluxes was gated. These experiments were conducted at several different substrate temperatures, on graphite (HOPG), and on so-called epitaxial graphene (graphene on SiC). First, for continuous exposure to $W(CO)_6$ and Se we observe, after an short incubation period, continuous growth of both the W and Se intensities. Analysis of this data indicates a stoichiometry consistent with WSe_2. We also find diffraction features consistent with the crystalline phase of WSe_2, where the basal plane is in the plane of the substrate. Particularly interesting is what we see when one of the reactants is gated: We have found that growth is halted by gating the incident flux of $W(CO)_6$, while the film is stable in the presence of a flux of Se_n. The physical properties of these thin films are essentially the same as those grown using continuous exposure to both reactants. We find a much different result when the flux of Se_n is gated: the absence of Se, but the presence of $W(CO)_6$, leads to *loss* of Se, and an increase in the amount of W. Since the termination of both fluxes does not lead to the loss of either element, it must be that $W(CO)_6$ is providing the species that leads to the loss of Se. The most likely scenario is that a ligand exchange reaction occurs producing the gas phase species, SeCO(*g*). Perhaps our most exciting result involves the growth of WSe_2 on epitaxial graphene. In these experiments, in addition to measuring the X-ray fluorescence, we also measured *in situ* and in real time the intensity at the anti-Bragg condition, which we have shown to be are very effective way to monitor thin film crystal growth. We observe strong and sustained oscillations, indicating layer-by-layer growth of WSe_2 of up to at least 5 monolayers. This is a very exciting result, and it indicates the effective use of synchrotron radiation to examine the growth of TMD thin films.

9:40am **SA+2D+AC+AS+TF-TuM6 Nanostructured Surface of Multilayer Graphene on Cubic-SiC***, **Victor Aristov**,* ISSP RAS, Chernogolovka, Russia, Russian Federation*; H.-C. Wu,* BIT, Beijing, China*; O.V. Molodtsova, S.V. Babenkov,* DESY, Hamburg, Germany*; A.N. Chaika,* ISSP RAS, Chernogolovka, Russia, Russian Federation

The results of atomically resolved scanning tunneling microscopy, low energy electron diffraction, low energy electron microscopy, micro-LEED and angle resolved photoelectron spectroscopy studies of graphene synthesized on cubic-SiC will be presented. Uniform few layer graphene was fabricated on SiC/Si wafers using Si-atom sublimation followed by SiC surface layer graphitization during high-temperature annealing in ultrahigh vacuum. Using the new dynamic-XPS end-station, based on the Argus spectrometer installed on the high-brilliance soft X-ray P04 beamline at PETRA III (DESY) one can control layer-by-layer graphene growth in real time following the evolution of the photoemission spectra with an acquisition time of ~ 0.1 sec/spectrum. Recording spectra during graphene growth on the SiC/Si(001) wafer, one can stop the process as soon as the desired number of graphene layers is reached. Angle-resolved photoemission measurements allowed us to extract the information about the electronic structure and the stacking order of the few-layer graphene on SiC(001). The preferential directions of the nanodomain boundaries coincide with the directions of carbon atomic chains on the SiC(001)-c(2x2) reconstruction, fabricated prior to graphene synthesis. Electrical measurements conducted on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene. Our measurements demonstrate that the self-aligned periodic NBs can induce a charge transport gap up to 1.3 eV at low temperatures. The transport gap opening produces high current on-off ratio of 10^4. This development may lead to new tuneable electronic nanostructures made from graphene on cubic-SiC, opening up opportunities for a wide range of new applications.

This work was supported by the RAS, RFBR grants No 140200949 and 140201234, by the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211, by a Marie Curie IIF grant No 12/IA/1264, by SPP 1459 of DFG.

11:00am **SA+2D+AC+AS+TF-TuM10 Full-field Photoelectron Spectromicroscopy of Ferroelectric Surfaces*, Nicholas Barrett,*** CEA Saclay, France **INVITED**

Advanced low energy electron optics combined with synchrotron radiation has transformed photoelectron emission microscopy (PEEM) into a powerful technique for the microscopic study of material surfaces. High lateral, wave-vector and energy resolution makes it possible to probe spatial variations in the chemical and electronic structure of nanoscale materials.

Perovskite based ferroelectrics are one important family of oxide materials requiring such analysis. Their robust polarization, switchable by an external field, makes them extremely interesting candidates for post-CMOS electronics.

First, the principles of fully energy filtered PEEM will be presented. By a combination of both direct and reciprocal space imaging the surface charge, work function, topography, chemistry and band structure of ferroelectric materials can be studied. This will then be illustrated by several examples.

The surface charge and hence the ferroelectric polarization can be estimated from the the work function as measured in PEEM. There is a critical film thickness in $BiFeO_3$ below which the film polarization drops to zero despite constant tetragonality, suggesting the formation of stripe domains in ultra-thin films [1].

The band structure of ferroelectric domains in $BaTiO_3$(001) are studied using spatially resolved reciprocal space PEEM and synchrotron radiation. The dispersion relations can be correlated with domain chemistry and in- and out-of-plane ferrolectric polarization [2].

The ferroelectric stability as a function of temperature of piezo force microscopy written domains has been studied using threshold PEEM. A Curie temperature of 490°C is recorded which is also dependent on the poling voltage.

We will conclude with a brief demonstration of an operando PEEM experiment, opening up the perspective of studying the changes in functional oxide properties under electric stimulation.

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11:40am **SA+2D+AC+AS+TF-TuM12 Electron Confinement at Magnetic Oxide Interfaces: Insight from Photoemission Spectroscopy*, Martina Mueller,*** Forschungszentrum Juelich GmbH, Germany **INVITED**

Recent advances in the fabrication of oxide heterostructures with atomic-scale precision has enabled interface and size control of complex oxide materials, for which unique phenomena with no bulk analogues have been demonstrated. In designated heterostructures, two-dimensional electron systems can be confined at oxide interfaces -- typically along the growth direction – which offer possible alternatives to conventional semiconductors in terms of functional (e.g. spin-polarized) electronic transport properties. Using redox-controlled synthesis [1, 2], the electronic properties of oxide heterostructures and interfaces can be engineered -- in terms of quality that were thought to be unique to semiconductors.

The basic idea of electron confinement applies to complex oxides just as to conventional semiconductors, but the physics is much richer. In metal oxides, confined electrons are subject to strong electron-electron interactions leading to a variety of physical phenomena that can be accessed, modified and controlled. For example, using oxides with intrinsic magnetic order allows to explore spin-related phenomena in low dimensions.

We present how to create two-dimensional electronic systems (2DES) in all-oxide heterostructures using EuO, a ferromagnetic insulator [1]. By interfacing Eu metal to $SrTiO_3$, a non-magnetic insulator, a redox reaction takes place at the interface which involves the oxidation of Eu metal into ultrathin EuO [2], and the reduction of Ti cations. This redox process strongly suggests that mobile electrons are created at the resulting interface. Using synchrotron-based soft, hard and angle-resolved photoemission spectroscopy [3] we probe the electronic structure and chemical composition at the EuO/STO interface and give a direct indication of a redox-created 2DES. The observed electronic confinement in all-oxide heterostrctures provides a route for controlling spin functionality for emerging applications.

[1] G. Prinz, T. Gerber, A. Lorke, M. Müller, submitted (2016)

[2] T. Gerber, M. Müller *et al*, J. Mater. Chem. C, 4, 1813 (2016)

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2D Materials Focus Topic
Room 103B - Session 2D-TuA

Novel Quantum Phenomena in 2D Materials

Moderators: Yoshi Iwasa, University of Tokyo, Japan, Kristian Thygesen, Technical University of Denmark

2:20pm **2D-TuA1 Time-dependent Density-functional Theory Simulation of Local Currents in Pristine and Single-defect Zigzag Graphene Nanoribbons***, **S He**, A. Russakoff, Y. Li, K. Varga,* Vanderbilt University

The spatial current distribution in H-terminated zigzag graphene nanoribbons (ZGNRs) under electrical bias is investigated using time-dependent density-functional theory solved on a real-space grid. A projected complex absorbing potential is used to minimize the effect of reflection at simulation cell boundary. The calculations show that the current flows mainly along the edge atoms in thehydrogen terminated pristine ZGNRs. When a vacancy is introduced to the ZGNRs, loop currents emerge at the ribbon edge due to electrons hopping between carbon atoms of the same sublattice. The loop currents hinder the flow of the edge current, explaining the poor electric conductance observed in recent

3:00pm **2D-TuA3 Studies of Conductance in Graphene Defects and Junctions using Complex-Injecting Potentials and TDDFT***, **Cody Covington**, K. Varga,* Vanderbilt University

In order create nanoscale electronic devices, there is a need for making high quality electrical connections between functional regions or specific defects[1]. However, connecting dissimilar materials such as graphene and metals[2] may pose complications from differing densities of states and work functions, and predicting how the system is effected computationally can be challenging given the system size. To address these challenges, studies of the electrons flow through heterogeneous material junctions, using complex potentials on a real-space grid and Time-Dependent Density Functional Theory have been performed. By confining an electron into the conduction band at a single point and propagating the system in time, the wavefunction for the system in a specific conducting state can be solved. Considerations for junctions and use of injecting and absorbing potentials in regions of diminished electron density will be presented.

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3:20pm **2D-TuA4 Excited Biexcitons in Two-Dimensional Transition Metal Dichalcogenides***, **Daniel Kidd**, D. Zhang, K. Varga,* Vanderbilt University

Recently, experimental measurements and theoretical modeling have been in a disagreement concerning the binding energy of biexctions in transition metal dichalcogenides. While theory predicts a smaller binding energy (~20 meV) that is lower than that of the trion, experiments find values much larger (~60 meV), actually exceeding those for the trion. In this work, we show that there exists an excited state of the biexciton which yields binding energies that match well with experimental findings and thus gives a plausible explanation for the apparent discrepancy. Ground and excited states of the five-body exciton-trion are also investigated and shown to be bound.

4:20pm **2D-TuA7 Electron Talbot Effect on Graphene***, **Jorge Salas**,* Vanderbilt University

The Talbot effect for a graphene sheet as a grating, using electron matter waves, is simulated using density functional theory and solving the Helmholtz equation. The obtained Talbot images show focusing effects suggesting possible applications for reshaping electron wave-packets and interferometry [1].

[1] Salas, J. A., Varga, K., Yan, J.-A. & Bevan, K. H. Electron Talbot effect on graphene. Phys. Rev. B 93, 104305 (2016).

4:40pm **2D-TuA8 Femtosecond Hot Electron-Phonon Interactions of Single Layer Graphene and the undelying Substrate***, **Zina Jarrahi**, J.L. Davidson, N.H. Tolk,* Vanderbilt University

We study the effect of substrate on the femtosecond transient electron and phonon dynamics of single layer graphene transferred on finely polished diamond, sapphire and quartz. Through a comprehensive set of fluence and energy dependent ultrafast optical conductivity measurements, we show that the temporal evolution of the hot carriers in graphene, differ *significantly* depending on the underlying substrate. We observe much faster(slower) relaxation and less(more) pronounced band filling dynamics for graphene on diamond(quartz). We demonstrate that the differences in the temporal evolution of the carrier temperature and inter/intraband transition interplay, cannot be accounted for by invoking the different static Fermi-levels of graphene on each substrate. These substrate-dependent dynamics are explained, using a multi-channel cooling picture, involving surface phonons of the substrate, intrinsic optical phonons of graphene, their competing scattering rates, phonon frequencies and the varying Fröhlich coupling strength of the different substrates. In this regard, the sub nm roughness of our studied substrates, enable a strong coupling between the phototexcited carriers in graphene and the surface vibrational modes of the polar substrates. We observe an increase in the carrier relaxation times as photoexcited carrier density is increased. This further confirms the existence of an additional relaxation mechanism through the substrate that competes with the intrinsic phonons of graphene to not only reduce the electron temperature but also carrier and optical phonon lifetimes. These results offer significant potential to selectively activate the desired energy relaxation channels in graphene and tune the carrier and optical phonon lifetimes, by simply varying the substrate and fluence regime. This knowledge will pave the road towards designing graphene-based (opto)electronics with highly tailored functionalities suited for specific device requirements.

5:00pm **2D-TuA9 New Opportunities in Two-Dimensional Material Research***, **Yuanbo Zhang**,* Fudan University, China **INVITED**

Two-dimensional (2D) atomic crystals, best exemplified by graphene, have emerged as a new class of material that may impact future science and technology. The reduced dimensionality in these 2D crystals often leads to novel material properties that are vastly different from that in the bulk. We refer to such a recurring scheme as “less is different”. In this talk I will illustrate this scheme with two 2D materials that we found particularly interesting – black phosphorus and 1T-TaS_2. These two layered materials have vastly different properties. Black phosphorus is a 2D semiconductor, and its superior material quality has recently enabled us to observe the quantum Hall effect. 1T-TaS_2, on the other hand, is a metal with a rich set of charge density wave phases. We explore their electronic properties while the doping and dimensionality of the 2D systems are modulated.

5:40pm **2D-TuA11 Ultrafast Carrier Dynamics in the Quasi-2D Metal Dichalcogenide SnS_2***, **Oliver Monti**, C. Eads, D. Bandak,* University of Arizona*; D. Nordlund,* SLAC National Accelerator Laboratory*; M. Neupane,* US Army Research Laboratory

We use soft x-ray resonant photoemission and core-hole-clock spectroscopy to investigate the ultrafast carrier dynamics in SnS_2. We show that carriers delocalize on a time-scale of a few hundred attoseconds near the conduction band minimum, but remain localized over an order of magnitude longer in higher lying bands. On the basis of density functional theory calculations we are able to show that this is consistent with the 2D nature of SnS_2. Moreover, we show that these experiments map the wavefunction in the unoccupied bands. Our measurements represent the first of their kind on the carrier dynamics in such materials.

6:00pm **2D-TuA12 MBE Growth of WTe_2 for Novel Electronic and Topologically Protected Devices***, **Lee Walsh**, R. Yue, A.T. Barton, H. Zhu, L. Cheng, R. Addou, J. Hsu, J. Kim, M. Kim,* University of Texas at Dallas*; L. Colombo,* Texas Instruments*; R.M. Wallace, C.L. Hinkle,* University of Texas at Dallas

Transition metal dichalcogenides (TMDs) are 2D materials which belong to a class known as van der Waals materials where the adjacent layers are held together by weak van der Waal’s interactions and, in principle, have no surface dangling bonds, which permits a relaxed growth requirement in terms of lattice matching. This relaxed lattice-matching criteria allows us to couple these materials based primarily on their band alignment and electronic properties. WTe_2 is a TMD with an equilibrium structure in the distorted octahedral (1T’) phase. This 1T’ phase of WTe_2 is a semi-metal and hence may be implemented as a 2D metal in an all-2D heterostructure for new devices. Monolayer 1T’ WTe_2 has been separately predicted to be a Weyl semi-metal and to behave as a relatively wide bandgap (>0.1 eV) topological insulator, possessing helical edge states which have a number of interesting properties including time reversal symmetry, spin-momentum locking, and ballistic transport[1,2]. The trigonal prismatic (2H) phase of WTe_2 is viewed as an integral part of the tunnel field effect transistor (TFET) device due to its bandgap and effective mass and has been theoretically predicted to provide low power operation and sub 60 mV subthreshold swing. WTe_2 is truly a remarkable material with intriguing electronic properties owing to its strong spin-orbit coupling and layered crystal structure.

In this work, we demonstrate the first report of WTe_2 growth by molecular beam epitaxy (MBE) on a variety of substrate materials (Bi_2Te_3, MoS_2, and graphite). We will discuss the optimal MBE growth conditions (substrate temperature, flux rates etc.) along with in-depth structural and chemical characterization of the resultant single crystal thin films. Characterization was conducted via reflection high energy electron diffraction, transmission electron microscopy, scanning tunneling microscopy/spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy. Challenges associated with Te incorporation and simple device and transport measurements will be presented.

This work is supported in part by the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA. It is also supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST. This work was also supported in part by the Texas Higher Education Coordinating Board's Norman Hackerman Advanced Research Program.

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Plasma Science and Technology
Room 104B - Session PS+2D-TuA

Plasma Processing for Nanomaterials and 2D Materials

Moderator: Sumit Agarwal, Colorado School of Mines

2:20pm **PS+2D-TuA1 Analysis of Microplasma Reduction of Aqueous Silver and Gold Salts to Colloidal Nanoparticles**, ***Caroline De Vos,*** Université Libre de Bruxelles, Belgium*; M.J. Gordon,* University of California, Santa Barbara*; R.M. Sankaran,* Case Western Reserve University*; F. Reniers,* Université Libre de Bruxelles, Belgium

The remarkable stability of microplasmas at atmospheric pressure and their non-thermal operation facilitate the introduction of liquids such as water for water treatment, medical, and material applications. Recently, there has been interest in the reduction of metal salts in aqueous solutions by microplasmas to produce colloidal nanoparticles (NPs). It is generally accepted that some active species from the plasma react with the solution phase and either directly reduce the metal cation or produce a reducing species. However, it remains unclear how exactly the metal cation is reduced to produce NPs.

In this study, we carried out experiments to understand the formation of silver (Ag) and gold (Au) NPs from their respective metal salt precursors with or without stabilizing capping molecule by reactions at the interface of a microplasma and the aqueous solution phase. The NPs were characterized after synthesis by ultraviolet-visible (UV-vis) absorption spectroscopy and transmission electron microscopy (TEM), and the chemical composition of the solution was characterized before and after microplasma treatment by ionic conductivity, electrochemical potential, and UV-vis absorption spectroscopy.

Our results show that both Ag and Au NP formation are directly proportional to the plasma current and process time. The calculated reduction efficiency based on the number of electrons injected and the number of Ag^+ reduced is only ~50% while the reduction efficiency for the Au precursor was ~25%. Another difference between the two metals is that plasmon band for Au was found to increase even after the plasma treatment was stopped. This was corroborated by a measured decrease in the concentration of the Au complex, confirming that reduction continues to occur without the plasma, presumably because of a long-lived reducing species generated in solution.

Assuming electrons are the important charge carriers, electrons can reduce metal cations, but can also reduce water to form OH radicals which in turn react to form hydrogen peroxide (H_2O_2). H_2O_2 is known to be a weak reducing agent and could also reduce the metal salts but based on our experiments and reduction potentials, we believe that H_2O_2 could only induce the formation of Au NPs.

To gain more insight into the different mechanisms involved, the gas phase above the plasma-liquid system was analysed by optical emission spectroscopy (OES); a variety of species were observed (OH, O, H, NO, N_2) and ultimately linked to the reactions occurring in the liquid phase.

This work was supported by the Belgian Federal Government (IAP research project P7/34 – Physical Chemistry of Plasma Surface Interactions).

2:40pm **PS+2D-TuA2 Controllable Optical Properties of Plasmonic TiN Nanoparticles Synthesized by a Scalable Non-Thermal Plasma Method***,* ***Alejandro Alvarez Barragan****, L. Zhong, L. Mangolini,* University of California Riverside

Titanium nitride is a refractory material with optical properties similar to those of gold. It has therefore attracted significant interest, since TiN nanoparticles are expected to show localized surface plasmon resonance in the visible/near-infrared range, all while overcoming the cost and thermal stability limitations of gold. For instance, they are a very attractive substitute of gold nanoparticles in biomedical applications [1]. Most of the methods involving TiN nanopowder synthesis use effective but complicated chemical routes [2,3]. In this contribution, we present a highly scalable method for the production of TiN nanoparticles using a non-thermal plasma process. A low-pressure non-thermal plasma reactor is used to continuously nucleate and grow crystalline TiN nanoparticles starting from a mixture of ammonia and titanium tetrachloride. Besides achieving a remarkable production rate (~50 mg/h), we were also able to control the particle size and stoichiometry with great precision by tuning process parameters such as gas composition and plasma input power. This finding is of paramount importance because the plasmonic peak position is highly dependent on these two parameters [4]. Absorption measurements of the as-synthesized particles show clear plasmonic resonance in the near-infrared region, ranging between 800 and 1000nm when dealing with the largest and smallest particles, respectively. XRD and high resolution TEM/EDS characterization also provides insight on the nitrogen content of the samples and its close correlation to particle size. The role of process parameters on the surface of the particles, which in turn affects their plasmonic properties, will be discussed extensively.

References

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3:00pm **PS+2D-TuA3 Plasma Prize Talk: Nonthermal Plasma Synthesis of Nanocrystal Materials***, N.J. Kramer, K. Schramke, T. Chen, H. Fu, S. Ehrenberg, K. Reich, B. Shklovskii,* ***Uwe Kortshagen***[*]*,* University of Minnesota **INVITED**

Nonthermal plasma synthesis of nanocrystals is particularly suited for covalently bonded materials that require high temperatures to be produced with good crystallinity. Several years ago, we showed that plasma produced silicon nanocrystals are capable of high-efficiency photoluminescence, different from bulk silicon material. More recently, the capability of nonthermal plasmas to produce substitutionally doped nanocrystal materials has attracted attention, as substitutional doping had presented a significant challenge both for liquid and gas phase synthesis due to effects such as self-purification.

