

# Friday Morning, November 3, 2017

## 2D Materials Focus Topic

Room: 15 - Session 2D+MI+NS+SS+TF-FrM

### Nanostructures including Heterostructures and Patterning of 2D Materials

**Moderators:** Huamin Li, University of Buffalo, SUNY, Arkady Krasheninnikov, Helmholtz Zentrum Dresden-Rossendorf, Germany

8:20am **2D+MI+NS+SS+TF-FrM1 Electro-optics with 2D Semiconductors and Heterostructures**, *Goki Eda*, National University of Singapore, Singapore **INVITED**

Despite being only a few atoms thick, two-dimensional (2D) semiconductors such as monolayer MoS<sub>2</sub> and phosphorene exhibit distinctly strong light-matter interaction compared to their bulk counterparts. Excitons and their complexes with giant oscillator strength play a fundamental role in mediating the strong coupling between light and a 2D semiconductor. These excitons are stable at room temperature and make 2D semiconductors attractive for a number of photonic devices including ultra-fast photo-detectors, optical modulators, on-chip photonic circuits, flexible photovoltaic devices, chiral light emitters, single photon sources, and ultra-low threshold lasers<sup>1</sup>. In order for these devices to be integrated for photonic devices, practical schemes for electrical generation, manipulation, and detection of excitons need to be developed. We create artificial quantum wells based on van der Waal heterostructures and investigate the dynamics of 2D excitons under various conditions to achieve the desired photonic functionalities. In this talk, I will start by discussing our findings on the ultrafast dipole-dipole energy transfer processes involving 2D excitons. I will show that exciton-exciton energy transfer in hetero-bilayers is among the fastest measured in nanomaterials<sup>2</sup>. Peculiar optical effects arising from strong exciton-plasmon coupling in 2D semiconductors hybridized with metal nanoparticles will also be discussed<sup>3</sup>. Finally, our recent efforts in realizing electro-optical (electroluminescence, electro-absorption, and Pockels effect) devices will be discussed. I will share our views on the potential advantages of 2D semiconductors over other materials and discuss our outlook for further studies.

#### References:

1. F. Xia et al. "Two-dimensional material nanophotonics" Nat. Phot. 8, 899 (2016).
2. D. Kozawa et al. "Efficient interlayer energy transfer via 2D dipole coupling in MoSe<sub>2</sub>/WS<sub>2</sub> heterostructures" Nano Lett. 16, 4087 (2016).
3. W. Zhao et al. "Exciton-plasmon coupling and electromagnetically induced transparency in monolayer semiconductors hybridized with Ag nanoparticles" Adv. Mater. 28, 2709 (2016).

9:00am **2D+MI+NS+SS+TF-FrM3 Understanding Variations in Circularly Polarized Photoluminescence in Monolayer Transition Metal Dichalcogenides**, *Kathleen McCreary*, *M. Currie*, *A.T. Hanbicki*, *B.T. Jonker*, Naval Research Laboratory

The unique electronic band structure in monolayer transition metal dichalcogenides (TMDs) provides the ability to selectively populate a desired conduction band valley by exciting with circularly polarized light. The subsequent valley population can be interrogated by measuring helicity-resolved photoluminescence (PL). A high degree of circular polarization has been theoretically predicted for resonant excitation of TMDs, yet rarely observed experimentally. In fact, a wide range of values for the degree of circularly polarized emission ( $P_{\text{circ}}$ ), has been reported for monolayer TMDs, although the reasons for the disparity are unclear. Here we investigate the room-temperature  $P_{\text{circ}}$  in several TMD monolayers synthesized via chemical vapor deposition. The samples include as-grown WS<sub>2</sub>, as-grown WSe<sub>2</sub>, and WS<sub>2</sub> monolayers that have been transferred to a fresh substrate. In each system, a wide range of  $P_{\text{circ}}$  and PL intensity values are observed. There is a pronounced inverse correlation between  $P_{\text{circ}}$  and PL intensity: samples that demonstrate weak PL emission and short exciton relaxation time exhibit a high degree of valley polarization. We attribute these effects to sample-dependent variations in the exciton radiative and non-radiative lifetime components. The short exciton lifetime results in a higher measured polarization by limiting opportunity for depolarizing scattering events. These findings clarify the disparities among previously reported values and suggest a means to engineer valley polarization via controlled introduction of defects and non-radiative recombination sites.

