

# Monday Morning, October 19, 2015

## 2D Materials Focus Topic

Room: 212C - Session 2D+EM+NS+PS+SP+SS+TF-MoM

## 2D Materials: Growth and Fabrication

**Moderator:** Cory Dean, Columbia University, Peide Ye, Purdue University

8:20am **2D+EM+NS+PS+SP+SS+TF-MoM1 Growth and FTIR Characterization of 2D Hexagonal Boron Nitride on Metal Substrates, Boris Feigelson, V.M. Bermudez, J.K. Hite, Z.R. Robinson, V.D. Wheeler, K. Sridhara, S.C. Hernandez, US Naval Research Laboratory**

Atomically thin two dimensional hexagonal boron nitride (2D h-BN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance. The development of 2D h-BN growth is still in the early stages and largely depends on rapid and accurate characterization of the grown monolayer or few layers h-BN films.

In this work, the IR-active out-of-plane vibrational mode of 2D h-BN films grown in vertical reactor by atmospheric-pressure CVD on metal substrates (mainly Cu but also Ni) is exploited to identify 2D h-BN directly on substrates and studied both computationally and experimentally.

Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) data have been used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the  $A_{2u}(\text{LO})$  vibrational mode were, for the first time, found for thin 2D h-BN films in contact with Cu and Ni [1]. To unveil the nature of the discovered sub-bands, ab-initio calculations were performed and verified using 2D h-BN films grown on various Cu substrates with varying coverage and with individual crystallites of different shapes and size up to 4  $\mu\text{m}$ . It was shown that the lower-energy  $A_{2u}(\text{LO})1$  sub-band around  $819\text{ cm}^{-1}$  is related to 2D h-BN coupled with Cu substrate, while the higher energy  $A_{2u}(\text{LO})2$  sub-band around  $824\text{ cm}^{-1}$  is related to decoupled (essentially free standing) 2D h-BN. These findings demonstrate not only a new and facile method for immediate 2D h-BN identification and characterization, but also a method that provides a simple means to characterize the degree of coupling between 2D h-BN and the substrate. This approach also provides an opportunity to determine which growth conditions lead to the absorption of foreign species on the substrate prior to the h-BN deposition and which conditions can prevent the formation of the interfacial layer between h-BN and the substrate. Such interfacial layers, like oxidized Cu, were shown to result in easily-recognizable shifts in the  $A_{2u}(\text{LO})$  peak. The degree to which the interaction of the h-BN layer with the substrate is uniform and homogenous can also be assessed easily by examining the width and fine structure of the  $A_{2u}(\text{LO})$  band. The developed approach can also be used to study growth and formation of h-BN/graphene and other 2D heterostructures.

### References

1. B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, *Nanoscale* **7**, 3694 (2015)

8:40am **2D+EM+NS+PS+SP+SS+TF-MoM2 Effect of Surface Termination on the Growth of Graphene on Cu Single Crystal Substrates, Tyler Mowll, E.W. Ong, University at Albany-SUNY, P. Tyagi, GLOBALFOUNDRIES, Z.R. Robinson, College at Brockport-SUNY, C.A. Ventrice, Jr., SUNY Polytechnic Institute**

The most common technique for synthesizing single-layer graphene films with large lateral dimensions is chemical vapor deposition (CVD) on Cu foil substrates. The primary reasons for choosing Cu substrates are the extremely low solubility of carbon in Cu, which allows a self-limited growth of graphene, and the relatively low cost of the Cu foil substrates. However, the transport properties of the CVD grown graphene films are typically a couple of orders of magnitude lower than for graphene flakes mechanically exfoliated from graphite. One of the reasons for the reduction in transport properties is the presence of crystalline defects in the CVD grown films. These structural defects arise in part from the multidomain structure of the Cu films. In order to achieve a better understanding of the influence of the surface termination of the Cu substrate on the crystallization of graphene during the CVD growth process, a systematic study of graphene growth on Cu(100), Cu(110), and Cu(111) crystals has been performed. The growth process is performed in an ultra-high vacuum (UHV) chamber that has been modified to perform CVD growth at pressures as high as 100 mTorr. The precursor gas used is ethylene. This

growth procedure allows for the preparation of the clean surfaces in UHV, growth under typical CVD conditions, and characterization of the surface structure in UHV, without exposing the sample to atmospheric contaminants. Our results indicate that the Cu(111) surface has the lowest catalytic activity of the three surfaces for the decomposition of ethylene. In fact, the decomposition rate is so low that graphene growth is suppressed because of the sublimation of Cu at the elevated temperatures used to grow the graphene. By using an Ar overpressure, it was found that graphene could be grown on that surface. The surface symmetry of the Cu substrate has a strong influence on the rotational alignment of the graphene grains as they nucleate on each surface. For Cu(111), single-domain graphene growth can be achieved for ethylene pressures of 5 mTorr or less. For both Cu(100) and Cu(110), a minimum of two graphene domains is always observed.

9:00am **2D+EM+NS+PS+SP+SS+TF-MoM3 Thermally Annealed and Electropolished Cu Substrates for CVD Growth of 2D Materials: Graphene, h-BN and MoS<sub>2</sub>, Karthik Sridhara, Texas A&M University, B.N. Feigelson, J.K. Hite, US Naval Research Laboratory, A. Nath, George Mason University, M. Fuhrer, Monash University, Australia, D.K. Gaskill, US Naval Research Laboratory, H. Castaneda, L.O. Nyakiti, Texas A&M University**

The growth of two dimensional (2D) materials such as graphene, hexagonal boron nitride (h-BN) and molybdenum disulphide (MoS<sub>2</sub>) have been demonstrated by chemical vapor deposition (CVD) on polycrystalline catalytic copper substrates. These Cu foil substrates (25  $\mu\text{m}$  thick) are produced by metallurgical rolling leading to the formation of irregular ridges on the foil surface along with a film of native oxide on the surface. These processing artifacts are a limiting factor for controlled and reproducible large area (several  $\text{cm}^2$ ) growth of 2D materials. Greater control of growth can be achieved by controlling the density of nucleation sites and improving the catalytic activity of Cu by removing the Cu native oxide on the surface. Previous attempts to pre-treat the Cu substrate by using wet chemistry or thermal annealing to control growth has been weakly addressed.

