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.

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

[2] A.T. Hanbicki, G. Kioseoglou, M. Currie, C.S. Hellberg, K.M. McCreary, A.L. Friedman, and B.T. Jonker, Sci. Rep. **6**, 18885 (2016).

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

[1] J.C. Johannsen et al., Physical Review Letters 111, 027403 (2013).

[2] S. Ulstrup et al., Physical Review Letters 112, 257401 (2014)

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

[4] A. Grubisic Cabo et al., Nano Letters, 15, 5883 (20150).

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:

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References:

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[2] M. Neek-Amal, P. Xu, J.K. Schoelz, M.L. Ackerman, S.D. Barber, P.M. Thibado, A. Sadeghi, and F.M. Peeters, Nature Comm. **5**, 4962 (2014).

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