This presentation discusses the physics of plasma synthesis process. High photoluminescense quantum yields are achieved by careful surface functionalization through grafting alkene ligands to the nanocrystal surfaces. We also discuss the substitutional doping of silicon nanocrystals with boron and phosphorous using a nonthermal plasma technique. While the synthesis approach is identical in both cases, the activation behavior of these two dopants is found to be dramatically different. Finally, we present some experimental work on transport in films of highly phosphorous-doped nanocrystals, which indicates the approach to the metal-to-insulator transition.

This work was supported in part by the NSF Materials Research Science and Engineering Center under grant DMR-1420013, the DOE Energy Frontier Research Center for Advanced Solar Photophysics, and the Army Office of Research under MURI grant W911NF-12-1-0407.

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[*] **PSTD Plasma Prize**

4:20pm **PS+2D-TuA7 Initiated Plasma Enhanced Chemical Vapor Deposition of Metalloporphyrins: A Simple Route towards the Deposition of Metal Organic Covalent Networks**, ***Nicolas BOSCHER,*** Luxembourg Institute of Science and Technology, Luxembourg*; M. WANG, K. GLEASON,* Massachusetts Institute of Technology

Porphyrins and porphyrinoids are robust and versatile functional molecules with varying properties depending on their central metal ion and peripheral and axial substituents. They have proved to be useful in a wide range of applications, including the catalysis and photocatalysis of various chemical reactions, in molecular sensing, light harvesting applications, and for gas storage and gas separation applications. In addition to these functional assets, their rigidity and chemical stability make them ideal as building units for the formation of covalent and coordination metal-organic polymers, including metal-organic frameworks (MOFs). Nevertheless, the difficult processability of these poorly soluble and non-meltable materials makes difficult their integration into smart devices.

Provided the fact that the monomer to deposit possesses free-radical polymerizable bonds, initiated PECVD (iPECVD) promotes conventional chain-growth polymerisation pathways, ensuring an excellent retention of the monomer structure. Several works have highlighted the radical polymerizability of the exo-pyrrole double bond of the porphyrin rings. The propagation reaction occurs at the beta-position of the porphyrin ring, leading to the formation of a polymer of reduced porphyrins, i.e. chlorin. Based on this wet-chemistry result, we recently investigated the use of zinc (II) meso-tetraphenylporphyrin (ZnTPP) building units in an iPECVD process and formed a new kind of metal-organic covalent network (MOCN) thin films.

5:00pm **PS+2D-TuA9 Plasma-graphene Interaction and its Effects on Nanoscale Patterning***, A. Harpale,* University of Illinois at Urbana-Champaign*;* ***Huck Beng Chew,*** University of Illinois at Urbana Champaign **INVITED**

Graphene is the lightest and strongest known material, and is also an ideal thermal and electrical conductor. Despite its unique properties, graphene has to be patterned to achieve its full engineering and nanotechnological potential. Recent experiments show that a monolayer of graphene deposited on an SiO2 substrate and subjected to hydrogen plasma treatment either undergoes (a) selective etching from the edges of the graphene sheet while leaving the basal plane intact, or experiences (b) etching of both the edges and basal plane of the graphene sheet which results in the formation of nanoscale holes in graphene. The plasma-etched holes in (b) can be either circular or hexagonal, suggesting that the etching process can be isotropic or anisotropic. Here, we model the hydrogen-plasma etching of monolayer graphene on SiO2 substrates across the range of plasma energies using scale-bridging molecular dynamics simulations. Our results uncover distinct etching mechanisms, operative within narrow hydrogen-plasma energy windows, which fully explain the differing plasma-graphene reactions observed experimentally. Specifically, our simulations reveal very sharp transitions in the etching mechanisms with increasing hydrogen ion energy: selective edge etching at ion energies of ~1 eV, isotropic basal plane etching at ion energies of between 2 and 5 eV, and anisotropic etching at ion energies > 7 eV. Understanding the complex plasma-graphene chemistry and the relationship to plasma process parameters opens up a means for controlled patterning of graphene nanostructures.

5:40pm **PS+2D-TuA11 A Closer Look at Chemically Modified Graphene***,* ***Sandra Hernández,*** Naval Research Laboratory **INVITED**

Graphene has been a research focus due to its numerous unique properties which have motivated vast interdisciplinary research in the search of materials for next-generation technologies. With its unique atomically thin nature, graphene has enabled a closer look at material surface interactions and highlighted the importance of surface interfaces, defects and adsorbates. Purposeful and native defects have demonstrated to have advantageous or adverse influences on the chemical, electrical, optical, mechanical and even magnetic properties of graphene. On the other hand, control of the localization of defects and their arrangement onto ordered and extended structures has enabled new graphene-based materials with novel properties. Surface functionalization has provided the ability to manipulate the material attributes, offering a range of opportunities for the chemically modified materials. It is clear that fundamental understanding of the modification of graphene relies on the understanding of the chemical functionalization dynamics, kinetic barriers, chemical transitions, and diffusion energies experienced by the added adsorbates with the graphene surface as well as the influence of the substrate on each. Plasmas provide both ease and versatility by enabling a single tool process on a wide range of background gases. In particular, electron-beam generated plasmas can introduce different functional groups over a large coverage range with atomic layer precision, providing the ability to tailor the locality of the surface chemistry on graphene opening up a wide range of reactivity studies and synthesis capabilities. Such unique ability allows for precise nano-engineering of the surface chemistry effecting local electronic properties, electron transfer kinetics, and surface reactivity; opening up a wealth of opportunities in device performance, chemical sensing, bottom-up material growth, plasmonics, and catalysis applications.

This work is supported by the Naval Research Laboratory Base Program.

2D Materials Focus Topic
Room 103B - Session 2D+TF-WeM
2D Materials: Growth and Fabrication

Moderator: Masoud Mahjouri-Samani, Oak Ridge National Laboratory

8:00am **2D+TF-WeM1 Synthesis and Characterization of Two-dimensional WSe_2 Grown using Chemical Vapor Deposition***, **Avra S. Bandophadyay**, G.A. Lara Saenz, C. Biswas, A.B. Kaul,* University of Texas at El Paso

Semiconducting Transition Metal Dichalcogenides (TMDCs) have attracted a lot of attention recently, because of their interesting electronic, optical, and mechanical properties [1]. Among large numbers of TMDCs, monolayers of tungsten diselenides (WSe_2) are of particular interest since WSe_2 possesses a direct band gap (~1.6eV) and tunable charge transport behavior, which makes it suitable for a variety of electronic and optoelectronic applications. Direct synthesis of large domains of monolayer WSe_2 and their growth mechanism studies are important steps toward applications of WSe_2. In this work, we have synthesized Tungsten Diselenide via Chemical Vapor Deposition Method using WO_3 powder and Se pellets as the precursors. Selenium was placed at the upstream side of the furnace at a temperature zone of 260-270°C. The temperatures and distances of these two sources were carefully controlled and adjusted. We used silicon with 300 nm thermally grown SiO_2 as the substrate and it was placed at some distance from the WO_3 source. The substrates for growing WSe_2 are put at the downstream side, where the Se and WO_3 vapors were brought to the targeting substrates by an Ar/H_2 (4:1) flowing gas with a flow rate of 120sccm. The pressure was maintained at 5Torr throughout the experiment. The temperatures at the Se source, WO_3 source and Substrates are maintained 260°C, 950°C and 750-850°C respectively. After the growth, the temperature of the furnace was naturally cooled down to room temperature and the samples were taken out for characterization. The size and shape of the as-grown flakes were observed under an Optical Microscope. Raman spectroscopy was used to determine the number of layers by noting the location of the Raman peaks and the relative Raman shift. In this paper we will discuss our work on the synthesis and characterization of 2D WSe_2, where we have also succeeded in forming monolayer structures for electronic device applications.

References:

[1] A. B. Kaul, *Journal of Materials Research*, vol. 29, pp. 348-361, 2014.

[2] H.Sahin et al, Physics Review B, vol. 87, pp. 1654091-1654096, 2013.

8:20am **2D+TF-WeM2 Reduction of Graphene Oxide by a Selective Surface Modification Process via Chemical Route for Achieving Higher Proportion of Graphene***, K. Dave,* CSIR Centre for Cellular and Molecular Biology (CCMB), India*; **KyungHee Park**,* Chonnam National University, Republic of Korea*; M. Dhayal,* CCMB, India

The primary objective of the study was to target the removable of remaining oxygen available as carboxylic acid functionalities from the surface of first level of reduced graphene oxide. Hence, first we describes preparation of highly exfoliated graphene oxide (GO) from graphite which was further reduced by hydrazine and sodium borohydride. Further we used soda lime for removing carboxylic functional group from the surface of reduced GO by decarboxylation. X-ray photoelectron spectroscopic analysis confirm the synthesis of exfoliated graphene oxide by chemically introduced oxygen as -COOH), –OH and C-O-C. A very high % proportion of carbon atoms as carboxylic functionality observed in the synthesized GO whereas the reduction of it with NaBH4 and Hydrazine significantly reduced it. The use of soda lime had further reduced the carboxylic group in both the $NaBH_4$ and N_2H_4 reduced GO. Raman spectroscopic analysis showed two distinct peaks of graphene oxide and reduced graphene in Raman spectra which were correlated with breathing mode of sp^2 atom and graphitic carbonic sp2 of carbon atoms. A strong red shift in the G-band position was observed after oxidation of graphite into GO due to increase in the number of layers of graphene whereas the reduced GO by both reducing agent $NaBH_4$ and N_2H_4 had showed a decrease in the red shift of the D-band. Above finding confirms better conversion of GO into graphene due to increased SP_2 carbon proportion after selective reduction of the GO. In the future we planned to use these materials for biomedical applications.

8:40am **2D+TF-WeM3 Scalabale Production of Molybdenum Disulfide-based Biosensors***, **A.T. Charlie Johnson**,* University of Pennsylvania **INVITED**

We demonstrate biosensor arrays based on CVD-grown molybdenum disulfide (MoS_2) field effect transistors (FETs) coupled to a computationally-redesigned soluble variant of the µ-opioid receptor (MOR). By transferring dense films of monolayer MoS_2 crystals onto prefabricated electrode arrays, we obtain clean, high-quality FETs that allow reproducible protein attachment. The yield of MoS_2 FETs and biosensors exceeds 95%, with average mobility of 2.0 $cm^2V^{-1}s^{-1}$ (36 $cm^2V^{-1}s^{-1}$) under ambient (in vacuum). An atomic length linker chemistry enables target binding very close to the MoS_2 surface to maximize sensitivity. The biosensor calibration curve for a synthetic opioid peptide target indicates binding affinity that matches values determined using traditional techniques and a limit of detection ~ 3 nM. The combination of scalable array fabrication and rapid readout enabled by MoS_2 transistors offer the prospect of a solid-state drug testing platform for rapid readout of the interactions between novel drugs and their intended protein targets.

9:20am **2D+TF-WeM5 Growth of Graphene on Cubic Silicon Carbide on Silicon Substrates***, **Mehdi Rezaee**, G.L. Harris, J. Griffin, C. Taylor,* Howard University*; E. Hu, D. Bell,* Harvard University

Graphene is a two-dimensional sheet of sp^2 carbon atoms with extraordinary high mobility and quantum properties that makes it a promising candidate for future electronics. Large-scale production of graphene is paramount for the development of graphene-based electronics. This thesis focused on the synthesis and characterization of graphene layers. Two methods were used to grow graphene films. First, graphene films were epitaxially grown on silicon carbide substrates by thermal decomposition of SiC at high temperatures and low pressures. An in-house built reactor consisting of an induction furnace was used to form epitaxial films for electronic applications. Second, chemical vapor deposition was used for direct graphene synthesis on 3C-SiC using copper as a catalyst. In the thermal CVD processes, hydrogen and methane gases were used as precursors. Methane acts as a carbon source, while annealing and cooling were done in a hydrogen environment. Different polytypes of silicon carbide (6H-SiC and 3C-SiC) and their crystal orientations were exploited as substrates to form epitaxial graphene. A hetero-epitaxial 3C-SiC epilayer was first deposited on Si substrate using the chemical vapor deposition technique in the cold wall, low-pressure horizontal CVD reactor. The reactor temperature, argon pressure, flow rate and concentration of different gases (propane, silane, hydrogen and argon) was investigated to control the growth of 3C-SiC and graphene sublimation rate. The resulting graphene films were confirmed using Raman spectroscopy. Further, graphene films have been characterized with the tools of atomic force microscopy (AFM) and scanning electron microscopy (SEM). Mobility, electrical resistivity and carrier density measurements were taken using Hall effect measurements.

This work was supported by the STC Center for Integrated Quantum Materials, NSF Grant No. DMR-1231319 and the PREM NSF Program.DMR-1205608 grant.

9:40am **2D+TF-WeM6 Growth of Graphene on Cu Single Crystal Substrates***, **Tyler Mowll**,* University at Albany-SUNY*; Z.R. Robinson,* College at Brockport-SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Copper foils are frequently used to grow single-layer graphene by chemical vapor deposition (CVD). The primary reasons for this are the low costs of the Cu foils, the low solubility of carbon in Cu, and the relatively low cost of the equipment needed to grow the films. However, the polycrystalline nature of Cu foils can lead to numerous crystalline defects in the graphene, resulting in a reduction in the transport properties. To provide a systematic study of the CVD graphene growth process, a study of the growth of graphene on single crystal Cu substrates, with terminations along the (100), (110), and (111) planes, was performed. Synthesis was performed in an ultra-high vacuum (UHV) chamber using a modified setup to allow growth at pressures as high as 1 Torr. Ethylene was used as the precursor gas. To control Cu sublimation at the elevated growth temperatures, an Ar overpressure was used. This arrangement allowed for the preparation of clean Cu surfaces by sputtering and annealing the Cu crystals in UHV, followed by graphene growth at low pressure, and analysis with low energy electron diffraction in UHV without breaking vacuum. This avoided exposure of the crystal to atmospheric contaminants. It was found that surface termination plays a strong role in the rotational alignment of the nucleating graphene grains and the decomposition rate of the ethylene. It was observed that single-domain epitaxy is possible on Cu(111) when the ethylene pressure is 5 mTorr or less. However, growth on both Cu(100) and Cu(110) result in a minimum of two domains. In addition, ex-situ EELS is currently being performed on well-ordered epitaxial graphene films grown on Cu(111) and Cu(100) to determine the effect of the graphene-Cu interaction on the electronic properties of the graphene.

11:00am **2D+TF-WeM10 Atomic Layered Large Area Growth of 2D Monolayers Over Different Substrates***, **Joseph Waters**, S. Garg, S. Balci, S. Kim, P. Kung,* University of Alabama

Atomically-thin transition metal dichalcogenides (TMDCs) such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) are of great interest because of their unique semiconducting and optical properties. For example, unlike graphene, MoS_2 is a semiconductor whose band gap changes from indirect (~1.2 eV) to direct (~1.85 eV) as the material thickness reduces from bulk to a monolayer state. This makes MoS_2 promising for numerous optoelectronic and biosensing applications. TMDC monolayers have originally been realized through exfoliation. However, the ability to synthesize monolayers over larger areas than those achievable with exfoliation requires scalable techniques such as chemical vapor deposition.

Here, we report the large area growth of monolayer thin films of TMDCs, such as MoS_2 and WS_2, by low-pressure chemical vapor deposition in an oxygen-free inert argon atmosphere. The growth of these materials has been compared on various substrates, such as basal plane sapphire, (001) SiO_2/Si, and GaN/sapphire substrates. The effects of growth conditions, including growth temperature, on the characteristics of the resulting material have been studied. The physical properties of the monolayers have been characterized using electron microscopy and atomic force microscopy to study their topology over the various substrates, in conjunction with confocal micro-Raman and micro-photoluminescence spectroscopy to correlatively assess their optical characteristics. The terahertz time domain spectroscopy of MoS_2 and WS_2 monolayer thin films will also be presented. We will further discuss the impact of these monolayer materials for robust optoelectronic device applications.

11:20am **2D+TF-WeM11 Growth of Doped Graphene from Fullerene Precursors***, X. Fei, J. Neilson, V. Lopez,* California State University Northridge*; H.J. Gao,* Chinese Academy of Sciences, People's Republic of China*; L. Gan,* Peking University, People's Republic of China*; **Li Gao**,* California State University Northridge

Heteroatom-doped graphene materials have potential applications in electronic devices, energy storage and conversion systems, and gas storage. Chemical doping with various heteroatoms is an effective strategy for tuning the properties of graphene in order to expand its applications. Toward the practical applications as well as fundamental studies of doped graphene materials, it is an urgent task to explore effective approaches to synthesize these materials with a high level of control over their doping properties. In this talk, we will discuss the synthesis of heteroatom-doped graphene materials from fullerene precursors. Initial success has been achieved on the iridium and ruthenium surfaces. The growth process and the properties of grown doped graphene materials are characterized by using scanning tunneling microscopy on the atomic scale. We will discuss how the growth process and the properties of grown doped graphene depend on precursor/metal systems and experimental conditions. This new synthesis approach is an important complement to the existing strategies for the preparation of heteroatom-doped graphene.

11:40am **2D+TF-WeM12 Evaluation of Precursor Chemistry for Controllable Growth of Molybdenum Disulfide by Pulsed Chemical Vapor Deposition***, **Berc Kalanyan**, J.E. Maslar, W.A. Kimes, B.A. Sperling, E. Garratt, B. Nikoobakht, R. Beams, S.J. Stranick, A.V. Davydov,* National Institute of Standards and Technology (NIST)

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs), e.g., MoS_2, are of increasing interest for next-generation nanoelectronic and optoelectronic devices due to their thickness dependent optical and electrical properties. For many applications, high volume manufacturing of devices based on TMDs will require deposition techniques that are capable of reproducibly growing wafer-scale films with monolayer control. To date, TMD deposition processes largely rely on powder vaporization and transport, with minimal control over precursor fluxes and chemistry. A detailed understanding of metal and chalcogen precursor chemistry in relation to film properties remains an important step toward the design of highly-controllable deposition processes suitable for large-scale 2D synthesis.

We aim to identify promising chemistries for chemical vapor deposition (CVD) processes for TMDs. We focus on MoS_2 CVD using organometallic and organosulfur compounds in a research grade single-wafer deposition system equipped with *in situ* optical diagnostics. The precursor flux is measured using optical mass flow meters installed on the delivery lines while deposition chemistry is characterized in the reactor volume above the deposition surface using *in situ* Fourier transform infrared (FTIR) spectroscopy. As-deposited and annealed films are characterized with *ex situ* techniques, including Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy.

Large-area thin films of MoS_2 were prepared from (η^5-ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum, cycloheptatriene tricarbonyl molybdenum, bis(ethylbenzene) molybdenum, 1-propane thiol, and diethyl disulfide sources. Film composition and growth rates on SiO_2 and c-plane Al_2O_3 were characterized for each compound as a function of precursor exposure time. Gas phase reaction chemistry and thermal stability of precursors were evaluated using FTIR spectroscopy. The full-width at half-maximum values for in-plane (E_{2g}^1) and out-of-plane (A_{1g}) Raman modes for MoS_2 were used as indicators of film quality. By relating film properties to gas-phase chemistry for various metal precursors, we will highlight precursor design and process conditions that lead to high quality CVD films.

12:00pm **2D+TF-WeM13 *In-situ* Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of hexagonal Boron Nitride Monolayers on Pd(111)***, **Pedro Arias**, A. Ebnonnasir, F. Fankhauser,* University of California at Los Angeles*; C. Ciobanu,* Colorado School of Mines*; S. Kodambaka,* University of California Los Angeles

Using *in-situ* ultra-high vacuum variable-temperature scanning tunneling microscopy (STM), we investigate the chemical vapor deposition kinetics of hexagonal boron nitride (hBN) monolayer growth on Pd(111) substrates as a function of substrate temperature, borazine flux, and deposition time. All of the experiments were carried out on sputter-deposited Pd(111)/Al_2O_3(0001) thin films. In each experiment, STM images were acquired while resistively heating the Pd(111) samples on the STM stage at temperatures between 300 K and 773 K and in the presence of borazine (10^{-7} ~ 10^{-6} Torr) for times between 60 s and 2500 s. We observe the nucleation and growth of chemisorbed (and presumably partially dissociated) borazine islands on the Pd surfaces. From the STM images, we measured the island density and size as a function of time, temperature, and borazine flux. We find that both the island density and size increase with increasing borazine flux and deposition time. We also find that borazine islands form on Pd(111) 'up-steps.' After achieving monolayer coverage of borazine, the samples are annealed in ultra-high vacuum at 1020 K for 60 seconds to form hBN monolayers. We then determined of the number density of rotational domains in the hBN layers, based upon which we identify the deposition parameters critical to the growth of single-domain hBN layers on Pd(111).