In this work, electropolishing combined with prior thermal annealing at  $1030^\circ\text{C}$  for 5 hrs under  $\text{H}_2$  is used to control the degree of roughness of cold rolled polycrystalline Cu foils, and subsequently, to explore the influence of electropolishing on the growth of 2D materials: graphene, h-BN and MoS<sub>2</sub>. Electropolishing dissolves a thin surface layer of Cu, which contains surface defects and contaminants. This helps in decreasing the density of spontaneous nucleation sites by producing a morphologically uniform and contaminant-free surface. Secondary effects, etch pits which are ascribed to  $\text{O}_2$  bubbling at random nucleation sites on Cu surface, are mitigated by using additives, such as acetic acid and ethylene glycol, in the  $\text{H}_3\text{PO}_4$  electrolyte. Thermal annealing and electropolishing results in this work reveal that a roughness of  $\sim 1.2\text{ nm}$  ( $R_a$ ) can be achieved as measured by Atomic Force Microscope (AFM) along with a greatly planarized Cu foil. AFM will also be used to establish the Cu substrate morphology and its relationship to the growth of 2D materials. Fourier Transform Infrared, and Raman spectroscopy will be used to confirm the existence of the 2D material. Preliminary growth studies of h-BN on these high quality Cu substrates demonstrate improved growth, as assessed by the metrics of size and count of h-BN crystals from Scanning Electron Microscopy (SEM) micrographs [1]. This work will demonstrate that thermal annealing followed by electropolishing leads to optimization of Cu foil surface resulting in the larger crystal size and a reduction in nucleation sites that induce 2D material crystal growth [1].

[1] K. Sridhara. "Growth of hexagonal boron nitride on electrochemically prepared polycrystalline Cu substrates." M.S. Thesis, University of Maryland, College Park, MD, 2014.

9:20am **2D+EM+NS+PS+SP+SS+TF-MoM4 In Situ Optical Diagnostics During Molybdenum Disulfide Chemical Vapor Deposition, Berc Kalanyan, J.E. Maslar, W.A. Kimes, B.A. Sperling, National Institute of Standards and Technology (NIST), R. Tieckelmann, T. Orzali, SEMATECH, R. Beams, S.J. Stranick, A.V. Davydov, National Institute of Standards and Technology (NIST)**

Two dimensional (2D), layered transition-metal dichalcogenides (TMDs), e.g., MoS<sub>2</sub>, are of increasing interest for next-generation nanoelectronic and optoelectronic devices. These materials have thickness dependent optical and electrical properties that make them suitable for a variety of applications including integrated circuits. For many applications, high volume manufacturing (HVM) of devices based on TMDs will require deposition techniques that are capable of reproducibly growing wafer-scale, 2D TMD films with monolayer control. To date, such a capability has not been widely demonstrated with typical TMD deposition processes.

This work aims to identify promising chemistries for HVM TMD chemical vapor deposition (CVD) processes. We focus on MoS<sub>2</sub> CVD using a variety of precursors (including organometallics, elemental sulfur, and organosulfur compounds) in a research grade single-wafer deposition system equipped with *in situ* optical diagnostics. The precursor flux is measured using optical mass flow meters installed on the delivery lines while deposition chemistry is characterized in the reactor volume above the deposition surface using *in situ* Fourier transform infrared (FT-IR) spectroscopy. As-deposited and annealed films are characterized with *ex situ* techniques, including Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy.

Stoichiometric MoS<sub>2</sub> films have been prepared from ( $\eta^5$ -ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum and elemental sulfur. As-grown films are smooth and continuous with major MoS<sub>2</sub> Raman modes present. Film thickness scales approximately with Mo precursor exposure time and few-layer films can be produced using pulsed injection mode. Furthermore, optical *in situ* diagnostics allow us to relate metal precursor flux to film crystallinity and facilitate the study of precursor decomposition in the thermal boundary layer.

9:40am **2D+EM+NS+PS+SP+SS+TF-MoM5 Controlled Interfaces in 2D Materials**, **Arend van der Zande**, University of Illinois at Urbana Champaign **INVITED**

Interfaces are ubiquitous in material science and technologies. For example, grain boundaries often dominate the mechanical and electrical properties in crystalline materials, while interfaces between dissimilar materials form the fundamental building blocks to diverse technologies, such as building electrical contacts in transistors and PN diodes in solar cells. Interfaces become even more important in 2D materials such as graphene and transition metal dichalcogenides, where the lack of dangling bonds enables material stability down to a single monolayer. In this entirely surface-dominated limit, the usual rules governing 3D interface devices, such as depletion regions, break down.

In this talk, we will discuss our work on engineering in- and out-of-plane 2D materials interfaces. We will first examine the structure of atomically-thin membranes and the impact of defects such as grain boundaries on the mechanical, optical, and electronic properties. We fabricate out-of-plane interfaces by stacking 2D materials to form heterostructures, which we utilize to tailor the bandgap in 2D materials and build new optoelectronic devices such as tunable photodiodes. Looking to the future, the rapidly expanding family of 2D materials with a diverse set of electronic properties provide a promising palette for discovering emergent phenomena and a motivation for developing overarching design principles for understanding and controlling interfaces in 2D.

10:40am **2D+EM+NS+PS+SP+SS+TF-MoM8 Obtaining Clean Suspended CVD Graphene: Comparative Examination of Few Transfer and Cleaning Protocols**, **Alexander Yulaev**, National Institute of Standards and Technology (NIST), University of Maryland (UMD), *G. Cheng, A. Hight Walker*, National Institute of Standards and Technology (NIST), *M. Leite*, University of Maryland (UMD), *A. Kolmakov*, NIST

Clean suspended graphene is used as supporting media in TEM, filtering membranes, and as electron transparent windows in ambient pressure electron spectroscopy and microscopy. CVD grown graphene is the most popular material for these applications due to its large-scale and high yield production. Multiple approaches such as sacrificial layer based methods [1] and direct transfer method on perforated carbon mesh by IPA droplet [2] have been implemented to transport graphene from copper or nickel foil onto a target substrate. However, the cleanliness of the suspended graphene remains to be an issue, and controversial results on lateral size of atomically clean graphene domains have been reported [2-5]. We conduct the comparative analysis of the most widely-used CVD graphene transfer and cleaning protocols. In particular, using extreme surface sensitivity of low energy SEM, we compare the standard PMMA based approach with direct graphene transfer method. We also propose alternative graphene transfer protocol which is based on employment of polycyclic aromatic hydrocarbon (PAH) as a sacrificial layer. The advantage of PAH method over others consists in facile sublimation of sacrificial layer upon heating PAH material within moderate temperature range of 100-150 °C. All three methods of graphene transfer were compared under the same conditions followed by similar graphene cleaning procedures by platinum catalysis [4] and activated carbon adsorption [5]. Both SEM and TEM study revealed the superiority of PAH method to achieve cleaner suspended CVD graphene. We envision that novel approach of graphene transfer can be employed under conditions when exposure of the sample to moisture is prohibited such as in battery research.

[1] "Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates", Ji Won Suk *et al.*, ACS Nano, 2011, 5 (9), pp. 6916.

[2] "A direct transfer of layer-area graphene", William Regan *et al.*, Appl. Phys. Lett., 2010, 96, 113102.

[3] "Low-energy electron holographic imaging of gold nanorods supported by ultraclean graphene", Jean-Nicolas Longchamp *et al.*, Ultramicroscopy 145 (2014) 80.