This work was supported by core programs at NRL and the NRL Nanoscience Institute, and by the Air Force Office of Scientific Research #AORD 14IOA018-134141.

9:20am **2D+MI+NS+SS+TF-FrM4 Multi-Junction Lateral 2D Heterostructures of Transition Metal Dichalcogenides**, *Prasana Sahoo*, University of South Florida, *S. Memaran*, Florida State University, *Y. Xin*, National High Magnetic Field Laboratory, *L. Balicas*, Florida State University, *H.R. Gutierrez*, University of South Florida

Here we demonstrate the successful synthesis of lateral in-plane multi-junction heterostructures based on transition metal dichalcogenides (TMD) 2D monolayers. The heterostructures were synthesized using a modified chemical vapor deposition approach. By only controlling the carrier gas composition, it is possible to selectively grow only one TMD at the time. This introduces an unprecedented flexibility in the CVD process and allows a good control of the lateral size of each TMD segment. Heterostructures only containing MoS<sub>2</sub>-WS<sub>2</sub> or MoSe<sub>2</sub>-WSe<sub>2</sub> multiple segments, were fabricated. We also demonstrate the synthesis of heterostructures based on homogeneous TMD ternary alloys (Mo<sub>x</sub>Se<sub>y</sub>-WS<sub>2</sub>Se<sub>z</sub>). Introducing ternary alloys in heterostructures opens the horizon of possible chemical combinations and applications of 2D optoelectronic devices. The band gap modulation as well as spatial chemical distribution were studied by Raman and photoluminescence mapping. The crystalline quality of the heterostructures were characterized within an aberration-corrected scanning transmission electron microscope. Basic devices were also fabricated to study the transport properties across the junctions. Depending of the growing conditions, diffuse and/or sharp seamless interfaces with high-crystalline quality can be produced.

9:40am **2D+MI+NS+SS+TF-FrM5 Novel Electronic, Optoelectronic, and Topological Properties of 2D Materials and Their Heterostructures**, *Xiaofeng Qian*, Texas A&M University **INVITED**

Low-dimensional materials exhibits dramatically distinct properties compared to their 3D bulk counterpart. 2D materials is such a fascinating platform with many exotic physical properties and unprecedented opportunities. In this talk, I will highlight some examples of interesting 2D materials and their heterostructures, including 2D multiferroics, 2D topological insulators and topological crystalline insulators, 2D nanostructured exciton funnels. First, I will present our discovery of 2D multiferroics in semiconducting Group IV monochalcogenide monolayers with giant spontaneous in-plane ferroelectric polarization and ferroelastic lattice strain that are strongly coupled. The multiferroicity and hence anisotropic 2D excitonic responses as well as low domain wall energy and migration barrier suggest their great potentials for tunable multiferroic functional devices such as 2D ferroelectric and ferroelastic memory, 2D ferroelastolectric nonvolatile photonic memory, and 2D ferroelectric excitonic photovoltaics. In the second example, I will highlight our discovery on 2D topological insulators in binary and ternary transition metal dichalcogenides, and topological crystalline insulators in monolayer IV-VI semiconductors. We found electric field, elastic strain, and van der Waals stacking are able to induce topological phase transition (TPT), among which the electric-field induced TPT can be utilized for realizing topological field effect transistor distinctly different from conventional MOSFET. In the third example, I will discuss how macroscopic responses of materials can be tuned and configured by nanostructuring such as inhomogeneous strain engineering and van der Waals Moire patterning. Both nanostructures can modify local atomistic configurations and generate spatially varying electronic structures, thereby introducing novel excitonic photon funneling effect. The latter could be exploited for developing more efficient photovoltaics and light-emitting diodes. Finally, I will highlight relevant experimental progresses as well as some critical challenges and opportunities in 2D materials and their nanostructures.

