2D Materials

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

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

Moderator: Sanghoon Bae, Massachusetts Institute of Technology

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

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

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

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

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

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

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

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

We present our work on dispersions of WS_2 and h-BN using cyclohexanone and terpineol (C/T) as the solvent to subsequently print prototype nanodevices. Current-voltage measurements, Raman spectroscopy, and photoluminescence spectroscopy were used to characterize the properties of these inks produced by various sonication techniques such as horn tip sonication, magnetic stirring and shear mixing. Both photodetector and capactive heterostructure devices were formed with these materials. From this analysis, the photoresponsivity and detectivity of the graphene-WS_2-graphene heterostructure devices were calculated to be ~ 0.86 A/W and ~ 10^{13} J, respectively. Capacitance-voltage (*C*-*V*) and *C*-frequency (*f*) measurements were also conducted, where the *V* was swept from – 6 V to + 6 V, while the change in *C* was measured from *f* ~ 20 kHz up to 3 MHz to gain insights into the nature of the graphene-WS_2 interface. An all-inkjet-printed graphene-h-BN-graphene capacitors were fabricated and leakage current density, $J_{Leakage}$, of up to ~ 0.072 μA/mm^2 and *capacitance density* of up to ~ 2.4 μF/cm^2 is reported. Finally, the influence of temperature, frequency, and LED illumination on the performance of the graphene-h-BN-based capacitor is explored with the help of *capacitance density*-voltage measurements at different parameters to promote the all-inkjet-printed capacitor for photosensitive detector applications.

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

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

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

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

11:20am **2D+EM+MI+NS-MoM10 Ultrasoft Slip-mediated Bending in Few-layer Graphene***, **Jaehyung Yu**, E. Han, E. Annevelink, J. Son, E. Ertekin, P.Y. Huang, A.M. van der Zande,* University of Illinois at Urbana-Champaign

A challenge and opportunity in nanotechnology is to understand and take advantage of the breakdown in continuum mechanics scaling laws as systems and devices approach atomic length scales. Such challenges are particularly evident in two-dimensional (2D) materials, which represent the ultimate limit of mechanical atomic membranes as well as molecular electronics. For example, after more than a decade of study, there is no consensus on the bending modulus of few layer graphene, with measured and predicted values ranging over two orders of magnitude, and with different scaling laws. However, comparing these studies is challenging because they probe very different and often fixed curvatures or magnitudes of deformation. To unravel the discrepancy, a systematic measurement of bending stiffness versus deformation is needed. The results have practical implications on predicting and designing the stiffness of many 2D mechanical systems like origami/kirigami nanomachines, stretchable electronics from 2D heterostructures, and resonant nanoelectromechanical systems.

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

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

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