[4] "Ultraclean freestanding graphene by platinum-metal catalysis", Jean-Nicolas Longchamp *et al.*, J. Vac. Sci. Technol. B 31, 020605 (2013).

[5] "Dry-cleaning of graphene", Gerardo Algara-Siller *et al.*, Applied Physics Letters 104, 153115 (2014).

11:00am **2D+EM+NS+PS+SP+SS+TF-MoM9 Low-Energy Electron Microscopy of Transition Metal Dichalcogenides Prepared by Various Methods**, **Sergio de la Barrera**, *S. Satpathy, R. Feenstra*, Carnegie Mellon University, *S. Wu, X.D. Xu*, University of Washington, *S. Vishwanath, X. Liu, J. Furdyna, D. Jena, H. Xing*, University of Notre Dame, *Y.-C. Lin, S.M. Eichfeld, J.A. Robinson*, Pennsylvania State University, *P. Mende*, Carnegie Mellon University

Recent work on two-dimensional materials has focused on transition metal dichalcogenides (TMDs), owing to their semiconducting behavior. Characterizing as-grown TMDs is crucial in improving the understanding of the effects of growth conditions, and ultimately improving material quality. Low-energy electron microscopy (LEEM) is a powerful tool for this purpose, providing real-space images with ~10 nm spatial resolution as well as selected-area low-energy electron diffraction ( $\mu$ LEED) of local crystal orientation at length scales down to ~1  $\mu$ m. Additionally, by varying the incident electron beam energy, low-energy electron reflectivity (LEER) spectra are extracted.

In this work, comparative LEEM results are presented from three TMD materials: MoS<sub>2</sub> prepared by exfoliation (onto Si), MoSe<sub>2</sub> grown by molecular beam epitaxy (MBE) (on epitaxial graphene), and WSe<sub>2</sub> grown by chemical vapor deposition (CVD) (also on epitaxial graphene). It is found that for TMDs generally, the LEER spectra do not exhibit the oscillatory behavior (in the 0 – 6 eV range) that is seen for both graphene and hexagonal boron nitride (h-BN) for various numbers of monolayers (MLs). This lack of oscillatory behavior is interpreted as being due to the weak coupling of the interlayer states localized in between the MLs, which is itself a result of the relatively large out-of-plane lattice parameter. Nevertheless, additional "band structure" features in the LEER spectra permit clear identification of the TMD materials relative to the substrates. The exfoliated flakes are seen to extend over many 10's of  $\mu$ m, the MBE-grown MoSe<sub>2</sub> forms a nearly continuous film, and the CVD-grown WSe<sub>2</sub> forms triangular islands several  $\mu$ m in extent.  $\mu$ LEED studies of the MBE-grown MoSe<sub>2</sub> and CVD-grown WSe<sub>2</sub> reveal preferential orientation with the underlying graphene substrates.

The reduced work functions of the TMD materials relative to the underlying substrate are clearly evident in the onset voltages for the LEER spectra (i.e. the onset shifts in accordance with the local work function of the surface). Most significantly, for the WSe<sub>2</sub> islands, a predominant "tail" is observed in this onset, extending about 5V below the usual onset location. This tail is tentatively interpreted as arising from charging of the islands, perhaps due to polar termination at the edges of the TMD islands. Comparison of the data with simulated LEER spectra will be presented, as a test of this model for edge charge of the islands.

Work supported by the Center for Low Energy Systems Technology (LEAST), one of six SRC STARnet Centers sponsored by MARCO and DARPA, and by NSF-EFRI-1433496.

11:20am **2D+EM+NS+PS+SP+SS+TF-MoM10 Atomically-Thin 2D Layers of Group IV Semiconductors**, **Joshua Goldberger**, The Ohio State University **INVITED**

Similar to how carbon networks can be sculpted into low-dimensional allotropes such as fullerenes, nanotubes, and graphene with fundamentally different properties, it is possible to create similar "allotropes" of Ge or Sn with unique optoelectronic properties as well. Here, we will describe our recent success in the creation of hydrogen and organic-terminated group 14 graphene analogues, from the topochemical deintercalation of precursor Zintl phases, such as CaGe<sub>2</sub>. We will discuss how the optical, electronic, and thermal properties of these materials can be systematically controlled by substituting either the surface ligand or via alloying with other Group 14 elements. Additionally, we have also developed an epitopotaxial approach for integrating precise thicknesses of Germanane layers onto Ge wafers that combines the epitaxial deposition of CaGe<sub>2</sub> precursor phases with the topotactic interconversion into the 2D material. Finally, we will describe

our recent efforts on the synthesis and crystal structures of Sn-containing graphane alloys in order to access novel topological phenomena predicted to occur in these graphanes.

# Monday Afternoon, October 19, 2015

## 2D Materials Focus Topic

Room: 212C - Session 2D+EM+MC+MS+NS-MoA

## 2D Materials: Devices and Applications

**Moderator:** Joshua Goldberger, The Ohio State University, Arend van der Zande, University of Illinois at Urbana Champaign

2:20pm **2D+EM+MC+MS+NS-MoA1 Designer Materials from the Assembly of 2D Layered Heterostructures, Cory Dean, Columbia University** **INVITED**

The capability to assemble two-dimensional (2D) materials into layered heterogeneous structures presents an exciting new opportunity in materials design. For example, encapsulating graphene with hexagonal BN yields enhanced transport properties with reduced environmental sensitivity, and allows for complex band structure engineering. This has enabled graphene to be exploited as a model experimental platform to study a wide range of fundamental physics arising both from conventional single-particle considerations, as well as more exotic emergent behaviour in the strongly interacting regime. Graphene however represents just one of a larger subset of layered materials, which are now receiving growing attention due to their diverse array of intrinsic properties. The opportunity to “mix and match” these disparate crystals to realize fundamentally new hybrid material properties provides an almost unbounded new direction as we look for quantum materials beyond graphene. In this talk I will outline some of the fundamental questions, and technical challenges facing these efforts and highlight some of our recent innovations in this direction. Implications for the development of new device geometries and scientific pursuits will be discussed.