10:20am **2D+MI+NS+SS+TF-FrM7 Imaging Nanoscale Heterogeneity at the Two-dimensional Semiconductor-Metal Heterointerface by Correlated Scanning Probe Microscopy**, *Deep Jariwala\**, California Institute of Technology, *A. Krayev*, *E. Robinson*, AIST-NT Inc., *M.C. Sherrott*, California Institute of Technology, *M. Terrones*, Pennsylvania State University, *H.A. Atwater*, California Institute of Technology

Transition metal dichalcogenides (TMDCs) of molybdenum and tungsten have recently attracted significant attention due to their band gaps in visible part of the spectrum for optoelectronic device applications. The ability to isolate these materials down to a monolayer with direct band-gap make TMDCs very attractive alternatives to graphene.

\* NSTD Postdoc Finalist

While a lot of investigation has been devoted to understanding of crystalline and electronic quality of TMDCs in devices, little is known about the spatial distribution of electronic quality and interfaces with metals. Conventional Raman spectroscopy and confocal Raman microscopy have proved to be useful tools in this regard. However, the spatial resolution of these techniques is diffraction limited to a few hundred nanometers only. Tip enhanced Raman scattering (TERS) provides spatial resolution down to few nanometers, along with increased sensitivity due to dramatic enhancement of the Raman signal by the plasmonic tip and is therefore a suitable technique to probe nanoscale heterogeneity in TMDC samples.

Here, we report observation of nanoscale heterogeneity in exfoliated WSe<sub>2</sub> flakes on plasmonic Au and Ag substrates using a combination of spatial mapping with TERS, contact potential difference, topography and conductance measurements. In TERS mapping of exfoliated WSe<sub>2</sub> flakes, we observe the presence of domains with enhanced or depreciated Raman signal compared to adjacent material. We also observe that WSe<sub>2</sub> demonstrates a resonant Raman response with 638nm excitation, the TERS spectra of these domains feature a single peak at around 250 cm<sup>-1</sup>, typical for non-resonant conditions. Distribution of these domains correlates extremely well with surface potential map, non-resonant areas being negatively charged compared to adjacent areas of WSe<sub>2</sub> that demonstrate a resonant Raman response.

We further correlate the TERS maps with concurrently recorded photocurrent maps, where we observe that domains showing both resonant and non-resonant Raman response, generated significant photocurrent, but of opposite polarities. Based on this observation, we conclude that in exfoliated layers of WSe<sub>2</sub>, there exist nanoscale semiconducting domains with opposite doping types when in contact with the underlying metal. This hitherto unobserved heterogeneity is therefore critical to understanding of the metal-two dimensional (2D) semiconductor contact and important for optoelectronic device design and performance. The results presented here show that cross-correlation of TERS with local conductivity, surface potential and photocurrent is a vital characterization technique for nanoscale inhomogeneities in 2D semiconductors and devices.

10:40am **2D+MI+NS+SS+TF-FrM8 Two-dimensional Circuitry Achieved by Defect Engineering of Transition Metal Dichalcogenides.** Michael G. Stanford\*, P.R. Pudasaini, A.N. Hoffman, P.D. Rack, The University of Tennessee Knoxville

Two-dimensional materials, such as transition metal dichalcogenides (TMDs), have demonstrated promising semiconducting properties. The electrical and optical properties of TMDs can be finely tuned by altering material thickness as well as chemical composition. Properties can also be tuned by defect engineering. In this work, a focused He<sup>+</sup> beam as well as a remote plasma source were utilized to introduce defects into TMDs such as WSe<sub>2</sub> and WS<sub>2</sub> with fine control. Scanning transmission electron microscopy reveals that defects introduced into the TMDs range from chalcogen vacancies (0D defects) to 1D defects and extended defect networks. Tailoring defect concentration enables tunability of the electronic properties with insulating, semiconducting, and metallic behavior each obtainable. By tuning electronic properties, we demonstrate direct-write logic gates such as resistor loaded inverters with a voltage gain of greater than 5. We also demonstrate the fabrication of edge-contacted field effect transistors by defect engineering homojunctions between metallic and semiconducting WSe<sub>2</sub> with on/off ratios greater than 10<sup>6</sup>. Defect engineering of TMDs enables the direct-write of complex devices into single flakes toward the goal of atomically thin circuitry.