Surface Science

Room 104D - Session SS+2D-WeM

Synthesis, Characterization, and Surface Science of Novel Materials and Interfaces

Moderator: Talat Rahman, University of Central Florida

8:00am **SS+2D-WeM1 Early Stages of the Thermal-Induced Mobility of Ag in SiC***, **Daniel Velázquez**, R. Seibert, J. Terry,* Illinois Institute of Technology

Tri-structural isotropic (TRISO) particles are the fuel of choice for very-high temperature reactor technology. At the core, these spherical particles consist of an inner fuel kernel of UO2, UC2 or a combination of both, which is coated radially outward by successive layers of low density pyrolytic graphite, an inner high density pyrolytic graphite layer, silicon carbide (SiC) and an outer high density pyrolytic graphite layer. SiC is the main diffusion barrier against the release of fission products due to its hardness and high melting point. Nonetheless, irradiation testing of TRISO particles indicates that trace amounts of metallic fission products, such as Ag (which as a ~41 day half-life), diffuse through SiC. Competing theoretical and experimental observations that indicate that Ag diffuses through the bulk and through grain boundaries. Diffusion through grain boundaries is usually amplified due to the formation of large grains upon crystallization by heating. This leads to the formation of triangular micro pits in thin films, suggesting that a 3D version of this form of crystallization could facilitate even more the release of Ag. Previously XAFS and XPS have shown that Ag remains metallic in a SiC matrix, indicating that bulk diffusion is perhaps interstitial rather than substitutional. In this work we discuss the mobility of Ag films enclosedon layers of 3C-SiC by analyzing SEM images taken before and after annealing. Image analysis supported by surface spectroscopic and crystallographic techniques are used in order to estimate the release of Ag through SiC for Ag interlayers at various thicknesses and annealing temperatures. Preliminary analysis by SEM/EDS show that upon annealing Ag escapes through the SiC surface by three different mechanisms, which roughly in chronological are: 1) escape through triangular pits and grain boundaries in SiC; 2) agglomeration and formation ofsub-surface blisters which eventually rupture; 3) diffusion through the bulk of SiC when the trapped amounts of Ag are insufficient to form large blisters. During the third mechanism, we still observed sub-surface mobility in the form of dendritic paths. When the starting amount of Ag is reduced sub-surface diffusion is limited and the release of Ag is dominated by the escape through the triangular pits of SiC and bulk diffusion.

8:20am **SS+2D-WeM2 Quantitative Chemical State base on XPS Energy Scan Image Applied to Ni Fe corroded Samples***, **Vincent Fernandez**, J. Keraudy,* Université de Nantes, France*; N. Fairley,* Casa Software Ltd, UK*; P.Y. Jouan,* Université de Nantes, France

1. Introduction

Corrosion is a natural phenomenon where metals have a tendency to revert back to their natural, lower energy state. During many years, the most effective corrosion protection systems were based on the use of chromate-rich surface treatments. However, recently, the legislation imposed by the european commission, REACH (Registration, Evaluation, Authorization and Restrictions of Chemicals) prohibited the use of hexavalent chromium. Many alternatives have been explored so far, including the protection with monolayer and/or multilayers of thin films (Cr, CrN, Ti, TiN, NbN) deposited by magnetron sputtering process. Corrosion is a physical-chemical interaction between the metal and its environment. Most hard coatings (TiN, CrN, NbN) possess an higher corrosion resistance than less noble materials like steel, Al or Mg alloys. When the coatings are deposited on such less noble substrates and exposed to a corrosive atmosphere (ex : NaCl), the coated parts suffer from serious corrosive attack (pitting corrosion) due to inherent coating defects or inhomogeneities . This kind of corrosion is localized to the defect area and is characterized by the anodic dissolution of the substrate material with a high anodic current density at the defect site. It is generally called galvanic corrosion. In this study, Nickel thin film (2 micrometers) was deposited on steel substrate (XC38) using Direct Current Magnetron Sputtering from a Ni target. In order to simulate the corrosive attack, the coated part was exposed to a corrosive medium, i.e salt spray test. The test was conducted under continuous spray (24 hours) conditions (5wt.% NaCl) at a temperature of 35 °C according to the ASTM B117 standard procedure.

The morphology and the chemical environment of the corrosion products were analyzed respectively by optical microscopy and XPS investigations.

2. Results

The samples have conducting and isolating regions to avoid spatial differential potential the samples were measured in a floating condition. The Parallel XPS images of 128 pixels by 128 pixels where done with FOV of 900 x 900 microns at an energy resolution of about 1eV and an energy step of 0.2 eV for O 1s, Na KLL, Ca 2p, C 1s, Ni 3p and Fe 3p with charge compensation. Ni and Fe were measure in one region. To treat the 735 images corresponding of more than 1.2 10^7 intensity points, images were smoothed and projected on PCA images. All images were projected on 6 abstract factors. Then images were converting in 81920 spectra. After spectra quantification, energies regions were converting back in quantitative images. Then Fe map was classified in 5 false colors part by intensity.

8:40am **SS+2D-WeM3 Novel Approaches to Form Organic-Inorganic Interfaces: Parallels between Coupling and Surface Modification Schemes in Vacuum and in Wet Chemistry***, **Andrew Teplyakov**,* University of Delaware

Recent interest towards controlled formation of organic-inorganic interfaces affected greatly the approaches used for surface modification of semiconductors. Despite substantial progress in designing chemical pathways for surface modification of these materials and synthetic capabilities to build a variety of precursor molecules, two major issues remain: 1) Can the same level of precision achieved for surface characterization in vacuum be achieved for surfaces modified by wet chemistry methods; and 2) Can the elemental and compound semiconductor surfaces be modified with chemical groups that are both oxygen- and carbon-free. These two questions will be addressed by drawing parallels between cyclocondensation processes on modified semiconductor surfaces and cycloaddition in vacuum. Mixed surface modification schemes will be discussed for silicon and ZnO materials to produce high-coverage chemical "hooks" and the use of these functionalities will be demonstrated for initial stages of film deposition or depositing large constructs (nanoparticles and buckyballs) by chemical addition to produce strong covalent bonds. The addition across double bonds of carbonaceous constructs and the production of chemical bonds by straightforward chemical reactions will be discussed. The reactions for producing amino-functionalities and the platforms for "click" reactions will be presented. The experimental evidence of the reactions will be based on infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and a combination of microscopic techniques. The selected results of the experimental work will be compared with the experimental observables predicted by density functional theory (DFT).

9:00am **SS+2D-WeM4 Adsorption of Hetero-bifunctional Urea on Ge(100)-2x1 Surface***, **Tania Sandoval**, S.F. Bent, A.M. Crow,* Stanford University

Organic functionalization of Group IV semiconductor surfaces is of interest due to the need for new pathways in surface chemistry modification. This is important in applications such as molecular layer deposition, molecular electronics, and biosensors where the ability to control and tune surface properties requires a deep understanding of the interactions between molecules and solid surfaces. In this study, adsorption of the heterobifunctional urea molecule on the Ge(100)-2x1 surface was investigated. Both the amine and carbonyl group of the urea molecule are known to react with the Ge surface. The aim of this study is to determine if any preferential reaction pathways exist and to understand the driving forces toward the final products.

Density functional theory (DFT) calculations suggest that NH_2 dissociation is the most thermodynamically favorable pathway for the single reaction. The reaction can occur through two possible precursor states: a nitrogen dative bond with the surface or an oxygen dative bond that can further undergo an enolization reaction. Interestingly, the oxygen dative bond is 7 kcal/mol more stable than the nitrogen bond, suggesting a preference for the latter reaction pathway. Furthermore, calculations show that the dual reactions provide less stabilization gain and a higher kinetic cost than single reactions, as the dual NH_2 dissociation has an activation barrier greater than 30 kcal/mol and only provides 5 kcal/mol of additional exothermicity, indicating that the urea molecule will likely react only through a single functional group. X-ray photoelectron spectroscopy (XPS) and multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy were used to determine the final reaction products. Results suggest that urea adsorbs on Ge(100) forming a mix of surface products. One of the products can be identified by the downshift in binding energy of the N(1s) XP peak and the Ge-H stretching mode in IR as NH_2-dissociated urea on Ge. This assignment is also consistent with the presence of a carbonyl group in the IR and XPS spectra, which is expected to remain unchanged in this surface configuration. Another reaction product exists that is evident by second O(1s) and C(1s) XPS peaks downshifted from that of the parent urea molecule, suggesting a loss of the carbonyl group by a reaction with a more electropositive atom. Moreover, coverage results support our DFT findings by suggesting that each urea molecule will occupy a Ge dimer by reacting through a single functional group per molecule.

9:20am **SS+2D-WeM5 Electronic Structure of Ferroelectric Nanodomains***, **Erie Morales**, C. Perez, M. Brukman, D. Bonnell,* The University of Pennsylvania

The local measurement of structure and properties enabled by scanning tunneling microscopy and atomic force microscopy in conjunction with systematic control of in situ environments has yielded insight into the fundamental behavior of ferroelectric compounds. Many atomic structures on BaTiO3 surfaces have been determined, the thermodynamic stability of structures on (001) surfaces has been described, and the polarization dependence of several classes of surfaces reactions has been demonstrated. In addition the polarization behavior at the nanoscale has received much attention.

Here we report unusual impact of local poling on the electronic structure of ferroelectric surfaces. Scanning Tunneling Microscopy in situ poling was performed on BaTiO3 (001) in ultra high vacuum (UHV). The voltage pulse produces apparent anti-parallel ferroelectric domains. Domain size can be controlled by changing conductivity of the crystal and/or by changing the bias set point; the smallest domain we pole is 24 nm. We use a 4-D analysis of geometric and electronic structure data to characterize the variations in electronic structure. Patterns of variations in the surface band gap are consistent with existing theoretical calculations of anti parallel domain orientations.

9:40am **SS+2D-WeM6 Using Data Analytics and Informatics in Understanding Enhanced Conductivity, Mobility, and Transparency in ITO Bearing ZrO_2 and reduced SnO_2*,* *Timothy Peshek,*** Case Western Reserve University*; J.M. Burst, T. Coutts, T.A. Gessert,* National Renewable Energy Laboratory

We deposited high quality tin-oxide-doped indium oxide (ITO) by RF magnetron sputtering with varying oxygen partial pressure in the sputter ambient and using targets with a nominal concentration of 5 wt% SnO_2, instead of a typical 10 wt%, and between 0-3 wt% ZrO_2. We demonstrate mobilities of \$>\$45 cm^2/Vs for sputtered ITO films at zero added oxygen. We demonstrate resistivities in the range of 10^{-5} Ω-cm at zero added oxygen with 1 wt% ZrO_2 added, mobilities at >55 cm^2/Vs and the films showed a modest increase in optical transmission with increasing Zr-content.orptio

Hypothetically the increase in mobility that apparently accompanies the addition of ZrO_2 yields enhanced optical clarity in the IR due to reduced free carrier absorption from reduced doping concentration for any given resistivity.

Anomalous behavior was discovered for films with no Zr-added, where a bimodality of high and low mobilities were discovered for nominally similar growth conditions. We examined this anomalous behavior using modern data science and visualization techniques of big data and materials informatics. We used these techniques to gain insights into the mechanistic behavior of the relationship between stoichiometry, process variables, material morphology and electrical properties. We will summarize these findings and describe the methods used in the analysis and a path forward for continuing utilizing data analytics in material characterization and learning.

11:00am **SS+2D-WeM10 Surface Composition and Atomic Structure of Topological Insulator Materials*, Jory Yarmoff*,** *W. Zhou, H. Zhu,* University of California - Riverside **INVITED**

A topological insulator (TI) is a two-dimensional material that behaves as an insulator in the bulk, but conducts along the surface via topologically protected surface states. TI's have attracted intense interest because of their fundamental importance combined with great potential for applications in areas such as spintronics and quantum computation. Because the critical electronic states in TI's are localized in the near-surface region, it is critical to understand their surface composition, surface atomic structure and surface chemistry, and there are several outstanding issues that have not been fully resolved. For example, the materials are often naturally doped leading to the Fermi energy residing in the conduction band. Some materials have also been observed to change over time, the so-called "aging effect". In addition, the surface termination of the prototypical TI, Bismuth Selenide (Bi_2Se_3), has been an area of recent debate. Although some studies have demonstrated that the cleaved surface is terminated with Se, as expected from the bulk crystal structure, there are other reports that show either a Bi-rich or mixed-termination.

We are using low energy ion scattering (LEIS), in conjunction with other surface analysis tools, to investigate the surface composition and atomic structure of TI materials prepared in numerous ways. LEIS is uniquely suited to measure surface termination and atomic structure, as it provides the elemental identification of the near-surface region and can be deployed to probe only the outermost atomic layer. We compared surfaces prepared by *ex situ* cleaving, *in situ* cleaving and Ar^+ ion bombardment and annealing (IBA) in ultra-high vacuum. LEIS measurements do not indicate any substantial differences between the Se-terminated surfaces prepared by IBA or *in-situ* cleaving. Samples inserted into the vacuum chamber following *ex-situ* cleaving are less well-ordered, show adsorbed oxygen and can be either Se-terminated or Bi-rich, which suggests a critical dependence on the level of contamination. We have also used molecular beam epitaxy to investigate the structure and stability of Bi overlayers grown on Bi_2Se_3. Additional experiments involve exposure of clean surfaces to gaseous species such as O_2, H_2 and Br_2.

11:40am **SS+2D-WeM12 Impact Collision Ion Scattering Spectroscopy of Bi_2Se_3 and Bi/Bi_2Se_3*, Weimin Zhou*,** *H. Zhu, J.A. Yarmoff,* University of California - Riverside

Bismuth selenide (Bi_2Se_3) and isolated bilayers of bismuth both behave as topological insulators, which are two-dimensional materials that conduct along the surface through topological surface states (TSS). These materials show great promise for use in spintronics and quantum computation. Because the TSS are located at the surface, it is important to understand the relationships between the surface atomic and electronic structures. Low energy ion scattering (LEIS) is a simple, but powerful surface sensitive technique that is ideal for structural analysis. LEIS, using Na^+ projectiles, is employed here in two distinct modes. First, time-of-flight (TOF) spectra are collected using low index incidence directions. This allows for a direct measure of the surface termination with minimal beam damage. Second, impact collision ion scattering spectroscopy (ICISS), which involves the collection of angular distributions using a large scattering angle, is employed to study the structure of the outermost few atomic layers. This work investigates the surfaces of clean Se-terminated Bi_2Se_3 and after a Bi bilayer has been grown on top by molecular beam epitaxy (MBE). Molecular dynamics (MD) simulations of ICISS are compared to the experimental data in order to ascertain the surface structures.

12:00pm **SS+2D-WeM13 Feature Scale Simulation for Materials Processing*, Paul Moroz,*** TEL Technology Center, America, LLC*; D.J. Moroz,* University of Pennsylvania

Modern materials processing often includes complex chemistries and surface interactions, and variety of species incoming to the wafer from gas and/or plasma in the chamber. It also often involves many time-steps, each one utilizing different chemistry and different gas/plasma parameters resulting in time-varying composition of fluxes coming to the wafer, and different energy and angular distributions of incoming species. Chemically or physically active species interact with material surfaces, generally resulting in etching, deposition, and implantation, and such processes might even happen together at the same time. The FPS3D feature scale simulator [1-3] is capable of handling very different and complex cases due to its special structure and numerical techniques, from atomic layer etching and atomic layer deposition to large-scale Bosch processing. Numerical models of surface and molecular interactions are flexible enough to describe most general cases. For this presentation, we selected three types of simulation cases. The first type considers simulation of mostly etching and implantation, such as during Si etching by chlorine-argon plasma. The 2nd type considers ALE (atomic layer etch) when etching is done by a cyclic process of surface passivation/activation with the following process of etching/removal of a single atomic layer per cycle or per a few cycles, allowing ultimate processing accuracy. The 3rd type of simulations considers deposition cases, such as Cu seed layer deposition. Some results will be presented for 2D simulations and some others – for 3D simulations.

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2D Materials Focus Topic
Room 103B - Session 2D+NS-WeA

Nanostructures including Heterostructures made of 2D Materials

Moderators: Charlie Johnson, University of Pennsylvania, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

2:20pm **2D+NS-WeA1 Single- and Few-Layer WTe_2 Nanosheets: New Raman Fingerprints, Nanomechanical Resonances, and Environmental Instability Studies***, **Fan Ye**, J. Lee,* Case Western Reserve University*; J. Hu, Z.-Q. Mao, J. Wei,* Tulane University*; P.X.-L. Feng,* Case Western Reserve University

Among recently emerging two-dimensional (2D) materials, 1T'-phase semi-metallic tungsten ditelluride (WTe_2) [4] possesses unique properties – large, non-saturating magnetoresistance [1] that originates from perfect balance between electrons and holes populations [2], a metallic to insulating transition under low temperature with varying number of layers [3] and superconductivity under high pressure [5]. These properties are not easily accessible in other 2D materials, thus making WTe_2 highly attractive for further investigations on their basic properties, especially in the single layer (1L) to few-layer regime.

In this work, we have systematically investigated new Raman signatures, nanomechanical properties [6], and environmental instability of single- and few-layer WTe_2. In Raman study, we have observed up to 12 peaks in few-layer WTe_2. We find clear softening, stiffening and invariant behaviors in the measured 12 Raman modes as thickness decreases from 8L to 1L. These Raman fingerprints could be an effective 'thickness indicator' for identifying layer number in atomically thin WTe_2. We have also investigated mechanical properties of few-layer suspended WTe_2 by measuring their resonances, and further determined its Young's modulus to be E_Y~80GPa. In addition, by employing surface sensitive material characterization tools such as Raman spectroscopy, XPS, and AES, we carefully study the degradation behavior of single- and few-layer WTe_2 in ambient conditions [7]. We find that oxidation is the main driving force of WTe_2 degradation and it is a self-limiting process. In particular, 1L WTe_2 quickly oxidize in ~13mins, while 2L and 3L WTe_2 exhibit relatively slower, saturating and self-limiting degradation process over two weeks.

This work paves the way for future investigations and utilization of the multiple new Raman fingerprints of few-layer WTe2, and for exploring mechanical control of WTe2 atomic layers.

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[7] F. Ye *et al.*, *In Submission* (2016).

3:00pm **2D+NS-WeA3 Laser-based Synthesis and Processing of Two-dimensional Monolayers and Heterostructures***, **Masoud Mahjouri-Samani**, C. M. Rouleau, A.A. Puretzky, D.B. Geohegan,* Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) materials, such as metal chalcogenides, graphene, and oxides, have emerged as an exciting class of materials with extraordinary physical, chemical, electrical, and optical properties. These classes of 2D materials have the potential to enable numerous new technological applications ranging from electronics to photonics. However, realization of this potential requires (i) novel synthesis approaches for growth of high-quality 2D materials, (ii) controllable chemical and structural modification of the crystals, and (iii) a fundamental understanding of their structural properties and device characteristics.

In this talk, I will demonstrate the use of non-equilibrium laser-based approaches to form and deliver atoms, clusters, or stoichiometric nanoparticles with tunable kinetic energies for the synthesis and processing of 2D layered semiconductors. Utilizing stoichiometric nanoparticles as feedstock, we have shown the growth of either small domain nanosheet networks (~ 20 nm) or large crystalline domains (~100 µm) of GaSe, $MoSe_2$, and WSe_2 with controlled orientation, number of layers, crystallite size, and growth location. We have also shown that atomic precursors with tunable kinetic energies can be used for doping, alloying, and conversion of 2D monolayers. I will show the structural, optical, and electrical properties of monolayer crystals modified by defect formation, healing, doping, and conversion processes. I will then highlight our newly developed method that enables the formation of patterned arrays of lateral heterojunctions between two different 2D semiconductors necessary for ultrathin electronics. These non-equilibrium approaches provide unique synthesis and processing opportunities that are not easily accessible through conventional methods.