3:00pm **2D+EM+MC+MS+NS-MoA3 Structural Semiconducting-to-Metallic Phase Transition in Monolayer Transition Metal Dichalcogenides Induced by Electrostatic Gating, Yao Li, K.-A. Duerloo, E.J. Reed, Stanford University**

Dynamic electrical control of conductivity in two-dimensional (2D) materials is one of the most promising schemes for realizing energy-efficient electronic devices. Monolayer transition metal dichalcogenides (TMDs) are 2D materials that can exist in multiple crystal structures, each of different electrical conductivity. Using density functional approaches, we discover that a structural semiconducting-to-metallic phase transition in some monolayer TMDs can be driven by electrical stimuli, including change of charge density and bias voltage. We find that a bias voltage approximately 0.5–1 V can trigger the phase transition in  $\text{MoTe}_2$ , while a larger voltage is required for the transition in other monolayer TMDs. The threshold bias voltage is strongly influenced by the substrate on which the monolayer is placed. Carefully choosing the substrate could greatly reduce the threshold bias voltage for the phase transition, and therefore consume much less energy, suggesting potential applications in electronics with very high energy efficiency. The dynamic control of this semiconducting-to-metallic phase transition can be achieved utilizing standard electronic devices like the electrostatic gating employed in a field-effect transistor. We have also calculated the phase boundary of a reported metallic-to-metallic phase transition in  $\text{TaSe}_2$  to compare with earlier STM experimental results and reasonable agreement is observed. Our findings open up the possibility of manufacturing ultrathin flexible two-dimensional phase change electronic devices with potential for higher energy efficiency than conventional electronic devices.

3:20pm **2D+EM+MC+MS+NS-MoA4 Use of Voltage-Contrast and Dynamical XPS for Characterization of Graphene-Based Devices in Operation, Sefik Suzer, Bilkent University, Turkey**

A noncontact chemical and electrical technique of XPS is performed to investigate a number of devices under operation. The main objective of the technique is to trace chemical and location specified surface potential variations as shifts of the XPS peak positions under operating conditions. To implement the measurements we apply D.C. (Voltage-Contrast) and/or A.C. (Dynamical) voltage biases externally to the sample, while recording XPS data. Accordingly, we extract chemically resolved static and/or time-resolved information related with certain electrical properties of materials and devices made from them. Details of the technique and applications to a number of graphene-based devices, configured in a transistor geometry with and without gating, will be presented.

4:00pm **2D+EM+MC+MS+NS-MoA6 Avalanche Photodiodes based on  $\text{MoS}_2/\text{Si}$  Heterojunctions, Oriol López Sánchez, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, G. Fiori, G. Iannaccone, Università di Pisa, Italy, D. Dumenco, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, E. Charbon, Delft University of Technology, Netherlands**

Avalanche photodiodes (APDs) are the semiconducting analogue of photomultiplier tubes offering very high internal current gain and fast response. APDs are interesting for a wide range of applications in communications, laser ranging, biological imaging, and medical imaging where they offer speed and sensitivity superior to those of classical p-n junction-based photodetectors. The APD principle of operation is based on photocurrent multiplication through impact ionization in reverse-biased p-n junctions. Here, we demonstrate APDs based on vertically stacked monolayer  $\text{MoS}_2$  and p-Si, forming an abrupt p-n heterojunction. With this device, we demonstrate carrier multiplication exceeding 1000 at 10 V reverse bias. Our devices show little degradation of SNR at high gains. These heterostructures allow the realization of simple and inexpensive high-performance and low-noise photon counters based on transition metal dichalcogenides.

4:20pm **2D+EM+MC+MS+NS-MoA7 From Black Phosphorus to Phosphorene, Peide Ye, Purdue University** **INVITED**

Phosphorus is one of the most abundant elements preserved in earth, constructing with a fraction of ~0.1% of the earth crust. In general, phosphorus has several allotropes. The two most commonly seen allotropes, white and red phosphorus, are widely used in explosives and safety matches. In addition, black phosphorus, though rarely mentioned, is a layered semiconductor and has great potentials in optical and electronic applications. Remarkably, this layered material can be reduced to one single atomic layer in the vertical direction owing to the van der Waals structure, known as phosphorene, where the physical properties can be tremendously different from its bulk counterpart. In this talk, we trace back to the 100 years research history on black phosphorus from the synthesis to material properties, and extend the topic from black phosphorus to phosphorene. The physical and transport properties are highlighted, aiming at further applications in electronic and optoelectronics devices.

5:00pm **2D+EM+MC+MS+NS-MoA9 Ambient Oxidation and Alumina Passivation of Exfoliated Black Phosphorus Transistors, Joshua Wood, S. Wells, D. Jariwala, K.-S. Chen, X. Liu, V. Sangwan, E. Cho, L. Lauhon, T.J. Marks, M.C. Hersam, Northwestern University**

Exfoliated black phosphorus (BP) is an elemental, two-dimensional (2D) nanomaterial with high carrier mobility ( $\sim 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ), a layer-dependent band gap ( $\sim 0.3$  to  $2.0 \text{ eV}$ ), and in-plane anisotropy. Further, 2D BP is air sensitive, culminating in undesirable surface reactions that degrade device performance. We find that unencapsulated, exfoliated BP flakes form oxidized derivatives following ambient exposure, as ascertained by X-ray photoelectron spectroscopy, atomic force microscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, and electrostatic force microscopy measurements. BP ambient oxidation is driven by oxygen-saturated  $\text{H}_2\text{O}$ , as we observe two-fold faster degradation for BP on hydrophobic substrates versus hydrophilic ones. After 48 hours of ambient oxidation, unencapsulated BP field-effect transistors (FETs) decline in mobility and current on/off ratio by factors of over 1000. In contrast, alumina (i.e.,  $\text{AlO}_x$ ) passivated BP flakes and FETs are robust and unoxidized for over seven months in ambient conditions. Alumina-passivated BP FETs possess mobilities of  $\sim 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , on/off ratios of 1000, and ambipolar transport, even following extensive ambient exposure [1]. This understanding of BP ambient oxidation—and how to prevent it—is also impacting ongoing work in solution-phase BP separation [2], BP chemical modification, and high-performance BP optoelectronic applications.

[1] J. D. Wood *et al.*, *Nano Lett.* **14**, 6964 (2014); [2] J. Kang *et al.*, *ACS Nano* **9**, 3596 (2015).

5:20pm **2D+EM+MC+MS+NS-MoA10 Electro-Acoustic Characterization of Transition Metal Dichalcogenide Films on  $\text{LiNbO}_3$ , Edwin Preciado, UC Riverside, F.J.R. Schülein, A. Wixforth, Universität Augsburg, Germany, A. Nguyen, D. Barroso, M. Isarraraz, G. von Son, I. Lu, L. Bartels, UC Riverside, H. Krenner, Universität Augsburg, Germany**  
We demonstrate mm-scale CVD growth of single layer molybdenum disulfide directly onto piezoelectric lithium niobate and present the fabrication of a hybrid FET – SAW (field effect transistor – surface acoustic

wave) device. Our experiments reveal close agreement between transport measurements utilizing conventional contacts and SAW spectroscopy. This approach will ultimately provide for a contact free transport characterization of 2D TMD films, avoiding concerns about the role of charge transfer at contacts as an artifact of such measurements.

