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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[2] M. N. Ali, *et al.*, *Nature***514**, 205-208 (2014).

[3] P. L. Cai, *et al.*, *Phys. Rev. Lett.* **115,** 057202 (2015).

[4] L. Wang, *et al.*, *Nat. Comm.***6**, 8892 (2015).

[5] X.C. Pan, *et al.*, *Nat. Comm.***6**, 7805 (2015).

[6] J. Lee *et al., Nanoscale*. **8**, 7854–7860 (2016).

[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 $2.61 \leq x \leq 2.72$. 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]

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[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)

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