4:20pm **2D+NS-WeA7 Pulsed Laser Deposition of Single Layer, Hexagonal Boron Nitride on Fiber-oriented Ag(111)/$SrTiO_3$(001)***, **Jeff Terry**, D. Velazquez, R. Seibert, L. Spentzouris,* Illinois Institute of Technology

We have grown thin films of hexagonal boron nitride (h-BN) of thickness 1-10 ML on fiber-oriented Ag buffer films on $SrTiO_3$(001) by pulsed laser deposition. We used Ag buffer films of 40nm thickness to substitute for expensive single crystal metallic substrates. Reflection high-energy electron diffraction (RHEED) was used to monitor the surface structure of the Ag films and to observe the formation of the characteristic h-BN diffraction pattern. Attenuated total reflectance spectroscopy showed the characteristic h-BN peaks at 780 cm^{-1} and 1367.4 cm^{-1}. Ex-situ photoelectron spectroscopy showed that the surface of the h-BN films was stoichiometric. Scanning electron microscopy showed that the h-BN films grew as large, sub-millimeter sheets with nano- and micro-sheets scattered on the surface. The h-BN sheets was easily exfoliated by the micromechanical adhesive tape method. The use of thin film Ag allowed us to adjust the surface morphology of the thin film prior to h-BN growth.

4:40pm **2D+NS-WeA8 Fracture Toughness Measurements of Graphene Oxide***, **Tobin Filleter**, C. Cao,* University of Toronto, Canada*; J.Y. Howe,* Hitachi High Technologies Canada Inc., Canada*; D. Perovic,* University of Toronto, Canada*; Y. Sun,* Univeristy of Toronto, Canada

Graphene Oxide (GO) is a functionalized form of graphene that we have recently shown to possess high tensile strength [1-2]. These studies on the strength of GO have revealed a size dependent mechanical behavior in which the strength is found to increase with decreasing thickness, a behavior which is controlled by a transition in the fracture mechanism [2]. In real engineering applications in which materials exhibit pre-existing flaws, the fracture toughness of a material is also a critical property in predicting the failure of the material. Here we present studies of GO with preexisting defects that enable the first measurements of the fracture toughness of GO nanosheets. Application of traditional experimental techniques used to measure the fracture toughness (and monitor the fracture behavior) of bulk materials is not feasible for the measurement of ultra-thin films such as GO. In this work, we apply a micro-electro-mechanical system (MEMS) based *in situ* transmission electron microscope (TEM) method to measure the fracture toughness of GO and directly characterize its fracture behavior through high resolution TEM imaging. GO nanosheets suspended on monolithic MEMS devices *in situ* TEM were first controllably etched by high-energy electrons to create well defined holes in the GO nanosheets used for fracture toughness measurements. After a defect was created, *in situ* TEM tensile tests allowed both measurement of the stress at the onset of fracture, as well as direct monitoring of the fracture response via TEM imaging.

[1] C. Cao, M. Daly, C. V. Singh, Y. Sun, and T. Filleter, "High strength measurement of monolayer graphene oxide", Carbon, vol. 81 (2015) p.g. 497-504

[2] C. Cao, M. Daly, B. Chen, J. Howe, C. V. Singh, T. Filleter, and Y. Sun, "Stengthening in graphene oxide nanosheets: bridging the gap between interplanar and intraplanar fracture", Nano Letters, vol. 15 (2016) p.g. 6528-6534

5:00pm **2D+NS-WeA9 Strain, Solitons, and Bimorphs with 2D Materials***, **Paul McEuen**,* Cornell University **INVITED**

Two-dimensional sheets combine many remarkable properties in a single, atomically thin package. For example, a graphene sheet can be made into a high-performance transistor, but it is also the ultimate realization of a thin mechanical sheet. In this talk, I will discuss some of the fascinating properties of heterostructures of these materials, touching on everything from creating the world's thinnest bimorph to the electronic and mechanical properties of interlayer strain solitons.

5:40pm **2D+NS-WeA11 Strain-Engineered Graphene Grown on Boron Nitride and Hexagonal Boron Nitride Grown on Graphite using High-Temperature Molecular Beam Epitaxy**, ***Alex Summerfield***, *A. Davies, T.S. Cheng, V.V. Korolkov, Y. Cho, C.J. Mellor, E.F. Smith, C.T. Foxon, A.N. Khlobystov,* University of Nottingham, UK; *K. Watanabe, T. Taniguchi,* National Institute for Materials Science (NIMS), Japan; *L. Eaves, S.V. Novikov, P. Beton,* University of Nottingham, UK

To scale up the production of graphene-hexagonal boron nitride (hBN) heterostructure devices, direct epitaxial growth of these materials will be necessary. As an alternative to commonly used techniques such as the exfoliation of graphene/hBN flakes or growth using chemical vapour deposition we have investigated high-temperature molecular beam epitaxy (HT-MBE) in order to produce high-quality graphene and hBN monolayers.

We show that graphene grown using HT-MBE on hBN surfaces form continuous domains with dimensions of order 20 µm, and exhibits moiré patterns with large periodicities, up to ~30 nm, indicating that the layers are highly strained. Topological defects in the moiré patterns are observed using atomic force microscopy (AFM) and attributed to the relaxation of graphene islands which nucleate at different sites and subsequently coalesce. In addition, cracks are formed leading to strain relaxation, highly anisotropic strain fields, and abrupt boundaries between regions with different moiré periods. These cracks can also be formed by modification of the layers with a local probe resulting in the contraction and physical displacement of graphene layers. The Raman spectra of regions with a large moiré period reveal split and shifted G and 2D peaks confirming the presence of strain.

We also demonstrate the epitaxial growth of high-quality hBN atomic layers on graphite using plasma-assisted HT-MBE. AFM reveals mono- and few-layer island growth, while conductive AFM measurements show that the grown hBN has a resistivity which increases exponentially with layer thickness comparable with exfoliated hBN samples. Furthermore, X-Ray photoelectron spectroscopy, Raman and spectroscopic ellipsometry confirm the formation of sp^2-bonded hBN with a band gap of 5.87 eV. Hexagonal moiré patterns of 15-17 nm are also observed on the hBN surface, suggesting that the grown layers may be strained due to the lattice mismatch with the graphite surface.

Our work demonstrates a new approach to the growth of epitaxial graphene/hBN and provides a route to the production of vertical superlattice structures for use in future devices.

6:00pm **2D+NS-WeA12 Metallic Edges in Atomically Thin WSe_2**, ***Rafik Addou***, *C.M. Smyth,* The University of Texas at Dallas; *Y.-C. Lin,* The Pennsylvania State University; *J. Noh,* The University of Texas at Dallas; *S.M. Eichfeld,* The Pennsylvania State University; *K.J. Cho,* The University of Texas at Dallas; *J.A. Robinson,* The Pennsylvania State University; *R.M. Wallace,* The University of Texas at Dallas

Transition metal dichalcogenides (TMDs) is a unique class of layered two-dimensional (2D) crystals with extensive promising applications. Tuning their electronic properties is vital for engineering new functionalities. Surface oxidation is of particular interest because it is a relatively simple and low-cost method compared with other processes involving complicated steps. By means of scanning tunneling microscopy and spectroscopy (STM and STS), and X-ray photoelectron spectroscopy (XPS), we show here the observation of metallic step edges in atomically thin WSe_2 monolayers grown by chemical vapor deposition (CVD) on epitaxial graphene (Gr). STM images show the shape and the structure of WSe_2 step edges and STS reveals their metallic nature. Photoemission demonstrates that the formation of metallic sub-stoichiometric tungsten oxide (WO_x, $x<3$) is responsible of high conductivity measured along the WSe_2 step edges. DFT Calculations [1,2] revealed that the $W_{18}O_{49}$ have a metallic behavior which is in excellent agreement with our photoemission estimated WO_x, with $2.61 \le x \le 2.72$. Our findings are in contrary with reported results of air-exposed WSe_2 edges with large band gap measured at ~3.1 eV. [3] We explain this discrepancy by considering the differences in WO_x stoichiometry. [1]

This work was supported in part by the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765.

[1] D. B. Migas *et al. J. Appl. Phys.* **108**, 093714 (2010)

[2] M. Remskar *et al. Adv. Funct. Mater.* **17**, 1974-1978 (2007)

[3] J. H. Park *et al. ACS Nano* ***10***, 4258–4267 (2016)

Advanced Surface Engineering
Room 101D - Session SE+2D+EM-WeA
Multifunctional Thin Films and Coatings

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Michael Stueber, Karlsruhe Institute of Technology, Germany

2:20pm **SE+2D+EM-WeA1 Investigation of H_2S Poisoning Process on Composite Material Made of Metal Oxides and Carbon Nanotubes**, ***Yichen Duan***, *A.V. Teplyakov,* University of Delaware

The composite material based on a combination of SnO_2, CuO and acid-treated carbon nanotubes is considered to be promising for H_2S sensing applications. By applying large dosage of H_2S (1% in volume) to the composite and evaluating the chemical changes spectroscopically via XPS, SEM and EDS, the poisoning mechanism of this type of sensing material is revealed. Specifically, metal sulfides (CuS and SnS_2), metal sulfate ($Sn(SO_4)_2$) and thiols are formed as the products following the introduction of H_2S. In fact, all the three components of the material are affected by H_2S. Moreover, when oxygen is present, metal sulfides can be reoxidized back into metal oxides while metal sulfate and thiols remain unchanged. The measurements of the model sensor response also support the assessment of the poisoning process.

2:40pm **SE+2D+EM-WeA2 Graphene-family Nanomaterials Co-assembled with Nanostructured Cobalt Oxide Polymorphs as Hybrid Supercapacitive Electrodes and Enzymeless Glucose Detection Platforms**, ***Sara Carrizosa***, *B. McDonald, S. Gupta,* Western Kentucky University

Graphene-family Nanomaterials Assembled with Cobalt oxides and Cobalt Nanoparticles As Hybrid Supercapacitive Electrodes and Enzymeless Glucose Detection PlatformsWe developed graphene/cobalt oxides and graphene/cobalt nanoparticles hybrid assembly highlighting the impacts of nanoscale surface morphology and microstructure producing tailored interfaces for improved electrochemical and electroanalytical properties. Molecular electrodeposition and facile hydrothermal synthesis techniques followed by thermal treatment are demonstrated to be effective approaches for nanoengineered electrochemical electrodes. Hybrid electrodes consisting of supercapacitive graphene nanosheets and pseudocapacitive nanostructured cobalt oxide polymorphs (CoO and Co_3O_4) as well as cobalt nanoparticles (CoNP) synthesized on two- and three-dimensional graphene nanosheets facilitate chemically bridged (covalently and electrostatically anchored) yet tunable graphene-cobalt interfaces. The intrinsic microstructure and surface of these hybrids were characterized by electron microscopy combined with elemental mapping, X-ray diffraction and Raman spectroscopy. The graphene/cobalt hybrid composites were investigated as asymmetric supercapacitor cathodes and as electroanalytical platforms for enzymeless detection of glucose. We demonstrate that Co3O4/ErGO and Co3O4/multilayer graphene hybrids are capable of delivering high specific capacitance of > 600 F g-1 at a current density of 10 A g-1 is achieved when the mass ratio of Co3O4 to ErGO is equal to 80:20 as compared with other hybrids with excellent cycling stability in voltage range 0–1.2 V. It can also detect glucose with ultrahigh sensitivity of 4.57 mA mM-1 cm-2 and a remarkable lower detection limit of < 50 nM in the following order Co_3O_4/rGO_{HT} < CoO/ErGO < CoNP/ MLGNiFoam < Co_3O_4/MLGNiFoam . We attribute all of these remarkable findings due to interplay of (a) open pore system beneficial to ion diffusion and transport kinetics owing to larger accessible geometric surface area, (b) three-dimensional topologically multiplexed and highly conductive pathways provided by MLG, ErGO and rGO_{HT} nanoscaffold architectures to ensure rapid charge transfer and electron/ion conduction (< 10 ms), and (c) synergistic integration of functional nanomaterials devoid of graphene sheets agglomeration with optimal transition metal (oxides) nanoparticles loading.

3:00pm **SE+2D+EM-WeA3 Cross-Bonding between Silicon, Silica and III-V Surfaces at the Nano-Scale Using Energy Analysis via Three Liquid Contact Angle Analysis (3LCAA) to achieve Hermetic Wet NanoBonding™**, ***Ashley Mascareno,*** SiO2 NanoTech LLC/Arizona State University Physics Dpt; *N.X. Herbots,* SiO2 NanoTech LLC; *C.F. Watson,* SiO2 NanoTech LLC/Arizona State University Physics Dpt

Mobile ions such as Na, percolate from saline environments into marine and atmospheric sensors and limit their reliability to less than a week. Implantable glucose monitors for diabetics require replacement about every 3-7 days, with finger blood samples re-calibration daily. Hermetic bonding can yield economic, medical, and human benefits by extending lifetime of such integrated sensors from days to years. Si-based surfaces such as thermally-grown amorphous a-SiO_2 on Si(100), and on III-V surfaces can be hermetically bonded with Wet NanoBonding™ to yield dense, hermetic cross-bonding. In Wet Nonbonding™, planarization is first accomplished at the nano-scale, then a-SiO_2 is etched with HF, while a 2 nm precursor β-$cSi_2O_4H_4$ phase is grown on Si(100) to initiate cross-bonding. Next, both surfaces are put into mechanical contact in a class 10 clean-room and nano-bonded under low temperature (T<180° C) steam pressurization.

Modifying the surface energy components of 2 surfaces can help optimize hermerticity by increasing the density of cross-bonding. Surface energy γ^T can be measured via 3 Liquid Contact Angle Analysis (3LCAA) using the the Van-Oss theory, which models γ^T for semiconductor and insulators in 3 interactions : (1) Lifschitz-Van der Waals molecular dipole interactions γ^{LW}, (2) electron donor interactions γ^+, and (3) electron acceptor interactions γ^-. Successful NanoBonding™ can occur between one surface with high γ^+ and one with high γ^-. 3LCAA extracts these from contact angles between several liquids with known surface energies and the surface. Sessile drop analysis with water, glycerin, and α-bromonaphthalene is conducted in a Class 100 hood using 4-8 drops per liquid for statistical accuracy. RCA cleaned Si(100) and Si(100) terminated with 2-nm β-$cSi_2O_4H_4$ via the Herbots-Atluri (H-A) process are used, in combination with Rapid Thermal Anneal and Oxidation (RTA and RTO), to grow a-SiO_2 [3]. The γ^T of hydrophilic RCA-cleaned Si(100) is 47.3±0.5 mJ/m^2 , 25% higher than the γ^T of ordered, hydrophobic β-$cSi_2O_4H_4$ Si(100) , 37.3±1.5mJ/m^2, and 30% higher than RTO oxides 34.5±0.5 mJ/m^2. Interactions from γ^{LW} account for 90-98±2% of γ^T in ordered oxides, but only 76.5±2.0% of those in hydrophilic surfaces. Thus, 3LCAA detects changes in surface reactivity from defects, impurities, and dangling bonds. While γ^+ accounts for little to none of γ^T for all but one surface, 180° C annealing during Wet NanoBonding significantly increases γ^+ in β-$cSiO_2$. Conversely, HF etching significantly increases γ^- for a-SiO_2. When matching acceptor with donor interactions between surfaces via 3LCAA, cross-bonding density appears to increase, and NanoBonding™

3:20pm **SE+2D+EM-WeA4 Porous Materials for Solid Phase Microextraction by Sputtering and Chemical Vapor Deposition**, ***Tuhin Roychowdhury,*** *A. Diwan, B. Singh, M. Kaykhaii, M.R. Linford,* Brigham Young University

Solid phase microextraction (SPME) is an important sampling tool. It consists of placing a coated fiber above a sample (headspace mode) or immersing it in a liquid such that molecules (analytes) of interest can be selectively extracted and concentrated. The captured species are then released by heating into a chromatograph for separation and identification. It is a 'green' method because no additional solvent is used in this process. We have developed a new class of SPME fibers that offer extraordinary capacity and speed. They are prepared by sputtering a material under conditions that lead to a nanoporous coating on the fiber. When silicon is sputtered under these conditions, its outermost surface can be additionally oxidized, leading to a high density of silanol groups than can be subsequently silanized. For example, the fibers can be derivatized with octadecyldimethylmethoxysilane by chemical vapor deposition (CVD), which creates a hydrophobic extraction medium. The performance of our 2 micron sputtered coatings has been compared to that of thicker (7 micron) commercial coatings. Our fiber consistently outperforms the commercial fiber, showing significantly higher capacity for alcohols, amines, aldehydes, and esters. Real world samples, e.g., hops and PAH from water, have also been analyzed. Different coating thicknesses have been prepared and evaluated. Sputtered coatings have been characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and wetting.

4:20pm **SE+2D+EM-WeA7 Ferroelectric Thin Films for Memory Applications**, ***Joyprokash Chakrabartty,*** Institut national de la recherche scientifique (INRS), Canada

Ferroelectric (FE) oxides draw attention in science community because of its spontaneous switchable polarization often used in electronic devices. FEs are earth abundant, easy to synthesis and low degradation of electronic properties while exposed to room atmosphere. One of its promising applications is in computer memory devices. FEs function as memory by storing data in its two polarization states normally defined as up and down state. However the challenges lie in enhancing data bit density at room temperature. Here we show four step ferroelectric polarization switching in $BiFeO_3$(BFO)/$SrRuO_3$(SRO)/$BiMnO_3$(BMO) heterostructure thin films which act as FE memory devices. All crystalline films are grown on (100) oriented Niobium doped SrTiO3 (NSTO) single crystal substrates by pulsed laser deposition. Our experimental results show a promising device concept, unique in FE memories that can enhance the data storage capacity in heterostucture capacitor devices at room temperature.

4:40pm **SE+2D+EM-WeA8 Thermoelectric and Optical Properties of Advanced Thermoelectric Devices from Ni/Bi_2Te_3/Ni and Ni/Sb_2Te_3/Ni Thin Films**, ***Satilmis Budak,*** *Z. Xiao, J. Cole, A. Kassu, D. Price, T. Davis, T. Strong, J. Gray,* Alabama A&M University

Thermoelectric devices were prepared from Ni/Bi_2Te_3/Ni and Ni/Sb_2Te_3/Ni thin films using DC/RF magnetron sputtering and E-beam deposition systems. Thermoelectric devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thin film devices were characterized using Seebeck coefficient measurement systems; four probe van der Pauw measurement system to measure resistivity, sheet resistance, density, mobility and type of the charge carrier concentration. In addition to the Seebeck coefficient and van der Pauw measurements, the laser thermal conductivity system was used for the thermal conductivity measurements. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM). Raman Spectroscopic technique is used for identification of inherent molecular specificity and analysis of chemical compositions of the films. The resonant features of the scattering spectra measured under the 532 nm and 785 nm wavelength excitation lasers are analyzed.

Acknowledgement

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5:00pm **SE+2D+EM-WeA9 Effects of Composition and Strain on Band Gaps of Pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge**, ***Nalin Fernando,*** New Mexico State University; *R. Hickey, J. Hart, R. Hazbun, D. Zhang, J. Kolodzey,* University of Delaware; *S. Zollner,* New Mexico State University

Ge-Si-Sn alloys are interesting for CMOS applications for a variety of reasons. For example, adding Sn to Si-Ge lowers the band gap, which reduces parasitic contact resistance. Also, the lattice constant of Ge-Sn alloys increases when adding Sn. Therefore, such alloys could be used to impart strain on PMOS devices with Ge channels. We used deformation potential theory to determine the compositional dependence of the direct, indirect, E_1, and $E_1+\Delta_1$ band gaps of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge and theoretical predictions are validated through spectroscopic ellipsometry measurements of the band gaps of pseudomorphic $Ge_{1-y}Sn_y$ on Ge grown by MBE.

The band structure of Ge is a strong function of strain and alloy composition, and a transition from an indirect to a direct band gap has been observed for y~6-10% for relaxed $Ge_{1-y}Sn_y$ indicating the possibility of widespread applications of Ge-based photonic devices. The pseudomorphic nature of the Ge-based alloy layer on a substrate is important to keep dislocation densities low at the interface to improve the performance of the device. Band gap engineering of Ge by controlling strain and alloying with Si and Sn has attracted great interest since a $Ge_{1-x-y}Si_xSn_y$ ternary alloy with two compositional degrees of freedom allows decoupling of the lattice constant and electronic structures.

The pseudomorphically grown $Ge_{1-x-y}Si_xSn_y$ layer on Ge experiences a biaxial stress due to the lattice mismatch between the alloy layer and the Ge. The strain resulting from the stress affects the band structure of the alloy.

Deformation potential theory is used to determine the compositional dependence of the band gaps of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge as a function of Si (x) and Sn (y) compositions. The predictions of the deformation potential theory are validated for pseudomorphic $Ge_{1-y}Sn_y$ (for Si=0) on Ge through measurements of the optical properties. The complex pseudodielectric functions of pseudomorphic $Ge_{1-y}Sn_y$ alloys grown on Ge by MBE were measured using ellipsometry in the 0.1-6.6 eV energy range for Sn contents up to 11%, to investigate the compositional dependence of the band gaps. Critical point energies (CP) and related parameters were obtained by analyzing the second derivative spectrum of the dielectric function. Our experimental results for E_g^{dir}, E_1 and $E_1+\Delta_1$ gaps are in good agreement with the theoretically predicted CP energies. We will discuss the strain and compositional dependence of the band gaps and the effects of the growth temperature of the Ge buffer layer on Si to the band gaps.