## **Accelerating Materials Discovery for Global Competitiveness Focus Topic**

**Room: 114 - Session MG+2D+MI+NS+TF-MoA**

### **Design and Discovery (Bio and Other Interfaces)**

**Moderator:** Sean Jones, National Science Foundation (NSF), Lynnette Madsen, National Science Foundation (NSF)

3:00pm **MG+2D+MI+NS+TF-MoA3 Rational Accelerated Design of Polymer Dielectrics, Rampi Ramprasad**, University of Connecticut  
**INVITED**

To date, trial and error strategies guided by intuition have dominated the identification of materials suitable for a specific application. We are entering a data-rich, modeling-driven era where such Edisonian approaches are gradually being replaced by rational strategies which couple predictions from advanced computational screening with targeted experimental synthesis and validation. Consistent with this emerging paradigm, we propose a strategy of hierarchical modeling with successive down-selection stages to accelerate the identification of polymer dielectrics that have the potential to surpass 'standard' materials for a given application. Specifically, quantum mechanics based combinatorial searches of chemical space are used to identify polymer repeat units that could lead to desirable dielectric properties, followed by configurational space searches to determine the 3-dimensional arrangement of polymers (and their properties) built from the desirable repeat units. Successful synthesis and testing of some of the most promising identified polymers and the measured attractive dielectric properties (which are in quantitative agreement with predictions) strongly supports the proposed approach to material selection.

3:40pm **MG+2D+MI+NS+TF-MoA5 Method to Make a Stable Copper-Carbon Alloy, Ivan Shchelkanov, D.N. Ruzic, I. Jasiuk**, University of Illinois at Urbana Champaign

Modern industry demands advanced materials with enhanced properties. To expand a range of available materials the covetic alloy is studied. Covetic is a novel alloy invented and patented by Third Millennium Metals, LLC (TMM). This is a new hybrid material made of a carbon and a metal, where the carbon forms a super lattice structure inside a metal. The base metal can be copper, aluminium, lead, tin or other low-melting point metals. In normal conditions the metal does not wet and does not form chemical bond with the carbon. However, the amount of carbon in the covetic alloy exceeds carbon solubility in the metal by several orders of magnitude. Such a composition is achieved by supplying a current to a volume of molten metal while it is being blended with micron size carbon particles. The alloy is prepared in vacuum.

The process of covetic formation is influenced by chemical composition of the base metal, a cast volume temperature change rate, external electric and magnetic fields, compound viscosity, surface and interphase tension coefficient, density, and thermal and electric conductivities of the metal and carbon particles. A part of the process of covetic alloy formation, which involves carbon particles dissolving, can be compared to phenomena occur in dust plasma. This assumption provides a possibility to visualise processes of microparticles spatial distribution and decomposition into single atoms with subsequent formation of a carbon super lattice inside the metal lattice.

The current work focuses on: the electric current influence on the alloy structure formation and carbon atoms distribution inside the metal; copper covetic hardness, conductivity, and tensile strength change as a function of carbon composition; and a phenomenological model for covetic alloy formation.

4:00pm **MG+2D+MI+NS+TF-MoA6 Development of Nanoporous Solid Phase Microextraction (SPME) Fibers by Sputtering, Matthew Linford, C.V. Cushman, B. Singh, A. Diwan**, Brigham Young University  
Solid phase microextraction (SPME) is a solventless, fast, easy and relatively inexpensive sample preparation technique that integrates sampling, extraction and preconcentration of samples such as food, waste water, air, and biological fluids in one step. However, commercial SPME coatings may be expensive, show relatively short lives, extract limited numbers of compounds, and have relatively low thermal and mechanical

stability. The aim of this study is to develop an SPME device that is thinner, robust, long lasting, has higher mechanical strength, greater thermal and solvent stability, and is devoid of the other drawbacks of commercial coatings. We describe a new method for the preparation of nanoporous SPME coatings via the oblique-angle sputtering of silicon and subsequent functionalization with silanes. The thickness of the sputtered coatings was controlled by varying the sputtering time. To increase the density of -OH groups on the surfaces, the coatings were treated in piranha solution and then reacted with n-octadecyldimethylmonomethoxysilane to render the surfaces hydrophobic. The coatings were robust and were characterized at each step in the process using XPS, water contact angle goniometry, spectroscopic ellipsometry, and scanning electron microscopy. Our sputtered, silanized fiber yielded comparable and/or better extraction efficiencies than a commercial 7  $\mu\text{m}$  PDMS fiber, especially for higher molecular weight species. In the case of a series of primary alcohols, and aldehydes, our fiber outperformed the commercial PDMS fiber by a factor of 2 - 3. In the evaluation of two real world samples: a sea water extract and beer, our fiber showed unique selectivity. Our 1.1  $\mu\text{m}$  fiber yielded comparable signals to 65  $\mu\text{m}$  PDMS-DVB and 85  $\mu\text{m}$  CAR-PDMS commercial fibers for higher molecular weight analytes. For a ~2.2  $\mu\text{m}$  fiber, the performance of our fiber increased substantially.

### **Thin Film**

**Room: 111 - Session TF+2D+MG+NS-MoA**

### **ALD, CVD, MLD, and PLD on Special Materials**

**Moderator:** Giovanna Scarel, James Madison University, Mark Davidson, University of Florida

2:20pm **TF+2D+MG+NS-MoA1 Optical Enhancement of Polyethylene Terephthalate Films Modified by Organometallic Vapor Infiltration, Halil Akyildiz**, North Carolina State University, *J.G. Simmons*, Redstone Arsenal, *H.O. Everitt*, Duke University, *J.S. Jur*, North Carolina State University

Polyethylene terephthalate is recyclable thermoplastic polymer that has wide application area including packaging, textiles and insulation applications. Due to the ring structures on the backbone of the polymer it shows weak luminescence in the blue spectrum upon UV light absorption by pi electrons. It has previously been shown that vapors of organometallic ALD precursors are able to infiltrate and react with the polymer to form organic inorganic hybrid materials. Infiltration of trimethylaluminum into PET to form polymer-alumina coordination complexes enhanced the photoluminescence and internal quantum efficiency of the material. In this study we present how the polymer morphology (i.e. crystallinity) and the infiltration temperature are able to affect the optical properties of the resulting PET films. Four unique emission bands are observed in pristine PET films; (2) stronger emissions in high crystallinity films attributed to the crystalline regions of the polymer and (2) peaks that show stronger emission in low crystallinity films attributed to the amorphous regions. After the low temperature infiltration (60  $^{\circ}\text{C}$ ) emissions attributed to the amorphous regions demonstrate increases intensity, indicating that the infiltration reaction is predominant in the amorphous regions of the polymer. After infiltration at 150  $^{\circ}\text{C}$ , a very high red shift is observed alongside a complete emission spectra changes, suggesting the reactions taking place at high temperatures are different than low temperature processing. This detailed understanding of the photoluminescence behavior of the hybrid films can provide insight for use of these hybrid materials with a bandgap ideal for unique optical applications.