11:00am **2D+MI+NS+SS+TF-FrM9 Scanning Tunneling Microscopy and Spectroscopy Studies of Atomically Precise Graphene Nanoribbons on Semiconducting Surfaces.** Ximeng Liu, A. Radocea, T. Sun, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, M. Pour, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, N. Aluru, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, A. Sinitskii, Nebraska Center for Materials and Nanoscience, University of Nebraska - Lincoln, J.W. Lyding, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign

Graphene nanoribbons (GNRs) with atomically smooth edges, controllable geometry and therefore tunable electronic band gaps have ignited enormous interest due to their high potential for future electronic devices. Among different techniques for GNR characterization, scanning tunneling microscopy and spectroscopy (STM/STS) provide both topographic details and local electronic structure with atomic resolution. Large-scale production of two different kinds of chevron-type GNRs (the double-wide (w) GNRs and the extended chevron (e) GNRs) was realized by a solution synthesis method

[1]. Dry contact transfer technique [2] was implemented for depositing the solution-synthesized GNRs onto clean InAs (110) and hydrogen-passivated Si(100) semiconducting surfaces under ultrahigh vacuum conditions. For both GNRs, their structures were confirmed by high resolution STM imaging. The band gap of the eGNRs was determined to be 2.6eV via STS. For the wGNRs, detailed analysis and mapping of the electronic density of states both spatially and energetically was carried out with STS and current imaging tunneling spectroscopy. We found that the electron orbital shapes at the GNR edges are different from those at the centers, in agreement with computational simulations. The measured band gap of the wGNRs was only 2eV, which may result in a great improvement in conductivity. In addition, these GNRs are found to be transparent to the substrate when scanned at a small tip-sample separation, indicating a strong interaction when GNRs are pushed towards the substrate.

References:

1. Vo, T. H.; Shekhirev, M.; Kunkel, D. A.; Morton, M. D.; Berglund, E.; Kong, L. M.; Wilson, P. M.; Dowben, P. A.; Enders, A.; Sinitskii, A., Large-Scale Solution Synthesis of Narrow Graphene Nanoribbons. *Nat. Commun.* **2014**, *5*, 3189.
2. Ritter, K. A.; Lyding, J. W. The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. *Nat. Mater.* **2009**, *8* (3), 235–42.

11:20am **2D+MI+NS+SS+TF-FrM10 Perfectly Perforated Monolayer WSe<sub>2</sub>.** Kirby Smithe, C. Bailey, Stanford University, A. Kravayev, AIST-NT Inc., E. Pop, Stanford University

One of many prospective applications of 2D transition metal dichalcogenides (TMDs) is catalytic splitting of water for hydrogen generation. Strain in TMD layers, chalcogen atom vacancies, and increased length of the edges of TMD flakes all play an important role in increased catalytic activity, with the latter being the most effective way for improving performance. One possible way to achieve increased ratios of edge length to surface area is to use small flakes, preferably a few hundred nm across. Unfortunately, such small flakes are difficult to manipulate, and the structure of such flakes should also differ from the perfect structure of the inner areas of larger flakes<sup>1</sup>. Here we report that WSe<sub>2</sub> monolayers, grown by chemical vapor deposition (CVD) on Si/SiO<sub>2</sub> and transferred from the original substrate by means of dissolving the sacrificial SiO<sub>2</sub> layer, contain a significant concentration of perfect triangular holes. The result is confirmed by correlating the data of topography, the surface potential, friction and tip enhanced Raman spectroscopy (TERS) characterization of transferred flakes. The ratio of edge length to surface area in such perforated flakes could be up to 3 to 4 times higher compared to homogenous continuous flakes. These perforated flakes can be transferred to any surface, including corrugated ones, which should inevitably cause some strain that is also beneficial for hydrogen catalytic activity. The perfect triangular shape of the holes suggests high quality of the atomic structure of the hole edges, which also implies that the perforated flakes can be used as templates for growth of distributed in-plane heterostructures of different TMDs.

1. Nature Commun., Wei Bao\*, Nick Borys\*, et al. "Visualizing nanoscale excitonic relaxation properties of disordered edges and grain boundaries in monolayer molybdenum disulfide," *6*, 7993 (2015)

\* National Student Award Finalist

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