This work was supported by AFOSR (FA9550-13-1-00222). FTIR measurements were performed at CINT.

5:20pm **SE+2D+EM-WeA10 MBE Growth of Hexagonal Boron Nitride for use in Novel Electronic Devices**, ***Adam Barton***, *R. Yue, C.M. Smyth, R. Addou, L. Cheng, R.M. Wallace, J. Kim, M. Kim, J. Hsu, K.J. Cho,* The University of Texas at Dallas; *L. Colombo,* Texas Instruments; *C.L. Hinkle,* The University of Texas at Dallas

2D materials offer unique opportunities in device fabrication due to the weak van der Waals interaction between crystalline layers that allows for the growth of high-quality heterostructures with significantly less impact from lattice mismatch with the substrate. Hexagonal boron nitride (hBN) has a honeycomb structure similar to graphene except with alternating boron and nitrogen atoms. The hexagonal rings are composed of six sp^2-hybridized atoms (three boron atoms and three nitrogen atoms). The electronic structure results in a bandgap of 5-7eV, a low-κ dielectric constant of 2-4ε_o, and an electron affinity of roughly 2 eV. These electronic properties make hBN an exciting material for a wide range of applications in electronic devices. In particular, we are interested in coupling hBN with transition metal dichalcogenides (TMDs) for low-power tunnel FET applications. Previous publications have primarily utilized chemical vapor deposition (CVD) to grow hBN on catalyzing transition metal substrates (Co, Ni, Cu, etc.) at growth temperatures ranging from 800-1200°C. However, these substrates and growth temperatures are not practical for the majority of device applications. Chalcogen loss in TMDs, for example occurs well below those temperatures.

In this work we report on our recent findings on the growth and characterization of hBN thin films grown by molecular beam epitaxy (MBE). This will include a detailed discussion of the growth mechanism on a variety of substrates (MoS_2, HOPG, WSe_2, Bi_2Se_3, and sapphire) using substrate growth temperatures ranging from 300-800°C. The impact of the source fluxes, substrate temperatures, and in particular, the presence of atomic hydrogen during growth will be presented. The hexagonal phase of BN is achieved as determined by diffraction, Raman, and XPS. AFM, TEM, and RHEED are also used to assess film quality and the experimentally determined bandgap and band alignment will be presented. We will also present our recent work on coupling hBN with ALD-deposited Al_2O_3 to enable higher-k gate dielectrics on top of 2D materials heterostructures.

This work is supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST. This work was also supported in part by the Texas Higher Education Coordinating Board's Norman Hackerman Advanced Research Program.

5:40pm **SE+2D+EM-WeA11 Passivation of Interfaces Between High-k Dielectrics and SiGe: *Ex Situ* Wet Sulfur Clean vs. *In Situ* Plasma Nitridation**, ***Kasra Sardashti***[*], *M.S. Clemons,* UC San Diego; *M. Yakimov,* SUNY College of Nanoscale Science and Engineering; *K. Tang,* Stanford University; *S. Oktyabrsky,* SUNY College of Nanoscale Science and Engineering; *P.C. McIntyre,* Stanford University; *L. Dong, N. Yoshida,* Applied Materials, Inc.; *A.C. Kummel,* UC San Diego

Silicon-Germanium is a promising channel material to be used in novel CMOS device architectures such as FinFET and Nanowire FET, due to its high hole mobility. Moreover, it enables control of carrier mobility by mechanical stress and band gap by variation in Si/Ge content in multilayer design. One of the important issues to address in the integration of SiGe in the MOS devices is formation of low-defect interfaces with very thin high-k gate dielectrics such as Al_2O_3, HfO_2 and ZrO_2. Due to adverse effect of Ge sub-oxide (GeO_x) formation and subsequent Ge out-diffusion on the performance of the devices, robust strategies to control the Ge reactions during and after oxide deposition are essential to further the development of SiGe FETs. This study determines the effects of two passivation methods on the quality of the interfaces between SiGe and high-k dielectrics: 1) Ex-situ wet sulfur passivation using $(NH_4)_2S$ solution; 2) In-situ NH_3 plasma nitridation. Al_2O_3 and HfO_2 were deposited on SiGe surfaces by atomic layer deposition (ALD). Electrical and chemical properties of the interfaces were evaluated by capacitance-voltage (C-V) spectroscopy, angle-resolved photoelectron spectroscopy (AR-XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Both sulfur passivation and plasma nitridation resulted in smaller density of interface traps with a large majority of the trap energy levels adjacent to the valence band edge. Ex-situ sulfur passivation was found to improve the interface quality by reducing the extent of GeO_x formation at the high-k/SiGe interface, therefore constraining the extent of Ge out-diffusion within the oxide. The mechanism is distinct; sulfur forms much stronger bonds to Ge than to Si due to the d-orbitals on the Ge; this promotes selective oxidation of the Si and prevents formation of GeOx. Using plasma nitridation, a thin layer of SiON forms selectively at the high-k/SiGe interfaces, preventing the presence of thermally-unstable species such as GeOx and GeON. In addition, SiON can act as a physical diffusion barrier to Ge out-diffusion. The nitridation is selective due to the higher enthalpy of formation for Si vs Ge oxynitrides. Both ex-situ sulfur passivation and in-situ NH_3 plasma nitridation were found to be effective approaches in preparing low-defect Al_2O_3/SiGe and HfO_2/SiGe interfaces; the different chemical mechanisms show there are multiple paths to selective bond formation to SiGe which can be utilized to engineer low-defect stable interfaces.

6:00pm **SE+2D+EM-WeA12 Enhanced Voltage Control of Perpendicular Magnetic Anisotropy in Magnetic Tunnel Junctions Using Ultrathin PZT Composite Oxide Tunneling Barriers**, ***Kevin Fitzell***, *X. Li, K. Wong, G. Yu, S. Robbennolt, S.H. Tolbert, P.K. Amiri, K.L. Wang, J.P. Chang,* University of California at Los Angeles

In contrast to manipulating magnetization with applied current, using an applied electric field can significantly reduce the required energy and result in less heat generation, leading to increased energy density. This can be accomplished using the voltage-controlled magnetic anisotropy (VCMA) effect, which forms the basis of next-generation magnetoelectric MRAM devices. Specifically, applying an electric field across a CoFeB/MgO interface can decrease the perpendicular magnetic anisotropy field as a result of the altered electron density at the interface, thus destabilizing the magnetization state and allowing for its efficient and deterministic reorientation with a small applied magnetic field. This operation principle stands in contrast to that of STT-RAM, which uses upwards of 100 fJ to write a single bit (300,000 times more energy than the actual energy barrier to switching).

Previous research on CoFeB/oxide interfaces has shown that increasing the dielectric constant of the oxide layer also increases the sensitivity of the interfacial magnetic anisotropy energy to an applied electric field. Lead zirconate titanate (PZT), having excellent ferroelectric properties including a large dielectric constant, is therefore a prime candidate for integration into such oxide layers in an attempt to maximize the VCMA effect. Using atomic layer deposition (ALD), PZT was thus incorporated into magnetic tunnel junctions having MgO/PZT/MgO multilayer composite tunneling barriers. Our group has shown that MRAM devices fabricated using these MgO/PZT/MgO tunneling barriers resulted in a 40% increase in the VCMA coefficient (and thus substantial energy savings) over magnetic tunnel junctions simply employing MgO tunneling barriers, despite the PZT layer being amorphous. Our most recent work has focused on the crystallization of these ultrathin PZT layers, which would cause an even larger dielectric response (even greater energy savings) and open an avenue toward four-state memory devices relying on the ferroelectric polarization of the PZT.

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[*] **National Student Award Finalist**

2D Materials Focus Topic
Room 103B - Session 2D+MI-ThM

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

Moderators: Paul Sheehan, US Naval Research Laboratory, Zhaohui Zhong, University of Michigan, Ann Arbor

8:00am **2D+MI-ThM1 Mechanics and Fracture of 2D Materials with Defects and Grain Boundaries***, **Zhao Qin**, G.S. Jung,* Massachusetts Institute of Technology*; S. Wang,* University of Oxford, UK*; F.J. Martin-Martinez,* Massachusetts Institute of Technology*; J.H. Warner,* University of Oxford, UK*; M.J. Buehler,* Massachusetts Institute of Technology

Two dimensional materials including graphene, silicene, MoS2 and so forth represent ideal materials composed of a single layer of atoms organized in a lattice form. Their unique geometry and intriguing mechanical and thermal properties make them perfect candidates for nano scale engineering applications. The robustness of the materials, especially those with defects is important to prevent their catastrophic failure and contribute to their durability in usage. Here we combine both large-scale molecular dynamics simulations based on reactive force fields and experiments via transmission electron microscopy to investigate their fracture behavior under extreme mechanical loading conditions. We focus on how defects and grain boundaries in 2D materials affect the critical conditions and the dynamics process of their fracture. Our results reveal that certain forms of atomic defects and grain boundaries are beneficial to enhance the mechanical strength of 2D materials that are subjected to cracks. For example, we find that poly-crystalline graphene under fracture releases up to 50% more energy than the pristine graphene. We find that grain boundaries increase the critical energy release rate to fracture by reducing stress concentration and making branches near the crack tip. We find atomic defects can cause crack deflections during crack propagation, effectively extending the crack length during propagation and thus increase the energy dissipation. Together, these molecular irregularities taking place at the atomic scale level can significantly affect the lattice characteristics of the 2D materials at larger scale levels and thereafter enhance their fracture toughness, making its crack propagation different from pristine ones, and such a mechanism explains the reduced crack propagation speed by adding vacancies as what is seen in experiments.

8:20am **2D+MI-ThM2 Effects of Non-local Screening and Effective Mass Anisotropy on Excitons in 2D Materials***, I.I. Oleynik, **Joseph Gonzales**,* University of South Florida

The optical excitations in semiconductors are substantially influenced by electron-hole interactions resulting in formation of excitons. Although the exciton binding energies in the bulk are much smaller that the fundamental band gaps, the excitonic effects in 2D materials are significantly amplified due to combined effect of quantum confinement and non-local screening of electron-hole interactions in two dimensions. An effective mass theory of 2D excitons, which takes into account the combined effect of the anisotropy and non-local 2D screening, is used to systematically investigate the variation of monolayer exciton binding energies E_x across a representative set of layered chalcogenides, both isotropic, such as $MoTe_2$, $MoSe_2$, WSe2, and WS_2, and anisotropic including phosphorene, TiS_3, ReS_2, and $SnSe_2$. The markedly different values of E_x are correlated with corresponding variations in atomic polarizabilities of constituent atoms.

8:40am **2D+MI-ThM3 2D Materials: A New Platform for Strong Light-Matter Interactions***, **Ajit Srivastava**,* Emory University **INVITED**

A recent addition to low-dimensional materials are monolayer transition metal dichalcogenides (TMDs), such as WSe_2, with an atomically thin, honeycomb lattice and optical band gaps. In addition to spin, charge carriers in TMDs exhibit a “valley” degree of freedom which can be optically addressed using circularly polarized light, opening up exciting possibilities for “valleytronics". Another curious aspect of TMDs lies in the non-trivial geometry of their band structure which gives rise to equal but opposite Berry curvature, an effective magnetic field in the momentum space. Owing to unusually strong Coulomb interactions in truly 2D limit, optical spectra of monolayer TMDs is dominated by tightly bound excitons which are expected to strongly couple to light and form stable polaritons - half light, half matter excitations.

In this talk, I will begin by presenting our recent results on valley Zeeman effect, where in analogy to spins, valleys shift in energy with magnetic field. Next, I will discuss our theoretical results on how the non-trivial geometry of Bloch bands modifies the excitonic fine structure of TMDs resulting in an orbital Zeeman effect in reciprocal space and a Lamb-like shift of levels. Finally, I will present our recent results on the observation of microcavity polaritons confirming the strong light-matter interactions in these materials. The presence of valley degree of freedom, non-trivial geometry of bands, and the possibility of introducing non-linearities in form of quantum emitters makes polaritons in TMDs particularly appealing for studying correlated many-body physics and topological states of matter.

9:20am **2D+MI-ThM5 Electronic Transport and Localization in Nitrogen-Doped Graphene Devices Using Hyperthermal Ion Implantation***, **Adam Friedman**, C.D. Cress,* Naval Research Laboratory*; S.W. Schmucker,* National Research Council postdoc working at Naval Research Laboratory*; J.T. Robinson, O.M.J. van 't Erve,* Naval Research Laboratory

Chemical alteration of graphene facilitates doping and may add a usable transport gap. For most published studies, atomic species (e.g., fluorine or hydrogen) are chemically bonded to the surface out-of-plane, breaking the sp^2 symmetry and replacing it with an sp^3 bond. These methods produce functionalized graphene, rather than substitutionally-doped graphene, where the former is typically only chemically stable for days (e.g., fluorine) or weeks (e.g., hydrogen) or less, depending on environmental conditions. Hyperthermal ion implantation offers a controllable method of producing high-quality substitutionally doped graphene with nitrogen, an n-type dopant that has great potential for graphene electronics and spintronics applications where high carrier concentration, uniform doping, and minimal vacancy defect concentration is desired [1]. Here we examine the transport properties of monolayer graphene sheets as a function of implantation beam energy and dose. We observe a transition from weak (metal) to strong (insulator) localization that varies as a function of carrier concentration, and we find that the transition is suppressed near the Dirac point for higher amounts of nitrogen [2]. For nominally equivalent doses, increased N ion energy results magnetoresistance magnitude increases, reaching a value as approximately -5.5% at 5,000 Oe, which we discuss in the context of dopant concentration and defect formation. We use a model for the temperature dependence of the conductivity that takes into account both temperature activation, due to the formation of a transport gap, and Mott variable-range hopping, due to the formation of defects, to further study the electronic properties of the doped films as a function of dose and N ion energy. We find that the temperature activation component dominates the behavior, further indicating that the implanted nitrogen, rather than defects, is responsible the observed result.

[1] C.D. Cress, et al. ACS Nano 10, 3714 (2016).

[2] A.L. Friedman, et al. Phys. Rev. B, 93 161409(R) (2016).

9:40am **2D+MI-ThM6 Metal Contacts to Transition Metal Dichalcogenide Films: Understanding and Avoiding the Formation of a Schottky-like Barrier***, M. Gomez, J. Martinez, M. Valentin, E. Preciado, V. Klee, C. Merida, **Ludwig Bartels**,* University of California - Riverside

We utilize a combination of X-ray photoelectron spectroscopy, transport measurements and optical as well as acoustic excitation to study the impact of the formation of metal contacts to transition metal dichalcogenide films on the electronic structure of the films. Photoelectron spectroscopy permits us to follow the formation of a Schottky-like barriers with increasing metal film thickness on the Angstrom scale. We utilize core level spectroscopy to indicate the evolution of the MoS_2 valence band during metal deposition. Our findings indicate that single layer MoS_2 films adopt the character of the metal (Fermi-level pinning) resulting in a Fermi-level position in the MoS_2 semiconducting gap that is – depending on the metal work function –indicative of a *p*-type semiconductor, even though the native carriers in an MoS_2 film are electrons. As a consequence, metal-TMD-metal junctions may best be understood as *p-n-p* junctions. Numerous ancillary measurements support this hypothesis.

11:00am **2D+MI-ThM10 Multilayer Graphene Suspension Over Millimeter Size Openings and Mechanical Testing***, **Joseph Rowley**, R.F. Davis, R.R. Vanfleet,* Brigham Young University*; J. Abbott,* Moxtek, Inc.

Because of it's high ultimate tensile strength, a single atomic layer of graphene has been able to suspend micron size holes reliably. However, to extend into regimes where devices have dimensions measured in millimeters, a single layer of graphene is insufficient. Films made from a few layers of graphene, although not as strong as pristine single layer graphene, have been shown to still retain a high level of strength. Using chemical vapor deposition on a nickel catalyst, we have fabricated many layer graphene films and suspended these membranes over millimeter size holes. Mechanical properties were measured on suspended films using a custom bulge test instrument.

11:20am **2D+MI-ThM11 Modeling Excitons in Transition-Metal Dichalcogenides***, F. Tseng,* NRC Research Associate*; E. Simsek,* George Washington University*; **Daniel Gunlycke,*** Naval Research Laboratory

Using a triangular lattice exciton (3ALE) model, we explore exciton states in semiconducting monolayer transition-metal dichalcogenides. We show that the hydrogen model for excitons breaks down due to lattice effects and that the excitons are neither Wannier nor Frenkel excitons and instead span an intermediate size regime. The model is formulated on sparse form in direct space, leading to a computationally efficient N log(N) scaling and the ability to calculate over lattice grids with tens of thousands of sites, more than sufficient to converge exciton states in this intermediate exciton regime. In this presentation, we will also discuss the Coulomb potential generated from a dielectric substrate and how the exciton binding energies could be tuned by the thickness and permittivity of an oxide layer.

11:40am **2D+MI-ThM12 Characterization of Collective Ground States in Single-layer NbSe$_2$***, **Miguel M. Ugeda,*** CIC nanoGUNE, Spain*; A.J. Bradley,* University of California at Berkeley*; Y. Zhang,* Advanced Light Source, Lawrence Berkeley National Laboratory*; S. Onishi, W. Ruan, Y. Chen, C. Ojeda-Aristizabal,* University of California at Berkeley*; H. Ryu,* Advanced Light Source, Lawrence Berkeley National Laboratory*; M.T. Edmonds, H.Z. Tsai, A. Riss,* University of California at Berkeley*; S.K. Mo,* Advanced Light Source, Lawrence Berkeley National Laboratory*; D. Lee, A. Zettl,* University of California at Berkeley*; Z. Hussain,* Advanced Light Source, Lawrence Berkeley National Laboratory*; Z.X. Shen,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory*; M.F. Crommie,* University of California at Berkeley **INVITED**

Layered transition metal dichalcogenides (TMDs) are ideal systems for exploring the effects of dimensionality on correlated electronic phases such as charge density wave (CDW) order and superconductivity. In bulk NbSe$_2$ a CDW sets in at T_{CDW} = 33 K and superconductivity sets in at T_c = 7.2 K. Below T_c these electronic states coexist but their microscopic formation mechanisms remain controversial. In this tal I will present the electronic characterization study of a single 2D layer of NbSe$_2$ by means of low temperature scanning tunneling microscopy/spectroscopy (STM/STS), angle-resolved photoemission spectroscopy (ARPES), and electrical transport measurements (1). I will show that 3x3 CDW order in NbSe$_2$ remains intact in 2D. Superconductivity also still remains in the 2D limit, but its onset temperature is depressed to 1.9 K. Our STS measurements at 5 K reveal a CDW gap of Δ = 4 meV at the Fermi energy, which is accessible via STS due to the removal of bands crossing the Fermi level for a single layer. Our observations are consistent with the simplified (compared to bulk) electronic structure of single-layer NbSe$_2$, thus providing insight into CDW formation and superconductivity in this model strongly-correlated system. Furthermore I will show that CDW order is also present in 2D semiconducting TMDs around 1D mirror twin boundaries (2).

(1) M. M. Ugeda, et al., Nature Physics 12, 92 (2016).

(2) S. Barja, et al., Nature Physics, in press (2016).

2D Materials Focus Topic
Room 103B - Session 2D-ThA
Surface Chemistry, Functionalization, Bio and Sensor Applications of 2D Materials

Moderator: Li Tao, The University of Texas at Austin

2:20pm **2D-ThA1 Nanoelectronic Heterodyne Sensor: A New Electronic Sensing Paradigm***, **Zhaohui Zhong**,* University of Michigan, Ann Arbor **INVITED**

Nearly all existing nanoelectronic sensors are based on charge detection, where molecular binding changes the charge density of the sensor and leads to sensing signal. However, there are several fundamental limitations to the charge-detection based electronic sensors. The examples include the ionic screening effect in high ionic strength solution, and the sensitivity-speed tradeoff for vapor phase sensing. In this talk, I will discuss our group's recent works on a new paradigm of electronic sensing by exploring the heterodyne mixing response between the molecular dipole and a nanoscale transistor. First, we successfully demonstrated that the fundamental ionic screening effect can be mitigated by operating single-walled carbon nanotube field effect transistor as a high-frequency heterodyne biosensor. Electrical detection of streptavidin binding to biotin in 100 mM buffer solution is achieved at a frequency beyond 1 MHz. The results should promise a new biosensing platform for point-of-care detection, where biosensors functioning directly in physiologically relevant condition are desired. Second, we demonstrated the concept of nanoelectronic heterodyne sensor for vapor detection in a graphene device. The dipole detection mechanism is confirmed by a plethora of experiments with vapor molecules of various dipole moments, particularly, with cis- and trans-isomers that have different polarities. Rapid (down to 0.1 s) and sensitive (down to 1 ppb) detection of a wide range of vapor analytes is achieved, representing orders of magnitude improvement over state-of-the-art nanoelectronics sensors. Finally, we demonstrated electrical probing and tuning of the non-covalent physisorption of polar molecules on graphene surface by using graphene nanoelectronic heterodyne sensors. Our results provide insight into small molecule-nanomaterial interaction dynamics and signify the ability to electrically tailor interactions, which can lead to rational designs of complex chemical processes for catalysis and drug discovery.