2:40pm **TF+2D+MG+NS-MoA2 Organic and Hybrid Organic-Inorganic Thin Film Deposition by Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation, Adrienne Stiff-Roberts**, Duke University  
**INVITED**

Over the past fifteen years, matrix-assisted pulsed laser evaporation (MAPLE) has been developed to deposit organic thin films[1-6], inorganic nanoparticles, and hybrid organic-inorganic nanocomposites[4, 7-9]. One variation of the MAPLE technique, resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE), reduces the laser energy (e.g., Er:YAG laser ~2.94 $\mu\text{m}$  peak wavelength) in order to minimize polymer degradation. In addition, because the frequency of the IR laser energy is resonant with OH bond vibrational modes in water, a frozen emulsion (comprising a mixture of the guest material dissolved in an organic solvent and water) is used as the target. Therefore, the unique advantage of emulsion-based RIR-MAPLE is that most of the energy from the IR laser is absorbed by water in the frozen emulsion, which evaporates and gently transfers the guest material to the substrate with minimal solvent exposure and degradation.

In the case of hybrid organic-inorganic nanocomposites, inorganic nanoparticles are embedded in a polymer matrix to achieve specific materials properties or functionality; however, nanoparticles that are mixed with a polymer in solution tend to aggregate due to a polarity difference with polymers[10]. In contrast, RIR-MAPLE is fundamentally different from solution processing and reduces nanoparticle phase segregation by eliminating the need to co-dissolve nanoparticles and polymers into a single common solvent; and by depositing the nanoparticles and polymers in a relatively dry state.

We will demonstrate the capability of RIR-MAPLE to deposit continuous nanoparticle films with the same optical properties as nanoparticles in solution and to minimize nanoparticle phase segregation in hybrid films. We will also demonstrate hybrid organic-inorganic thin films deposited by RIR-MAPLE for application to solar cells. This work is supported in part by ONR.

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3:40pm **TF+2D+MG+NS-MoA5 Integrating Ultrathin ALD/ALE Films with 1D and 2D Materials to Enable New Device Structures, Virginia Wheeler, N. Nepal**, U.S. Naval Research Laboratory, *A. Nath, George Mason University, A.D. Koehler, Z.R. Robinson, J.K. Hite, K.M. Daniels, M.A. Mastro*, U.S. Naval Research Laboratory, *E. Self, P. Pintauro, Vanderbilt University, J.D. Caldwell, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy Jr.*, U.S. Naval Research Laboratory

## INVITED

As device features continue to approach nanoscale dimensions, requisite structures continually grow in complexity often resulting in 3D architectures, nanowires, and/or 2D van der Waals materials. This reduction in size leads to new phenomena, such as quantum confinement effects in electronics or strong localization of light in nanophotonics, which can potentially enable new devices. Realization of novel device structures that exploit these effects requires integration of scalable thin films of various electronic materials onto nanostructures. Atomic layer deposition (ALD) is the preferred method to conformally coat nominally planar as well as complex, high surface area nanostructures with abrupt interfaces, wafer-scale uniformity, and angstrom-scale control of thickness. Additionally, ALD is a low temperature process which allows incorporation with many temperature sensitive nanostructure materials that are not compatible with other deposition techniques. Alternatively, a slightly higher deposition temperature can facilitate atomic layer epitaxy (ALE) of crystalline thin films with all the same beneficial characteristics of ALD. However, the inert nature of 1D and 2D materials often inhibit direct application of ALD/ALE films with desired coverage and uniformity. In this work, we will discuss crucial aspects of ALD/ALE growth, such as surface functionalization and *in situ* nucleation sequences, required to obtain uniform, conformal films on nanostructured substrates.

The essential requirements for integration of ALD/ALE layers with 1D and 2D materials will be evaluated through several case studies including: 1) integration of III-N films on graphene for a hot-electron transistor; 2) coating of carbon fibers for battery and electrode applications; and 3) functional oxide layers on SiC nanopillars to modify their optical response for several potential devices. The substrates in these cases have varying degrees of surface reactivity, so we will address the need for and our current *ex situ* and *in situ* approaches to obtaining sufficient reactivity between the substrate and ALD precursors. Moreover, it was found that ALD parameters (temperature, pulse and purge durations, etc.) impact the effectiveness of uniform, conformal coating of these structures. Other factors, such as sample suspension, are sometime critical to overcoming these limitations while still operating in ALD/ALE windows. Initial devices results will be presented, when appropriate, to demonstrate the feasibility of the integration of ALD thin films in new device structures.

4:20pm **TF+2D+MG+NS-MoA7 Development of the Optical Properties of Silicon Rich Oxide Films Growth by CVD Techniques for Possible Photovoltaic Applications, Karim Monfil-Leyva**, Benemérita Universidad Autónoma de Puebla, Mexico, *A.L. Muñoz-Zurita*, Universidad Politécnica Metropolitana de Puebla, Mexico, *E. Ojeda-Durán, A. Benítez, J. Carrillo-López, J.A. Luna-López, R.C. Ambrosio-Lázaro*, Benemérita Universidad Autónoma de Puebla, Mexico

Currently, electronics and semiconductor studies have focused a great effort to overcome the intrinsic disadvantages of bulk-Si to develop optoelectronic devices. In particular, the Silicon Rich Oxide (SRO) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or silicon-based light emitters. SRO can be deposited by several chemical vapor deposition techniques like Low Pressure Chemical Vapor Deposition (LPCVD) or Hot Filament Chemical Vapor Deposition (HFCVD). Silicon excess in SRO films obtained by LPCVD can be controlled by pressure ratio  $R_o = N_2O/SiH_4$ . Meanwhile, silicon excess in SRO films obtained by HFCVD can be controlled by changing the hydrogen flow ( $H_F$ ).

In this work, we report a study of the optical and structural properties of thin SRO films obtained by LPCVD and HFCVD. Silicon excess was changed by the pressure ratio  $R_o$  in the range of 15 and 45 (SRO15 to SRO45) and  $H_F$  was changed between 25 and 75 sccm. SRO LPCVD films were annealed at 1100 °C. Ellipsometry and step measurements were applied to calculate thickness and the refractive index. Fourier transform infrared (FTIR) measurements were obtained from SRO films to confirm a change on stoichiometry. Absorbance spectra of SRO films showed rocking and bending vibration modes similar to stoichiometric silicon dioxide but an asymmetric stretching mode revealed the non-stoichiometric nature of our semiconductor films. SRO films by LPCVD showed a strong photoluminescence (PL) at room temperature (RT) on two bands, a blue band from 400 to 550 nm or a red band from 575 nm to 875 nm depending on  $R_o$ . Blue and red emission bands were related to donor acceptor decays between traps promoted by defects. SRO films by HFCVD also showed a red band from 500 to 1100 nm (depending on the  $H_F$ ) and this emission was attributed to defects produced by the transport of the precursors. SRO films showed suitable optical properties for possible photovoltaic applications.

