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.

References

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