3:20pm **2D-ThA4 Study of the Photoresponse and Transport Properties of Photoexcited Carriers in MoS_2 Nanoflakes for Sensing Applications***, **Sourav Garg**, J. Waters, A. Shahab, M. Singla, S. Kim, P. Kung,* University of Alabama

Although graphene has been widely studied for its 2D properties, its zero band gap nature limits its potential role in semiconducting applications. Molybdenum disulphide (MoS_2) is a semiconductor whose bandgap changes from indirect to direct due to the disappearance of the inversion symmetry when the material is in a monolayer form and in addition this breaking of the symmetry between the K and K' valleys intensifies its use in valleytronic applications. Understanding the correlation between electrical and optical characteristics of MoS_2 is important in order to realize optoelectronic devices based on these materials, including for sensing and biological applications.

In the present work, we investigate and compare the electrical transport characteristics of MoS_2 in monolayer and bilayer forms under the influence of an optical excitation and temperature, through the realization and measurement of MoS_2 interdigitated patterned devices. MoS_2 monolayer and bilayer sheets were synthesized by chemical vapor deposition in an oxygen-free environment on basal plane sapphire substrates. Interdigitated metal contacts were realized using conventional optical lithography with channel lengths ranging from 5 to 10 micrometer. The response of the resulting device was characterized as a function of incident light intensity, wavelength, applied bias, and temperature. We further investigate the impact of these properties on the realization of chemical sensor devices using MoS_2.

4:00pm **2D-ThA6 Surface Engineering with Chemically Modified Graphene and other 2D Materials***, **Paul Sheehan**, SC. Hangarter, W.K. Lee, S.P. Mulvaney, J.T. Robinson, S.D. Tsoi, K.E. Whitener,* US Naval Research Laboratory **INVITED**

Atomically-thin 2D materials such as graphene, boron nitride, or transition metal dichalcogenides can radically alter the chemistry and physics of surfaces they are placed on. Indeed, the appropriate choice of 2D material and subsequent chemical functionalization can dictate all the principal surface forces including van der Waals, acid-base interactions, electric double layers, and even magnetism. For instance, while graphene completely screens the van der Waals forces of the underlying substrate, boron nitride is completely transparent to these forces. A second example is hydrogenation which enables rapid patterning of ferromagnetic domains in graphene. Such control over surface forces should enable us to master technologically critical processes ranging from ice formation to bacterial adhesion to oriented crystal growth. The methods we have developed for chemically functionalizing and patterning graphene will be presented as well as experimental and theoretical work describing how these changes control the various surface forces. Finally, we will discuss a new technique to transfer surface functionalities *in toto* from one substrate to another.

4:40pm **2D-ThA8 Passivation of Transition Metal Chalcogenide Surface *via* Sulfur Layer to Enhanced Metal Contact***, **JunHong Park**,* Univeristy of California, San Diego*; A. Rai,* University of Texas at Austin*; I.J. Kwak,* Univeristy of California, San Diego*; S. Bhattacharjee, K. Ganapathi, N. Bhat,* Indian Institute of Science, Bangalore*; S.K. Banerjee,* University of Texas at Austin*; A.C. Kummel,* University of California, San Diego

The performance of FETs based on transition metal chalcogenide (TMD) is limited by the contact resistance between metal and TMD channels, resulting from the interface degradation during metal deposition on TMDs, metal reaction at defect sites or work function differences between TMDs and metals. In this presentation, the amorphous sulfur layers are formed on MoS_2 to protect the surface of MoS_2 during metal deposition and form an interfacial layer between MoS_2 and metal. The MoS_2 (bulk) flake is emerged into ammonium sulfide 40 % $(NH_4)_2S$ in H_2O at 523 K (technique of Karr et al). Afterwards, the sulfur treated MoS_2 (bulk) is transferred into a UHV chamber to observe the atomic and electronic transformations of the surface *via* scanning tunneling microscopy (STM) and spectroscopy (STS). In the STM and STS, the sulfur-treated surface band gap is measured 1.85 ± 0.03 eV, while the bare MoS_2 bulk has 1.27 ± 0.02 eV band gap, consistent with existence of sulfur layer on MoS_2. Annealing the sample at 623 K for 60 mins results an increase in the band gap to 2.30 ± 0.03 eV. Additional annealing at 793 K of sulfur treated MoS_2 results in observation of crystalline sulfur clusters on MoS_2. However, this sulfur layer can be desorbed from MoS_2 by just direct hearing to 793 K for 1 hr without intermediate step, Afterward, no missing sulfur atoms are observed nor any surface residues; however, there are sulfur clusters inside of the large native defects. The amorphous sulfur layer can be used as interface control for contact deposition. The MoS_2 devices were fabricated to elucidate the impact of sulfur treatments on MoS_2 FETs. After sulfur treatment of multilayer MoS_2, the metal contacts are defined by electron beam lithography and deposition, afterwards the samples were annealed at 673 K for 15 mins. In the electronic measurements, the contact resistance of multilayer MoS_2 and metal decrease to half of non-treated MoS_2 FET. The present sulfur treatment can expand to other TMD materials to improve the contact of TMDs and metal by providing both defect passivation and an interfacial control monolayer to prevent TMDA reaction and an ultrathin metal-sulfide interfacial control layer.

5:20pm **2D-ThA10 Substrate Effects in CVD Synthesized Monolayer WS_2***, **Kathleen McCreary**, A.T. Hanbicki,* Naval Research Laboratory*; G. Kioseoglou,* University of Crete*; M. Currie, B.T. Jonker,* Naval Research Laboratory

The unique electronic band structure in single layer WS_2 provides the ability to selectively populate a desired valley by exciting with circularly polarized light. The valley population is reflected through the circular polarization of photoluminescence (PL). We investigate the circularly polarized PL in WS_2 monolayers synthesized on SiO_2/Si substrates using chemical vapor deposition (CVD).[1] The resulting polarization is strongly dependent on the sample preparation. As-grown CVD WS_2 (still on the growth substrate) exhibits PL emission from the neutral exciton and polarized emission that is unaffected by laser power. Removing WS_2 from the growth substrate and repositioning on the same substrate significantly impacts the optical properties. In transferred films, the excitonic state is optically controlled via high-powered laser exposure such that subsequent PL is from either the charged exciton state or the neutral exciton state, similar to the recently observed behavior in mechanically exfoliated WS_2 flakes.[2] Additionally, the neutral excitonic emission in transferred CVD films exhibits low polarization whereas the trion polarization can exceed 25% at room temperature, demonstrating the ability to optically control the degree of circularly polarized emission. The removal process may modify the strain, sample-to-substrate distance, and chemical doping in the WS_2 monolayer, and work is underway to determine how these factors influence the valley populations. This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AOARD 14IOA018-134141.

[1] K. M. McCreary, A. T. Hanbicki, G. G. Jernigan, J. C. Culbertson, B. T. Jonker, *Sci. Rep.***2016**, *6*, 19159.

[2] M. Currie, A. T. Hanbicki, G. Kioseoglou, B. T. Jonker, *Appl. Phys. Lett.***2015**, *106*, 201907.

5:40pm **2D-ThA11 Driving Mechanochemical Wear on Graphene Using Local Stress and Heat***, S. Raghuraman,* ***Jonathan Felts****,* Texas A&M University

Here we investigate the chemical dynamics of local graphene oxide reduction through the application of local temperature and stress using a heated atomic force microscope (AFM) tip. Specifically, a silicon AFM cantilever with an embedded Joule heater applies both local stress and heat to chemically functionalized graphene surfaces during tip sliding. The friction of the graphene sheet depends linearly on chemical group concentration, so monitoring friction force provides an *in situ* measure of chemical functionality on the surface over time. We demonstrate bond cleavage of oxygen via both local temperature and force during tip sliding on graphene oxide. Monitoring friction change over time for constant tip temperatures between 310 – 355 C and a load of 40 nN provides the kinetics of the reduction process, with an activation energy for bond scission of 0.7 ± 0.3 eV. Measurement noise contributed significantly to error and precluded determination of reaction order. In an effort to reduce measurement time and error, we introduce a new technique, called Scanning Thermal Desorption Microscopy (SThDM). The working principle of SThDM is similar to bulk thermal analysis techniques such as thermogravimetry or differential scanning calorimetry, where thermal kinetics are calculated from mass loss over time during a linear temperature ramp. We demonstrate the technique on graphene oxide during a linear temperature ramp between 50 - 450 C at low mechanical loads, providing an activation energy 0.62 ± 0.07 and a reaction order n ~ 1. Raising the applied load during the temperature ramp shifted the mass loss curve to lower temperatures, due to a lowering of the thermal energy barrier. The results show that the force lowers the energy barrier non-linearly--at odds with current models of mechanochemical atomic attrition found in the literature--where higher loads begin to impede the reaction rate. The results are compared to bulk measurements from the literature and current theoretical models of mechanochemical reactions. Based on the observed energy barriers and reaction order, a diffusion mechanism is proposed.

6:00pm **2D-ThA12 Functionalized Metallic Island Films as Enhancement Substrates for Raman and IR Microscopic Biosensing***, C. Kratz,* Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Germany*; D. Gkogkou, F. Rösicke,* Humboldt-Universität zu Berlin, School of Analytical Sciences Adlershof (SALSA), Germany*; T. Shaykhutdinov, T. Oates, A. Furchner,* Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Germany*; J. Rappich,* Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany*;* ***Karsten Hinrichs****,* Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Germany

Metallic island covered substrates for Surface Enhanced Infrared Absorption (SEIRA) [1] and Surface Enhanced Raman Scattering (SERS) [2] are excellent candidates for enhancement templates in biosensing applications. The specific enhancement behavior of the surfaces is due to their effective optical properties as well as localized and coupled surface plasmon effects. For a detailed understanding of this behavior Au and Ag silver island films on SiO_2/Si with a lateral gradient in size distribution were characterized by IR laser ellipsometry [3] and VIS ellipsometry [4] in combination with numerical and analytical calculations. Along the gradient of the metallic island film, measurements of the IR enhancement of vibrational bands of a Self-Assembling Monolayer adsorbed on the surface as well as a band of the SiO_2 below the island film were performed. The metallic island substrates increase the detection limit and enable new applications, anisotropic substrates allow to separate signals from solvated molecules from adsorbed ones. [2] On the way towards applications as biosensors, the effective and reliable functionalization of these surfaces is an important step. For this we studied a direct electrochemical functionalization of the metal particles from diazonium compounds [5-6] and an indirect route by transferring pre-functionalized graphene sheets to our substrates. [7] For quantitative evaluation the surfaces were characterized in a multi-method approach using UV-VIS ellipsometry, IR ellipsometry, IR microscopy, Raman spectroscopy and IR-AFM.

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[7] F. Rösicke et al, to be submitted.

MEMS and NEMS
Room 102B - Session MN+2D+NS-ThA
Focused Session on Atomic Layer Nanomechanics and 2D MEMS

Moderators: Wayne Hiebert, National Institute of Nanotechnology & University of Alberta, Canada, Max Zenghui Wang, Case Western Reserve University

2:20pm **MN+2D+NS-ThA1 Exploring New Degrees of Freedom by Reducing Dimensions***,* ***Lincoln Lauhon****,* Northwestern University **INVITED**

Nanomechanical resonators fabricated additively from 1-D and 2-D nanomaterials present a wealth of scientific opportunities beyond those of conventional resonators fabricated in a subtractive manner from dielectric thin films. This talk will describe the interesting mechanical behaviors of 1-D VO_2 nanowires and 2-D MoS_2 membranes measured by scanning fiber optic interferometry and modeled using finite element methods. In the first case, nanowire resonators provide a compelling platform to investigate and exploit phase transitions coupled to mechanical degrees of freedom because resonator frequencies and quality factors are exquisitely sensitive to changes in state, particularly for discontinuous changes accompanying a first-order phase transition. To that end, correlated scanning fiber-optic interferometry and dual-beam Raman spectroscopy were used to investigate mechanical fluctuations VO_2 nanowires across the first order insulator to metal transition (*Nano Lett.***14**, 1898 (2014)). Unusually large and controllable changes in resonator frequency were observed due to the influences of domain wall motion and anomalous phonon softening on the effective modulus. In addition, extraordinary static and dynamic displacements were generated by local strain gradients, suggesting new classes of sensors and nanoelectromechanical devices with programmable discrete outputs as a function of continuous inputs. The same interferometric measurement method has been extended to study thermally driven displacements in square few-layer MoS_2 membranes (*Nano Lett.***15**, 6727 (2015)). Mechanical mode frequencies can be tuned by more than 12% by optical heating with the above gap illumination, and modes exhibit avoided crossings indicative of strong inter-mode coupling. When the membrane is optically excited at the frequency difference between vibrational modes, normal mode splitting is observed, and the inter-mode energy exchange rate exceeds the mode decay rate by a factor of 15. Finite element and analytical modeling quantifies the extent of mode softening necessary to control inter-mode energy exchange in the strong coupling regime. The observation of strong coupling suggests the feasibility of coherent control of mechanical modes in TMDs resonators, which would provide novel basis for developing phononic devices or exploring mechanical motions that mimic quantum phenomena.

3:00pm **MN+2D+NS-ThA3 Manipulating Nonlinearities in 2D NEMS***,* ***Akshay Naik****,* Indian Institute of Science, India **INVITED**

Nanoelectromechanical systems (NEMS) are exquisitely sensitive to various stimuli and make fantastic sensors. NEMS devices fabricated using top down fabrication techniques have already demonstrated the ability to measure mass of individual protein macromolecules and their potential use in mass spectrometry applications. NEMS devices fabricated using atomically thin membranes have the potential to bring the resolution of these devices down to single Dalton. However, nonlinearities in these 2D NEMS are quite prominent and can dramatically reduce the dynamic range of these sensors. It is thus imperative to employ strategies to minimize the effect of nonlinearities as well as to exploit them to improve the performance of these devices.

In this talk, I'll present two distinct ways in which we manipulate the nonlinearities in these atomically thin NEMS devices and improve their performance for sensing and oscillator applications. In the first method

we manipulate bias voltages and strain in these devices to partially cancel out the nonlinearities present in the system. In the second method, we exploit the strong coupling between various vibrational modes to initiate internal resonance. The frequency stability, and thus the mass resolution, can be improved by orders of magnitude by operating these devices at internal resonances.

4:00pm **MN+2D+NS-ThA6 Wide Bandgap β-Ga_2O_3 Nanomechanical Resonators***, **Xu-Qian Zheng**, S. Rafique, J. Lee, L. Han, C.A. Zorman, H. Zhao, P.X.-L. Feng,* Case Western Reserve University

Among wide bandgap oxide semiconductors, β-Ga_2O_3 has recently been emerging as a promising candidate for future high-power electronics. Thanks to its direct wide bandgap, E_g≈4.9eV [1,2], power devices made of β-Ga_2O_3 may provide higher breakdown voltage even than that in high-power devices based on mainstream 4H-SiC and GaN materials. In addition to its excellent chemical and thermal stability [1, 2], β-Ga_2O_3 also possesses excellent mechanical properties (Young's modulus, E_Y≈300GPa) [3], providing opportunities for creating next generation nano- and micro-electromechanical systems (NEMS and MEMS) which can be suited for operations in harsh and extreme environments.

In this work, we describe the construction of β-Ga_2O_3 nanosheets and their suspended structures, toward the first demonstration of vibrating β-Ga_2O_3 drumhead nanomechanical resonators. The nanomaterials were synthesized on 3C-SiC film covered Si substrate using a growth temperature of 950°C for 1.5hrs. No metal catalyst was used for the synthesis of the nanomaterials. The nanosheets have a width of ~2-7μm and thickness of ~20-140nm. The crystal structure and the morphology of the nanosheets were investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). From high resolution FESEM image, it was confirmed that the nanosheets originated from the sidewall of the nanorods. The selected area electron diffraction pattern (SAED) taken along the [10-1] zone axis reveals that the synthesized nanosheets are single crystalline β-Ga_2O_3. We investigate the elastic properties and resonant characteristics of such devices, by measuring flexural-mode resonances using ultrasensitive laser interferometry. We fabricate circular drumhead β-Ga_2O_3 resonators with a diameter of ~3μm using a dry transfer technique. Then, by measuring undriven thermomechanical noise spectra of β-Ga_2O_3 resonators, we observe the resonance characteristics of such resonators at 37MHz to 66MHz in high frequency (HF) range with quality (*Q*) factors ranging 100 to 420. In addition, we observe static mechanical behaviors of β-Ga_2O_3. We perform nano-indentation on these drumhead structures using AFM tips to further study the elastic modulus of β-Ga_2O_3. By combining measured elastic properties from resonances and nano-indentation, this study provides quantitative understanding of mechanical properties of β-Ga_2O_3, and paves the way for future nanomechanical devices engineering based on this new crystal.

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4:20pm **MN+2D+NS-ThA7 Nonlinear Mode Coupling and Internal Resonances in MoS_2 Nanoelectromechanical System***, **Chandan Samanta**, P. Gangavarapu, A.K. Naik,* Indian Institute of Science, India

Molybdenum-disulphide (MoS_2), a layered material has attracted attention for nanoelectro- mechanical system (NEMS) applications due to its ultralow mass density and extraordinary mechanical properties. Along with this, its direct band gap of 1.8eV (for monolayer MoS_2) offers the possibility of a new kind of transducer where its mechanical properties can be strongly coupled to its optical properties in visible range. MoS_2-NEMS has been realized recently using optical detection technique. This approach has its own difficulties to drive the resonator into nonlinear regime. On the other hand, mechanical nonlinearities play a crucial role in the performance of NEMS as its dimension shrinks down to atomically thin membrane. A clear understanding of nonlinear effects and the ability to control them are important from both fundamental and application points of view. In this report, we demonstrate fabrication of few layer MoS_2-NEMS and its characterization by three distinct all electrical actuation and detection schemes. We are able to detect multiple vibrational modes in our devices using all the three schemes. We are also able to drive the devices deep into nonlinear regime. Our devices show strong nonlinear coupling between multiple modes. The nonlinear modal coupling is so strong that it leads to multiple internal resonances. Although, there is a report on internal resonance in micromechanical system (MEMS), there is no reported evidence of internal resonance in NEMS made from atomically thin membrane. The observed internal resonances in our devices open the possibility for realizing high stability oscillator in very high frequency range.

4:40pm **MN+2D+NS-ThA8 Very-High-Frequency (VHF) Molybdenum Disulfide (MoS_2) Nanomechanical Resonators Operating in Liquid***, H. Jia, **Rui Yang**, P.X.-L. Feng,* Case Western Reserve University

Micro/nanoelectromechanical systems (NEMS/NEMS) have demonstrated versatile device technologies for sensing applications by exploiting their miniaturized dimensions and increasing sensitivities upon scaling.[1,2] However, quite limited flexural-mode resonators (mostly cantilevers and doubly-clamped beams) have been reported, with only fundamental-modes are often utilized that suffer from very low quality factors (*Q*<5) in viscous media.[3-6]

In this work, we experimentally demonstrate the operation of molybdenum disulfide (MoS_2) nanoscale drumhead resonators (1–5μm in diameter, 50–60nm in thickness) in fluidic environment (water), which exhibit robust multimode resonances in the high- and very-high-frequency (HF/VHF) bands. We observe ~10 flexural modes up to ~150 MHz in water. The *Q* factors can easily exceed 10 for fundamental modes, and achieve as high as ~30 for higher modes.

Atomic-layer MoS_2, an emerging two-dimensional semiconductor, has attracted tremendous attention due to its ultralight weight and high surface-to-volume ratio. These attributes suggest that MoS_2 nanoresonators hold potential for ultrasensitive sensing capabilities even in fluids. Meanwhile, drumhead structure exhibits sealed air cavity and multimode resonance characteristics, which help maintain device performance in liquid.