5:00pm **TF+2D+MG+NS-MoA9 Radical-Enhanced Atomic Layer Deposition Enabled Multiferroic Composite Synthesis, C. Pham, Jeffrey Chang, J.P. Chang**, University of California at Los Angeles

Multiferroic materials, which exhibit controllable magnetic (ferroelectric) behavior via electric (magnetic) field, are of great interest due to their wide spectrum of new device applications such as non-volatile memory devices. Unfortunately, such behavior is extremely rare in natural single-phase systems. Furthermore, the properties of the few single phase multiferroic materials are too insignificant to be integrated into current device designs. Therefore, alternative strategies involving composite materials are proposed to combine the ferroelectricity and magnetism of different materials, achieving multiferroic behavior. By utilizing piezoelectric and magnetostrictive effects in different material phases, a strain-mediated approach shows great promise for applications. In such a strategy, the interface area per volume, as well as the material crystallinity of each constituent, will greatly influence composite properties. The conformal and high quality film growth with atomic layer deposition (ALD) shows great potential for enabling the multiferroic composites described above.

In this work, lead-free ferroelectric/antiferromagnetic BiFeO<sub>3</sub> (BFO) and ferrimagnetic CoFe<sub>2</sub>O<sub>4</sub> (CFO) thin films were grown on SrTiO<sub>3</sub> (001) (STO) substrate by radical enhanced ALD (REALD) using metalorganic precursors, Bi(tmhd)<sub>3</sub> (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), Co(tmhd)<sub>2</sub>, and Fe(tmhd)<sub>3</sub>. The use of oxygen radicals as an ALD oxidant provides extra process flexibility. Film crystallinities and properties were studied under different conditions. The BFO films showed epitaxial single crystalline growth in a (001) pseudocubic orientation after annealed at 650 °C while the CFO films are polycrystalline due to the lattice mismatch between the film and substrate (~1% for BFO and ~7% for CFO). The piezoelectric properties of BFO films were confirmed using PFM while weak ferromagnetic behavior was also observed. Tunable CFO magnetic properties were shown using thickness-related strain relaxation over the range of 5~90 nm.

Synthesis of multiferroic composites was enabled by REALD. When fixing the total thickness at 40nm, 2-2 BFO/CFO nanolaminate composites with an increasing number of sub-layers showed a controllable competition between magnetic and shape anisotropy. 0-3 CFO/PZT composites were enabled by growing conformal CFO ALD films onto mesoporous PZT medium. SEM confirmed the gradual and conformal coating with increasing ALD cycles. It was found that the pore necks limit the incorporation of CFO inside the mesoporous media as it blocks precursor penetration. The volumetric magnetic properties were found to exceed the values found in literature with 0-3 configurations.

5:20pm **TF+2D+MG+NS-MoA10 Plasma Enhanced Deposition of Nanocrystalline Silicon Thin Films from SiF<sub>4</sub> by RF-PECVD and MDECR: Key Aspects of Growth Dynamics**, *JK. Wang, P. Bulkin, I. Florea, J.L. Maurice, Erik Johnson*, LPICM-CNRS, Ecole Polytechnique, France

For the growth of thin-film hydrogenated silicon by low temperature plasma-enhanced chemical vapor deposition (PECVD), SiF<sub>4</sub> has recently attracted interest as a precursor for numerous reasons, most importantly due to the resilient optoelectronic performance of the resulting layers and devices, even when grown in a slightly oxygen-contaminated growth environment. Nevertheless, many questions remain concerning the critical factors determining the quality of hydrogenated microcrystalline silicon (μc-Si:H) thin films grown from this precursor.

To advance knowledge on this subject, we present studies performed on two very different types of PECVD reactor: a standard capacitively coupled RF-PECVD reactor, using a process gas mixture consisting of Ar/SiF<sub>4</sub>/H<sub>2</sub> and at deposition rates up to 4 Å/s, and a matrix-distributed electron cyclotron resonance (MDECR) PECVD reactor operating at much lower pressures but achieving a higher deposition rate (8 Å/s) and using simply an SiF<sub>4</sub>/H<sub>2</sub> mixture. In doing so, we reveal key details concerning the growth process. We underline recently obtained results concerning three critical experimental findings about the use of SiF<sub>4</sub> as a growth precursor: (1) the importance of temperature for high-deposition rate, low-pressure conditions, (2) the vital role of ion bombardment energy on the quality of growth, and (3) the vastly increased challenge of the nucleation process when using high-density plasma processes. The films generated in these studies have furthermore been studied by cross sectional HR-TEM, revealing more specific details about the changing nature of the films during growth, and the dependence of these dynamics on the maximum ion energy impinging on the surface. These studies - along with residual gas analysis studies and optical emission spectroscopy results - allow us to examine the precise growth mechanism of such films when using an SiF<sub>4</sub>/H<sub>2</sub> mixture.

# Tuesday Morning, October 20, 2015

## 2D Materials Focus Topic

Room: 212C - Session 2D+EM+NS+SS+TF-TuM

### Optical and Optoelectronic Properties of 2D Materials

**Moderator:** Andrea Young, University of California at Santa Barbara

8:00am **2D+EM+NS+SS+TF-TuM1 The Tri-Angular Lattice Exciton (3ALE) Model: Exciton Physics at the Atomic Scale**, *F. Tseng*, NRC Research Associate, *E. Simsek*, George Washington University, *Daniel Gunlycke*, Naval Research Laboratory

Descriptions of excitons in pristine semiconducting crystals usually rely on the hydrogen model adopted for excitons. Owing to the weak screening in monolayer transition-metal dichalcogenides, however, the electron and hole separation in the strongest bound excitons is on the atomic scale, necessitating atomistic treatment. In this presentation, we present a minimalistic exciton model that accounts for the lattice and the spin-orbit and exchange interactions, thus making this model appropriate across the spectrum from Wannier to Frenkel excitons. Using this model, we show that the exciton lifetimes could be extended by transitioning the excitons into excitonic dark states. Longer exciton lifetimes could make these materials candidates for applications in energy management and quantum information processing.

This work has been funded by the Office of Naval Research (ONR), directly and through the Naval Research Laboratory (NRL). E.S. and F.T. acknowledge support from NRL through the ONR Summer Faculty Program and the NRC Research Associateship Program, respectively.

8:20am **2D+EM+NS+SS+TF-TuM2 Opposite Dependence of Microwave-Induced vs. Field-Induced Imaging Contrast in NV<sup>-</sup> based Fluorescence Microscopy as Function of Optical Excitation**, *Etienne Goovaerts*, *S.K.R. Singam*, University of Antwerp, Belgium, *M. Nesladek*, Hasselt University, Belgium, *M. Giugliano*, University of Antwerp, Belgium

The charged nitrogen-vacancy (NV<sup>-</sup>) center is a remarkable defect in diamond which allows interrogation of spin state through its fluorescence. Among the proposed applications, background-free imaging based on fluorescent nanodiamond (FND) was demonstrated [1-3]. The FNDs emission can be discriminated from spurious fluorescence by switching on resonant microwaves (MW) and/or a static magnetic field [1-3], as demonstrated in cells [1] and potentially in small animals [2]. It is now important to understand the origin of the contrast in either of these approaches, and the optimal experimental parameters.