The MoS_2 resonators are directly immersed in water, and optothermally driven by an amplitude-modulated 405nm diode laser. The multimode resonances are interferometrically read out using a 603nm He-Ne laser. We observe ~10 flexural modes up to ~150 MHz with *Q* factors exceeding 10 for fundamental modes, and reach as high as ~30 for higher modes in water. We attribute the improved resonance performance (higher *f* and *Q*, as compared to cantilever beams) to the drumhead structure consisting of an air cavity on one side. We also demonstrate the degradation of resonance characteristics (*f*, *Q* dramatically drop) if water gradually leaks into the imperfectly-sealed nanodrum cavities.

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2D Materials Focus Topic
Room Hall D - Session 2D-ThP
2D Materials Poster Session

2D-ThP1 Vacuum Properties and Operation Stability of the RFQ Accelerator in J-PARC Linac*, **Takatoshi Morishita**,* Japan Atomic Energy Agency, Japan

The J-PARC accelerator comprises an injector linac, a 3-GeV Rapid-Cycling Synchrotron and a 50-GeV Main Ring. The beam energy of the linac has been upgraded from 181MeV to 400MeV in 2013. For the beam current upgrade, the new frontend (RF ion source, RFQ, chopping system) has been installed for 1MW operation at RCS. The new RFQ, which is designed for 50mA beam acceleration from 0.05MeV to 3MeV, has been high-power tested and beam acceleration tested at the test station before the installation. The existing RFQ, which is 30 mA design, was replaced to 50 mA RFQ in the accelerator tunnel in summer 2014. After two weeks vacuum pumping, the high-power RF conditioning has been started in the middle of September, then, the user operation started in the beginning of November, 2014. Since then, the RFQ operates without serious problems for more than one year, however, the operation stability with beam acceleration was not enough due to the sparking in the RFQ cavity. We consider that the impurities in the vacuum chamber are related to this sparking phenomena. In this paper, the relation between the sparking rates, the residual gas species in the cavity, beam operation parameters are described.

2D-ThP2 Inkjet Printing Of Liquid-Exfoliated, Highly Conducting Graphene Nanosheets*, J. Desai, M. Michel, C. Biswas, R. Hossain, **Jorge Catalan**, A.B. Kaul,* University of Texas at El Paso

Graphene consisting of just one sheet of carbon atoms arranged in a honeycomb lattice is a thinnest two-dimensional (2-D) material known since its discovery in 2004. It finds applications in printed electronics, flexible displays, fuel cells, solar cells and range of other applications due to its high strength and good thermal and electrical properties. Two-dimensional materials are formed from layered materials which can be defined as materials having strong in-plane covalent bonding but weak out-of-plane van der Waals bonding. Exfoliation, i.e., shearing of individual monolayers of layered materials to get two-dimensional materials, can lead to breakage of van der Waals bonding and production of thin atomic two-dimensional nanosheets. Liquid-phase exfoliation refers to exfoliation in suitable solvents. It is a versatile, scalable and sustainable route for production of 2-D nanosheets. Inkjet printing is a material-conserving deposition technique used for printing patterns and devices using liquid-phase materials. The present challenges in printed electronics include finding an appropriate common solvent for exfoliation and printing, printing highly conductive and uniform graphene patterns, preventing nozzle clogging and non-uniform spread of ink on substrate, promoting adsorption and preventing absorption of inks. In our work, we demonstrate highly conductive graphene patterns produced by liquid-phase exfoliation of layered graphite in N-Methyl-2-pyrrolidone (NMP) followed by inkjet printing. We have found an avenue to tailor the viscosity of NMP though the addition of PEDOT: PSS or Poly (3,4 ethylenedioxythiophene)-poly(styrenesulfonate), making it suitable for inkjet printing.. Our ink jet printed dispersions show a uniform microstructure, good optical absorbance values and higher concentration of graphene in our final exfoliated solvent using the novel techniques we have developed.

2D-ThP3 Electronic Transport Properties of Hybrid Graphene-C60 Structures*, S. Chugh, C. Biswas, **Avra S. Bandophadyay**, G. Lara, L. Echegoyen, A.B. Kaul,* University of Texas at El Paso

Since graphene was first mechanically exfoliated in 2004 using scotch tape [1], it has attracted intense interest due to its unique electrical, mechanical and thermal properties. Since then, rapid advances have been made in the large-area deposition of graphene films and its ensuing applications. At the same time, C_{60} fullerenes and their derivative structures also display remarkable chemical reactivity [2]. Various hybrid materials created by organic functionalization of fullerenes have generated intense attention, driven by the possibility of combining some of the outstanding properties of these zero-dimensional materials with those of higher order dimensionality [3]. In this work, we report on the electrophoretic deposition of C60 on the graphene. The synthesized graphene films were characterized using Raman spectroscopy and Scanning Electron Microscopy (SEM), and electrical contacts were made to the graphene flakes of varying sizes using a lift-off process. Then, C60 was synthesized and deposited via an electrophoretic deposition technique. Electronic characterization of the structures was conducted before and after the attachment of C60 over a wide range of temperatures. A comparative study was made to analyze the resistivity and conductivity as a result of the interaction with the Si/SiO2 substrate. Also, we discuss the potential application of graphene based C60 structures as flexible transparent electrodes in photovoltaic devices.

Keywords: Graphene, CVD, Raman Spectroscopy, SEM, electrophoretic deposition, C60

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2D-ThP4 Comparative Study of the Optical and Electrical Properties of Fluorine-doped Tin Oxide Films Obtained by Spray Pyrolysis Techniques*, **Karim Monfil-Leyva**, R.C. Ambrosio-Lázaro, J.A. Luna-López,* Benemerita Universidad Autónoma de Puebla, Mexico*; A.L. Muñoz-Zurita,* Universidad Politécnica Metropolitana de Puebla, Mexico

Research and development of Transparent Conducting Oxides (TCOs) has increased due to their many industrial applications. In particular, Fluorine doped Tin Oxide (FTO) is actually needed to develop semiconductor devices because this material has repeatable optical and electrical properties . This work shows a comparative study of the optical and electrical properties of FTO thin films obtained by electronic spray pyrolysis and ultrasonic spray pyrolysis techniques. A chemical solution for spraying purposes was prepared with stannic chloride (SnCl) dissolved in ethanol ($C_2H_6O_2$) mixed with ammonium fluoride (NH_4F). FTO thin films were deposited on glass substrates varying the distance from the nozzle to the hot plate. Spray pyrolysis system was controlled by an electronic trigger. Ultrasonic pyrolysis system was controlled by a resonant frequency. The transmittance and reflection properties were measured using an UV-Vis Spectrophotometer and the band gap energy was determined. The average transmittance in the visible range of FTO films was even above 85%. All FTO films were characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The X-ray diffraction patterns showed that main growth orientations were [110], [101] and [211]. SEM images showed homogeneous surface on FTO films but they also indicated a change on nano-cluster sizes and density according to the distance from the nozzle to the hot plate and according to the used spray pyrolysis technique. XRD results were used to calculate the grain size and lattice parameters. The chemical composition of the FTO films was also analyzed using Electron Diffraction Scanning (EDS) and the obtained atomic concentration was compared. Sheet resistance was measured using a four points arrangement and the minimum sheet resistance was 14 Ω/square. Optical and electrical results of the FTO thin films showed suitable properties for photovoltaic and optoelectronic applications using fast, cheap and large area deposition techniques.

2D-ThP5 Selective Molecular attachment for 3D Printing of 2D Circuits*, A.T. Juhl, N.R. Glavin, G.M. Leuty, R.J. Berry, R.R. Naik, M.F. Durstock, E.M. Heckman, R.S. Aga, E.B. Kreit,* Air Force Research Laboratory*; **Wenbi Lai**, C. Muratore,* University of Dayton

Recently, we utilized phage display techniques to identify peptides that selectively bind to 2D targets such as electrically conductive graphene and semiconducting MoS_2 in the forms of micro-scale fine powder, bulk crystals, and ultra-thin films (<1.5-5 nm). To examine the nature of peptide binding to these materials, we produced different ‘inks’ comprised of peptide molecules known to selectively bind to each material in solvents for printing on diverse surfaces including SiO_2, gold, and PDMS. Each ink only binds to one type of particle (graphene or MoS_2). We then exposed the substrates printed with peptides to suspensions of 2D particles.The particles demonstrate strong binding to the printed peptide surfaces, demonstrating a new scalable technique for large area device fabrication from 2D materials on diverse surfaces. To further understand peptide-MoS_2 surface binding mechanisms, molecular dynamics simulations employing a newly developed atomic force field predicting the surface energy of MoS_2 films were conducted. Integration of binding peptides into the model in conjunction with experimental results promote fundamental understanding of molecular interactions with MoS_2 and other TMD materials for development of novel sensors and devices.

2D-ThP6 Image Potential State of Graphene on Iridium Modulated by Oxygen Dosing*, **Yi Lin**, Y.Z. Li, J. Dadap, R. Osgood,* Columbia University

Image potential state are an important class of surface states, which can be used to probe the chemical and structural properties of metallic or dielectric crystals. Recently the existence of image states has been reported for graphene and graphene on metal such as the Fauster and

Osgood, Hoefer, and Petek Groups. However, understanding of the effects of adsorbates on Gr surfaces has not been extensively studied either theoretically or experimentally. An important issue is the change of the electronic structure of the image potential states at graphene-mental interface due to oxygen absorption. Thus we have recently carried out the study on the image potential system for graphene on iridium (111) as altered by oxygen dosing.

The epitaxial graphene on iridium is prepared by repeated cycles of temperature programmed growth (room-temperature ethene exposure 2×10^{-5} torr for 45 s and then flashing to 1450 K. This procedure is known to lead to self-limited growth such that exactly one graphene monolayer are formed on the single crystal Iridium substrate (*in situ* cleaned by many annealing and sputtering cycles). The oxygen adsorption is done simply by pure oxygen gas injection by 10^{-5} Torr. The cleanness of the iridium substrate, the growth of monolayer graphene on iridium and the absorption of oxygen are monitored by *in situ* low energy electron diffraction (LEED) patterns. Our 2PPE experiments are conducted using either monochromatic or bichromatic femtosecond pulses with the pump photon energy generally in the 4.2 eV range. An optical parametric amplifier, driven by 250 kHz Ti-sapphire laser, generates tunable laser pulses from 1.5-6.1 eV, pulse duration 90 fs and pulse energy 1 nJ. Photoemission electrons are detected along the M-G-M direction of the Brillouin zone using a spherical-sector energy analyzer with 50 meV energy resolution. Care is taken to prevent distortion of the photo-emitted electron energy distribution by space charge effects.

With this instrument, the state energy, its dispersion and the decay time of the first image potential states of the oxygen-absorbed graphene on iridium are measured. We compare our results of oxygen-dosed graphene on iridium with previous reported results of pure graphene on iridium. The shift of the states, the broadening of the dispersion and the change of the dynamic process are modeled and discussed, which provides new insight on using image states for surface probing, as well as the effects of dosing on image state physics.

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award Contract No. DE-FG 02-04-ER-46157.

2D-ThP7 Raman Spectroscopy and Optical Characterization of Thermoelectric Devices From Ni/Bi_2Te_3/Sb_2Te_3/Ni Thin Films, ***Aschalew Kassu***, *S. Budak, Z. Xiao, R. Hammond, X. Crutcher, A. Sharma,* Alabama A&M University

Thermoelectric devices from Ni/Bi_2Te_3/Sb_2Te_3/Ni thin films were prepared. The thin films are deposited by using DC/RF magnetron sputtering and E-beam deposition systems. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM). Raman spectroscopic technique is used for identification of inherent molecular specificity and analysis of chemical compositions of the films. The resonant features of the scattering spectra measured under the 532 nm and 785 nm wavelength excitation lasers are analyzed.

Acknowledgement

This research was supported by NSF with grant numbers NSF-HBCU-RISE-1546965, NSF-EPSCOR-R-II-3-EPS- 1158862, DOD with grant numbers W911 NF-08-1-0425, and Department of Homeland Security-Scientific Leadership Award, Grant No. DHS-SLA 2014-ST-062-000060

2D-ThP8 Thermoelectric Generators from SiO_2/SiO_2+Au Thin Films For Energy Harvesting, *S. Budak, Z. Xiao, M. Curley,* ***Justin Cole***, *C. Birchfield, M. Howard, B. Rodgers, T. Strong,* Alabama A&M University

Thermoelectric generators were prepared from multinanolayered SiO_2/SiO_2+Au thin films using DC/RF magnetron sputtering system. Thermoelectric devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The prepared devices were characterized using Seebeck coefficient measurement; four probe van der Pauw measurement resistivity and the laser thermal conductivity systems. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM+EDS). TE devices will also be characterized as if they are wave-guides. Mode index, propagation loss, refractive index profile with respect to the dose, depth of the thin films will be analyzed as a function of annealing temperatures.

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, NSF-EPSCOR-R-II-3-EPS-1158862, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

2D-ThP9 Advanced Thermoelectric Devices from Ni/Bi_2Te_3/Sb_2Te_3/Ni Thin Films for Energy Harvesting, *S. Budak, Z. Xiao, M. Curley,* ***Cody Birchfield***, *J. Cole, M. Howard, B. Rodgers, T. Strong,* Alabama A&M University

Thermoelectric devices were prepared from Ni/Bi_2Te_3/Sb_2Te_3/Ni thin films using E-beam deposition and DC/RF magnetron sputtering systems. Fabricated devices were annealed at different temperatures to form nanostructures in the multilayer thin films to increase both the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. The thermoelectric devices were characterized using Seebeck coefficient measurement system; four probe van der Pauw measurement resistivity system and the laser thermal conductivity system. The surface morphology of the fabricated thermoelectric films is characterized using Scanning Electron Microscope (SEM). TE devices will also be characterized as if they are wave-guides. Mode index, propagation loss, refractive index profile with respect to the dose, depth of the thin films will be analyzed as a function of annealing temperatures.

Acknowledgement

Research was sponsored by NSF with grant numbers NSF-HBCU-RISE-1546965, NSF-EPSCOR-R-II-3-EPS-1158862, DOD with grant numbers W911 NF-08-1-0425, and W911NF-12-1-0063, U.S. Department of Energy National Nuclear Security Administration (DOE-NNSA) with grant numbers DE-NA0001896 and DE-NA0002687.

2D-ThP10 VUV-photoassisted Chemical Doping on Graphene Oxide, ***Masahiro Soga***, *Y. Tu, T. Utsunomiya, T. Ichii, H. Sugimura,* Kyoto University, Japan

Chemical doping on graphene and its derivatives is a powerful technique for modulating their electronic properties[1]. Especially, nitrogen doping can help the electron transfer and enhance the electrocatalytic activity. Nitrogen doped graphene have been synthesized by thermal annealing approach and hydrothermal reduction of graphene oxide (GO) in the presene of N_2H_4 and NH_3 in general[1, 2]. However, these methods are high cost, complicated and suffer from toxic chemicals. In this research, nitrogen doped and reduced graphene oxide (N-rGO) was synthesized by vacuum ultraviolet (VUV) irradiation.

Colloidal dispersion of GO sheets was prepared by the modified Hummers' method. NH_3 aqueous solution (14.8 M) was added to the GO dispersion and was magnetically stirred for 24 hours. After that, the dispersion was centrifuged at 13.5 krpm for 10 min and washed ten times with ultra pure water, and then aqueous dispersion of nitrogen modified GO (N-GO) was obtained. the N-GO dispersion was spincoated on Si substrate and VUV light (λ = 172 nm, 10 mW cm^{-2}) was irradiated on this sample under high vacuum condition (< 10^{-3} Pa) for 64 min. The sample were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS).

XPS and FT-IR analysis of the samples revealed that chemically reactive oxygen functional groups in a GO sheet reacted with ammonia and the formation of C-N bond proceeded after stirring in NH_3 aqueous solutiom. After VUV irradiation, XPS and FT-IR analysis showed that N-GO was reduced and bonding configuration of nitrogen was changed.

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2D-ThP11 Tungsten Diselenide Nanoribbons Formed by Focused Helium Ion Beam Induced Etching, ***Michael G. Stanford***, *P.R. Pudasaini, A.T. Wong, A. Hoffman, D.G. Mandrus, P.D. Rack,* The University of Tennessee Knoxville

The helium ion microscope (HIM) has garnered much attention in recent years due to its high resolution and precision as a nanoprocessing tool. In this work, we introduce a focused helium ion beam induced etching (FIBIE) process which enables direct-write patterning of WSe_2. The etching process utilizes the XeF_2 precursor molecule to provide a chemical etch assist for rapid material removal. The FIBIE process enables the high fidelity patterning of WSe_2 with He^+ doses an order of magnitude lower than standard He^+ milling procedures. Of particular interest, transition metal dichalcogenide (TMD) nanoribbons exhibit unique magnetic properties depending upon edge termination. However, few experimental studies have been conducted on TMD nanoribbons due to difficulty of fabrication.

The FIBIE process enables the straightforward direct-write fabrication of aligned arrays of WSe_2 nanoribbons with dimensions as low as 8 nm. The WSe_2 nanoribbons demonstrate high optical anisotropy and electrical measurements are reported for the first time. We also study the magnetic properties and report magnetoresistance of devices fabricated from WSe_2 nanoribbon arrays.

2D-ThP12 Tuning the Electronic Structure of Metallic Single Crystal Surfaces through Ultra Thin Hetero-Junctions for Photocathode Applications*, **ZhengRong Lee**, R. Seibert, D. Velázquez, L. Spentzouris, J. Terry,* Illinois Institute of Technology

The development of photocathodes for the next generation of state-of-the-art laser-driven photoinjectors requires the use of photoemissive materials with specific characteristics depending upon their application (FELs, ERLs, Wakefield acceleration, etc.). The ability to tune the emissive properties of photocathodes to match the requiremets of the specific accelerator device could have a important impact in research and development. In this work we show that such photoemissive tunability can be achieve thorugh the engineering of single crystal metallic surfaces by coating them with metal-insulator heterojunctions of various thicknesses. Ultrathin multilayered MgO/Ag(001)/MgO films were grown by pulsed laser deposition, tuning the thickness n of the flanking MgO layers to 0, 2, 3, and 4 monolayers. We observed an increase in quantum efficiency and simultaneous decrease in work function with layer thickness. The scale and trend direction of measurements are in good but not excellent agreement with theory. Angle resolved photoemission data for the multilayered sample n = 3 showed that the emission profile has a metallic-like momentum dispersion. Deviations from theoretical predictions [K. Németh et al., PRL 104, 046801 (2010)] are attributed to imperfections of real surfaces in contrast with the ideal surfaces of the calculation.

2D-ThP13 Electronic Structure of Bulk WSe_2 and Multilayer WS_2*, **Iori Tanabe**,* University of Nebraska-Lincoln*; T. Komesu,* University of Nebraska - Lincoln*; E.F. Schwier,* Hiroshima Synchrotron Radiation Center*; M. Gomez, L. Bartels,* University of California - Riverside*; M. Zheng, Y. Kojima,* Hiroshima University*; E.M. Echeverria,* University of Nebraska-Lincoln*; A.V. Barinov, S.K. Balijepalli, V. Kandyba,* Elettra - Sincrotrone Trieste*; K. Shimada,* Hiroshima Synchrotron Radiation Center*; P.A. Dowben,* University of Nebraska - Lincoln

WSe_2 and WS_2 and the related transition metal dichalcogenides (TMDs) MX_2 (with M = V, Mo, W, Ta and X = S, Se, Te) are layered structures, where each plane consists of a hexagonal honeycomb lattice reminiscent of graphene or graphite. The distinguishing features of TMDs compared to graphene are that TMDs are semiconductors and TMDs monolayers have C_{3v} symmetry, not C_{6v} symmetry, since the metal and chalcogen planes are offset from each other. We investigated the valence band structure of bulk WSe_2 and multilayer WS_2 using angle resolved photoemission spectroscopy (ARPES). These ARPES studies of the electronic band structure of bulk WSe_2 and multilayer WS_2 provide a means to compare the effective hole mass and the splitting of the top of the valence band at K, due to spin-orbit coupling for various transition metal dichalcogenides. The splitting of the top of the valence band at K was measured to be 0.49±0.01 eV and 0.42±0.03 eV, for bulk WSe_2 and multilayer WS_2 respectively. In both cases, the splitting due to spin orbit coupling are far larger than that for MoS_2, but smaller than that for monolayer WSe_2. We found that the effective mass at the top of the valence band at K of WSe_2 and WS_2 were very small, which indicates very high intrinsic mobility and is consistent with expectations from density functional theory. The electron effective masses, as derived from angle-resolved inverse photoemission, are found to be much greater than anticipated.

2D Materials Focus Topic
Room 103B - Session 2D+NS-FrM

2D Materials: Device Physics and Applications

Moderator: Miguel M. Ugeda, CIC nanoGUNE, Spain

8:20am **2D+NS-FrM1 Direct Writing of 2D Flexible Electronic Devices via Illumination-based Techniques***, M.E. McConney, N.R. Glavin, A.T. Juhl,* Air Force Research Laboratory*; J.E. Bultman, J.J. Hu,* University of Dayton Research Institute/Air Force Research Laboratory*; M.F. Durstock,* Air Force Research Laboratory*; A.A. Voevodin,* University of North Texas*; **Christopher Muratore**,* University of Dayton

Ultra-thin two-dimensional (2D) semiconducting materials possess a combination of large, tunable electronic bandgaps, optical transparency, and mechanical flexibility, and will likely revolutionize electronic devices such as wearable sensors and flexible displays. A primary step in the development of such devices with integrated 2D materials is the development of scalable, transfer-free synthesis over large areas at low temperatures. Electrically insulating amorphous transition metal dichalcogenide (TMD) films can be deposited via physical vapor deposition on large area flexible substrates at room temperature, and crystallized with subsequent illumination with light. Focused laser light with a power density of ~1 kW $cm^2$is suitable for writing micron scale features in semiconducting transition metal dichalcogenides on polymer substrates. Broad band illumination from a xenon lamp can also be used over the large substrate areas (> 100 cm^2), or passed through a physical mask to print features only in desired locations. The semiconducting properties of 2D MoS_2 and WS_2 materials synthesized in this way have been characterized using conductive atomic force microscopy, and other techniques to observe the expected temperature dependence on electrical conductivity. Structure and composition of the materials can be controlled by altering the incident fluence as well as by controlling the ambient environment during illumination, as verified by Raman spectroscopy, X-ray photoelectron spectroscopy, cross-sectional and plan view transmission electron spectroscopy, and other techniques. Multiple layers of 2D materials can also be treated in this way. For example, both layers in a MoS_2/WS_2 heterostructure of 10 nm total thickness on a polymer (PDMS) substrate were crystallized upon laser illumination. Diverse 2D architectures and devices built from illumination-based crystallization techniques will be highlighted.

8:40am **2D+NS-FrM2 Resolving and Tuning Mechanical Anisotropy in Black Phosphorus Nanoelectromechanical Resonators***, **Zenghui Wang**, H. Jia, P.X.-L. Feng,* Case Western Reserve University

Black phosphorus (P) has emerged as a layered semiconductor with unique crystal structure featuring corrugated atomic layers and strong in-plane anisotropy in its physical properties. In particular, it is predicted to exhibit strong in-plane mechanical anisotropy, which shall lead to previously inaccessible dynamic responses in resonant 2D nanostructures [1], and new opportunities for studying carrier-lattice interaction in atomic layers. It is therefore of both practical and fundamental importance to systematically investigate the mechanical anisotropy in black P crystal and NEMS devices.

Enabled by the first demonstration of black P resonant nanostructures [2] with multimode responses, we show that the spatial mapping of the multimode resonance mode shapes [3] creates a new means for precise determination of black P crystal orientation (*i.e.*, the anisotropic zigzag and armchair axes) [4] . Further, the multimode technique enables simultaneous quantification of the anisotropic mechanical properties (*i.e.*, elastic moduli along both major crystal axes): combined with finite element method (FEM) modeling, we determine the Young's moduli of multilayer black P to be 116.1 GPa and 46.5 GPa in zigzag and armchair directions, respectively. In addition, we demonstrate that electrostatic gating induced straining can continuously tune the mechanical anisotropic effects on multimode resonances in black P electromechanical devices. Our results show that multimode resonant response manifests the unique mechanical anisotropy effect in black P nanodevices, and provides a new method for determine the material's crystal orientation and elastic properties *in situ*, independent from conventional optical, electrical, and nanoindentation calibration techniques.

[1] Wang, Z. & Feng, P. X.-L. Design of Black Phosphorus 2D Nanomechanical Resonators by Exploiting the Intrinsic Mechanical Anisotropy. *2D Materials* **2,** 021001 (2015).

[2] Wang, Z., Jia, H., Zheng, X.-Q., Yang, R., Wang, Z., Ye, G.J., Chen, X.H., Shan, J., & Feng, P. X.-L. Black Phosphorus Nanoelectromechanical Resonators Vibrating at Very High Frequencies. *Nanoscale.* **7**, 877 (2015).

[3] Wang, Z., Lee, J., & Feng, P. X.-L. Spatial Mapping of Multimode Brownian Motions in High Frequency Silicon Carbide (SiC) Microdisk Resonators. *Nature Communications* **5**, 5158 (2014).

[4] Wang, Z., Jia, H., Zheng, X.-Q., Yang, R., Ye, G.J., Chen, X.H., & Feng, P. X.-L. Resolving and Tuning Mechanical Anisotropy in Black Phosphorus via Nanomechanical Multimode Resonance Spectromicroscopy. *under review.* (2016).

9:00am **2D+NS-FrM3 2D Devices for Flexible and Topological Nanoelectronics***, **Li Tao**, W. Zhu, D. Akinwande,* The University of Texas at Austin **INVITED**

Two-dimensional (2D) buckled atomic sheets, such as silicene and phosphorene, yield collective properties of mechanical flexibility and tunable bandgap, which hold promise for advanced flexible and topological nanoelectronics. Silicene is the 2D silicon equivalent of graphene, and is predicted to offer a host of exotic electrical properties, such as quantum spin Hall effect, subjected to external fields. Despite great theoretical expectations on silicene, air-stability had prevented experimental device studies. Recently, our research progress debuts silicene transistors corroborating theoretically predicted ambipolar transport with Dirac band structure. Electrostatic characterization on non-optimized silicene transistors exhibited carrier mobility ~100 cm^2/V-s and 10× gate modulation in ambient condition. Without non-ideal limiting factors, e.g. phase boundary scattering and electron-phonon coupling, pristine free-standing silicene is predicted to offer intrinsic mobility ~1200 cm^2/V-s. Further optimization is on-going to shed light on the mobility upper bound achievable and aging evolution of silicene devices. It is likely with further experimental study that monolayer or multilayer silicene can be a platform for realizing advanced device concepts, e.g. topological bits, on flexible substrates. The unique allotropic affinity of silicene with crystalline bulk silicon suggests a more direct integration with ubiquitous semiconductor technology.

Phosphorene, few-layer black phosphorus (BP), is another promising candidate for flexible nanoelectronics. Phosphorene exhibits high carrier mobility (100 to 1000 cm^2/Vs) and tunable direct bandgap (0.3 to 2eV) even on plastic substrates, making it the most suitable contemporary 2D semiconductor that combines the merits of graphene and transitional metal dichalcogenides. We reported the first BP based flexible RF transistors with intrinsic f_T=20 GHz and f_{Max}=14.5 GHz, and such performance sustained under ex-situ bending test with tensile strain up to 1.5%. Raman spectroscopy analysis of few-layer BP under tensile strain up to 7% was carried out for the first time to reveal the strain effect on BP. Significant orientation dependence was observed while applying tensile strain along armchair (AC) and zigzag (ZZ) directions, exhibiting the trend of Raman peak shift well agreed with theoretical projections. This recent progress on silicene and phosphorene represent a renewed opportunity for future nanoscale flexible and topological electronics beyond what is available in graphene.

9:40am **2D+NS-FrM5 Optical Detectors Based on Bismuth Telluride Nanowire Arrays Capped by Graphene***, **Tito Huber**, T. Brower, O. Abana,* Howard University

Recently, research on graphene based photodetectors has drawn substantial attention. The gapless nature of graphene and low light absorption can cause low responsivity. The synergetic integration of graphene with other materials is a promising approach to overcome these shortcomings. There have been reports of broadband photodetectors based on heterostructructures of few-layer Bi(2)Te(3)/graphene devices that are very encouraging. Here we discuss a different approach, where single layer graphene caps the top of a bismuth telluride nanowire array (where the wire axis are perpendicular to the graphene surface) . Partially, our motivation was to test the exceptional thermoelectric properties of the interface. The room-temperature thermoelectric efficiencies of bismuth telluride compounds are the highest reported for any material, and, therefore, Bi(2)Te(3) nanowires are interesting as building blocks of nanoscale thermoelectric devices, as in this case. Graphene strong photothermoelectric response is also very well known. We employed devices composed of bismuth telluride nanowire arrays which are capped with single layer graphene. Dense arrays of 200-nm nanowires have been prepared by a nonlithographic fabrication technique consisting of the pressure injection of an alumina template with molten Bi_2Te_3, a method that can be successfully employed with 100-µm thick templates of pore diameters in the range of 2 to 200 nm. Bismuth telluride is a semiconductor with a small gap. The nanowire arrays electronic properties including magnetotransport and thermopower were characterized in separate experiments. The single layer graphene layer was fabricated by transfer by Graphenea. Graphene on the device was characterized using Raman spectroscopy. We observed the D, G and 2D peaks and broadening indicating that graphene is nearly intact. We also observed the Raman peaks of bismuth telluride. The incident surface features very low optical reflectivity and enhanced light trapping. Light trapping causes strong light absorption at the interface, an effect that counteracts the weak absorption of graphene and has not been mentioned in the literature before. The unique attributes of the thermoelectric arrays are the combination of strong temporal and optical wavelength dependences of the photocurrent. Under infrared illumination, the signal can be completely described by thermoelectric effects considering cooling rates given by heat diffusion through the array. We will discuss that, in addition, under visible illumination we observe a photovoltaic response. This work was supported by the National Science Foundation through PRDM 1205608 and STC 1231319

10:00am **2D+NS-FrM6 Graphene Nanoelectromechanical Resonators with Eletrothermal Excitation and Tuning***, F. Ye,* ***Jaesung Lee****, P.X.-L. Feng,* Case Western Reserve University

Graphene, a hallmark of two-dimensional (2D) materials, has been employed as an atomically thin building block for highly miniaturized nanoelectromechanical system (NEMS) and shown attractive potential for nanoscale actuators and sensors. Thanks to its exceptional elastic modulus (E_Y~1TPa), ultralow mass density (r~2200kg/m^3), and superior strain limits (e_{limit}~25%) [1], high performance and frequency tunable graphene resonators have been demonstrated using photothermal [2] and electrostatic actuation [3] schemes. In addition to excellent mechanical properties, graphene possesses high temperature stability [4] and negative thermal expansion coefficient [5], hence graphene resonators may inherently exhibit better performance under high temperature. In existing reports, graphene resonators are exposed in high temperature using annealing or Joule heating (*e.g,*, applying up to 1.8V from drain to source) only for thermal annealing [3], high temperature operation of graphene resonators has not been demonstrated yet.

In this work, we fabricate mono- and bi-layer (1L and 2L) graphene resonators and investigate their resonance characteristics at high temperature up to ~500 K using Joule heating. We conveniently use DC voltage to heat graphene resonators, and apply AC voltage to excite resonance motion. Then, we simultaneously measure temperature and resonance characteristic of graphene resonators using a home-built, integrated Raman spectroscopy and laser interferometry measurement system. We first test electrothermal frequency tuning and find that frequency of graphene resonators upshift from ~80MHz to ~86MHz as DC voltage increases from 0.5V to 2.5V. Unlike electrostatic force resonance tuning and excitation [3], we do not observe capacitive softening or loaded *Q* effects which may compromise performance of resonators. We then investigate mechanical nonlinearity of graphene resonators in high temperature by changing both DC and AC voltage. This study opens new capabilities for engineering tunable graphene NEMS resonators and oscillators for a number of emerging applications.

[1] C. Lee, *et al.*, *Science***321**, 385-388 (2008).

[2] J. S. Bunch, *et al.*, *Science.***315**, 490-493 (2007).

[3] C. Chen, *et al.*, *Nat. Nanotech.***4**, 861-867 (2009).

[4] K. Kim, *et al.*, *Phys. Status Solidi RRL***4** 302-304 (2010).

[5] M. Pozzo, *et al.*, *Phys. Rev.Lett.***106** 135501 (2011).

10:20am **2D+NS-FrM7 Pushing the Performance Limit of 2D Semiconductor Transistors***,* ***Xiangfeng Duan****,* California Nanosystems Institute, University of California, Los Angeles **INVITED**

Two-dimensional semiconductors (2DSCs) such as MoS_2 have attracted intense interest as an alternative electronic material in the post-silicon era. However, the on-current density achieved in 2DSC transistors to date is considerably lower than that of silicon devices. It remains an open question whether 2DSC transistors can offer competitive performance. To achieve a high performance (high on-current) device requires (1) a pristine channel with high carrier mobility, (2) an optimized contact with low contact resistance and (3) a short channel length. The simultaneous optimization of these parameters is of considerable challenge for atomically thin 2DSCs since the typical low contact resistance approaches either degrade the electronic properties of the channel or are incompatible with the fabrication of short channel devices. Here I will first review different strategies that have been developed to optimize these factors, and discuss how we can combine these strategies together to achieve high performance 2DSC semiconductor transistors. In particular, we will discuss a unique approach towards high-performance MoS_2 transistors using a physically assembled nanowire as a lift-off mask for creating ultra-short channel devices with pristine MoS_2 channel and self-aligned low resistance metal/graphene hybrid contact. With the optimized contact in short channel devices, we demonstrate that a sub-100 nm MoS_2 transistor can deliver a record a high on-current density comparing well with that of silicon devices, demonstrating thte exciting potential of 2DSCs for future electronic applications.

11:00am **2D+NS-FrM9 Low Temperature Al_2O_3 ALD on 2D Semiconductors***,* ***Il Jo Kwak****, J.H. Park, A.C. Kummel,* University of California at San Diego

2D semiconductors have attracted attention for future electronic devices due to their excellent electronic and optoelectronic properties. These devices require few nanometer thick and pin hole-free dielectric layers as gate insulators. However, due to the inert nature of 2D semiconductors such as graphene and Transition Metal Chalcogenides (TMDs), the dielectric layer selectively nucleates on defect sites or step edges. In the conventional atomic layer deposition (ALD) process on graphene or other 2D semiconductors, such non-uniform oxides result in large leakage currents in 2D semiconductor based device. Therefore, for successful integration into device, uniform and insulating gate oxides on 2D semiconductors should be prepared.

In this work, Al2O3 was directly deposited on HOPG and MoS2 surface by low temperature ALD with trimethylaluminum(TMA) and H2O or O3 without any seeding layer or surface treatments. Using short purge time between two precursor pulses at 50C, a CVD growth component was intentionally induced to provide more nucleation sites on the surface. The CVD growth component induces deposition of 1 nm Al2O3x particles on the surface which provide a uniform layer of nucleation centers. Before ALD, HOPG and MoS2 samples were cleaned by mechanical exfoliation method. For HOPG substrate, 50 cycles of ALD Al2O3 was deposited at 50C using 600ms of TMA and 50 ms of H2O pulse time with 500ms purge time between two pulses. In the case of MoS2, 300ms of O3 pulse was employed instead of H2O pulse. The same ALD recipes were performed on SiGe substrates in order to compared the quality of the oxide. After ALD process, MOSCAP devices were fabricated to measure the capacitance and leakage current of the oxide. Non-contact mode AFM was performed to check the topography of the oxide and the results showed that uniform and pin hole-free oxide layer was formed on the surface. The leakage current of the oxide on HOPG and MoS2 was as low as 10^{-5} A/cm^2 which was comparable to the oxide on SiGe substrates.

11:20am **2D+NS-FrM10 Atomic Layer Deposition of High-k Dielectrics on WSe_2 for High Performance Electronic Devices***,* ***Pushpa Raj Pudasaini****, M.G. Stanford, A. Hoffman,* The University of Tennessee Knoxville*; T.Z. Ward,* Oak Ridge National Laboratory*; D.G. Mandrus, P.D. Rack,* The University of Tennessee Knoxville

The performance of electronic and optoelectronic devices based on two-dimensional (2D) transition metal dichalcogenides (TMDs), such as tungsten diselenide (WSe_2) is significantly affected by the quality of the various interfaces present in the device. Historically, the performance of bottom-gate SiO_2 2D TMDs field effect transistor (FET) devices has been greatly limited by the carrier scattering due to the oxide trapped charges, surface roughness, and surface optical phonons, among others. One approach to mitigate this issue is to explore alternatives to SiO_2 which ideally would involve high-κ dielectrics, in which Coulombic impurity scattering is confirmed to be strongly shielded by the dielectric screening.

However, depositing high quality high-k dielectric film onto the surfaces of TMDs is very challenging due to the chemical inertness of the TMD basal planes. Here, we present an aluminum oxide and hafnium oxide top-gate on WSe_2, deposited using atomic layer deposition (ALD) both with and without hydrogen/oxygen plasma treatments and titanium seed layers. The top gated WSe_2 FET devices are fabricated by employing ALD deposited high k-dielectrics, with promising device characteristics having large current on-off ratio (~10^8), small threshold voltage (~5V) and relatively large field effect mobility (~70 cm^2/V.s) at room temperature. A high performance logic invertor device is also demonstrated.

11:40am **2D+NS-FrM11 Layer-dependent Measurements of Electronic Band Alignment for Individual MoS_2 Flakes Supported on SiO_2 using Photoemission Electron Microscopy (PEEM) with Deep Ultraviolet Illumination***, Morgann Berg,* Sandia National Laboratories*; K. Keyshar,* Rice University*; I. Bilgin, F. Liu,* Northeastern University, Los Alamos National Laboratory*; H. Yamaguchi,* Los Alamos National Laboratories*; R. Vajtai,* Rice University*; C. Chan,* Sandia National Laboratories*; G. Gupta,* Los Alamos National Laboratories*; S. Kar,* Northeastern University*; P. Ajayan,* Rice University*; T. Ohta,* Sandia National Laboratories*; A. Mohite,* Los Alamos National Laboratories

Tailoring band alignment layer-by-layer using heterojunctions of two-dimensional (2D) semiconductors is an attractive prospect for producing next-generation electronic and optoelectronic devices that are ultra-thin, flexible, and efficient. 2D layers of transition metal dichalcogenides (TMDs) in laboratory devices have already demonstrated properties favorable for electronic and optoelectronic applications. Despite these strides, a systematic understanding of how band alignment evolves from monolayer to multilayer for MoS_2, a model TMD system, is still missing owing to the lack of a suitable experimental approach. Quantitative determination of the electronic band alignment necessitates that measurements be performed in a controlled environment (such as vacuum) using a substrate that interacts minimally with the overlying TMDs (preferably insulating) to suppress the electronic influence of supporting substrates and prevent chemical modification of TMDs due to adsorbates (primarily water).

Here we report on the local band alignment of monolayer, bilayer, and tri-layer MoS_2 on a 285-nm-thick SiO_2 substrate, measured using a new approach to probe the occupied electronic states based on photoemission electron microscopy with deep ultraviolet excitation. The spatially-resolved, simultaneous measurements of the vacuum level and the valence band edge at the Brillouin zone center show that the addition of layers to monolayer MoS_2 increases the relative work function, and pushes the valence band edge toward the vacuum level. We also find n-type doping of few-layer MoS_2 and type-I band alignment across monolayer-to-bilayer and bilayer-to-trilayer lateral junctions. Our results differ from some earlier reports based on Kelvin probe and scanning photocurrent microscopies [Sci. Reports, 5, 10990 (2015), Nano Lett., 15, 2278 (2015)], and highlight the strong influence of environmental effects on the band alignment in MoS_2 homojunctions. We are now applying this exciting new metrology to systematically examine the ionization energies of a series of TMDs. The results will provide fundamental information necessary to assess the band alignments of TMD heterojunction devices, and to validate or refine existing theoretical predictions [APL, 103, 053513 (2013), J. Phys. Chem. C, 119, 13169 (2015)].

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12:00pm **2D+NS-FrM12 Visualizing Light Scattering in Silicon Waveguides with few-layer Black Phosphorous Photodetectors***, **Tianjiao Wang**, S. Hu,* Vanderbilt University*; B. Chamlagain, Z. Zhou,* Wayne State University*; S.M. Weiss, Y. Xu,* Vanderbilt University

We investigate the light scattering properties of a silicon nanobeam waveguide through wavelength- and polarization-dependent scanning photocurrent measurements of a black phosphorus (BP) photodetector on top of the silicon waveguide. The measured photocurrent responses exhibit similar patterns as the light intensity distribution calculated by finite-difference time-domain simulations, suggesting that the light scattering properties of the waveguide can be detected as photocurrent signals by the BP photodetector. Interestingly, no photocurrent signals are observed when the incident photon energy is below the bandgap of silicon, indicating that the photocurrent response generated in the BP photodetector is mainly attributed to the photo-excited electron-hole pairs in the silicon waveguide which can be injected into the BP and dominate its photocurrent generation. Our experimental results suggest that two dimensional (2D) material based photodetectors can offer an effective approach to visualize the light scattering properties of photonic structures by photocurrent mapping, which not only opens up avenues for learning about light matter interaction of photonic structures but also provides a way of engineering future 2D material based optoelectronic devices with integrated photonic structures.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index