NV<sup>-</sup> defects in single-crystal diamond as well as in FNDs were excited by a 532nm laser through the microscope objective. A compact spectrometer combined with appropriate filters allowed to measure the NV<sup>-</sup> and NV<sup>0</sup> emission. MW-induced contrast is achieved using a broadband circular antenna (i.d. 1mm) on a printed plate, and for field-induced contrast we use a small-sized permanent magnet (~300mT). They are placed closely behind the sample with in each case the magnetic field component along the optical axis of the objective.

For shallow implanted NV in (100) diamond as well as for FNDs the fluorescence is quenched by application of either resonant MWs or static field, with contrast levels systematically higher in the single crystal case than for deposited nanoparticles. The contrast values were measured for laser powers covering 6 orders of magnitude. After an initial rise at very low excitation (max. 13% in crystal, 7% in FND), the MW-induced contrast significantly decreases at higher laser powers. In parallel, field-induced contrast increases from about 12% to values of 38% and 20% for the single crystal and FNDs. This is described under steady state conditions using a 5-level model that includes radiative and nonradiative decay and ground state spin relaxation. The MW-contrast results from induced spin transitions in the triplet ground state while the field effect relies on state mixing within the ground and the excited triplets which change the decay rates. The analysis also shows that the applied excitation rates runs through 3 regimes from below the spontaneous relaxation rate, via an intermediate regime, to above the decay rate of the intermediate singlet.

This work demonstrates the advantages of field-induced contrast microscopy over the MW-induced approach. These become particularly important at high excitation rates which are more often applied in confocal microscopy.

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[2] A. Hegyi, E. Yablonovitch, Nano Lett. 2013, **13**, 1173

[3] R. Chapman, T. Plakhoitnik, Opt. Lett. 2013, **38**, 1847

8:40am **2D+EM+NS+SS+TF-TuM3 2D Materials and Heterostructures for Applications in Optoelectronics**, *Thomas Mueller*, Vienna University of Technology, Austria **INVITED**

Two-dimensional (2D) atomic crystals are currently receiving a lot of attention for applications in (opto-)electronics. In this talk I will review our research activities on photovoltaic energy conversion and photodetection in 2D semiconductors. In particular, I will present monolayer p-n junctions, formed by electrostatic doping using a pair of split gate electrodes, and MoS<sub>2</sub>/WSe<sub>2</sub> van der Waals type-II heterojunctions. Upon optical illumination, conversion of light into electrical energy occurs in both types of devices. I will present measurements of the electrical characteristics, the photovoltaic properties, and the gate voltage dependence of the photoresponse. In the second part of my talk, I will discuss photoconductivity studies of MoS<sub>2</sub> field-effect transistors. We identify photovoltaic and photoconductive effects, which both show strong photoconductive gain. We envision that the efficient photon conversion, combined with the advantages of 2D semiconductors, such as flexibility, high mechanical stability and low costs of production, could lead to new optoelectronic technologies.

9:20am **2D+EM+NS+SS+TF-TuM5 Excitations and Ultrafast Charge Response in Bilayer Transition-Metal Dichalcogenides**, *Volodymyr Turkowski*, *T.S. Rahman*, University of Central Florida

We analyze the absorption spectrum and ultrafast charge dynamics in bilayer 2L-MoS<sub>2</sub>, 2L-MoSe<sub>2</sub> and MoS<sub>2</sub>-WS<sub>2</sub> systems by using time-dependent density functional theory in the density-matrix representation. In particular, we calculate the values of the binding energies of excitons in these structures for both intra- and inter-layer electron-hole excitations and demonstrate that, similar to the case of a single layer, these energies can be as large as hundred(s) of meVs. We also analyze the ultrafast dynamics of the electrons, holes and excitons in the photoexcited bilayers. We pay special attention to the ultrafast hole transfer in these systems and find transfer times of the order 100fs, in agreement with the experimental finding for the MoS<sub>2</sub>-WS<sub>2</sub> system. We perform a detailed *ab initio* study of the spatially- and time-resolved charge density in the systems during the hole transfer and conclude that sulfur and selenium orbitals play an important role in the process. Finally, we discuss possible applications of the results in light harvesting technologies.

Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

9:40am **2D+EM+NS+SS+TF-TuM6 Automatic Localization and Identification of 2D-Material Flakes by Spectroscopic Imaging Ellipsometry**, *Sebastian Funke*, *P.H. Thiesen*, Accurion GmbH, Germany, *G. Greg Hearn*, Accurion Inc.

With the rising of 2D materials in surface sciences, the localization of mono- to few-layers of 2D materials, such as graphene, Molybdenum disulfide, hexagonal boron nitride is a time consuming task. With the help of imaging spectroscopic ellipsometry flakes of 2D materials can be found and its layer numbers can be differentiated.

Therefore a spectroscopical mapping of the sample is done. At selected wavelengths nulling ellipsometry for each pixel in the field of view is done to measure  $\Delta/\Psi$ . The measurement of all pixels is done simultaneously. To cover larger areas than the field of view a XY-patterning is done automatically. For each XY-position spectroscopic  $\Delta/\Psi$  maps are obtained. Every pixel of a  $\Delta/\Psi$  map represents the spectroscopic angle  $\Delta/\Psi$  respectively. By comparing the spectral  $\Delta/\Psi$  values for each pixel with the ellipsometric model of e.g. graphene monolayer, flakes of graphene monolayers on the sample can be found. To ensure, that only flakes are found, a grid with a threshold is used. The threshold indicates the number of pixels in the grid that need to fit to the model.

In the talk we present the capability of imaging ellipsometry to localize and identify monolayer to few-layers of 2D Materials. Flakes of MoS<sub>2</sub> with a size smaller than 10  $\mu$ m can be localized. Monolayer of graphene can be distinguished from bilayers of graphene. To improve the time factor, the use of a Scheimpflug corrected objective is presented. Further investigations on different 2D materials, e.g. h-BN and the implementation of a Raman System is in progress.



11:00am **2D+EM+NS+SS+TF-TuM10 Systematic Hydrogen Intercalation of Epitaxial Graphene for THz Plasmonics, Kevin Daniels,** National Research Council postdoc working at NRL, *A. Boyd*, American Society for Engineering Education postdoc working at NRL, *R.L. Myers-Ward, D.K. Gaskill*, Naval Research Laboratory

Epitaxial growth of graphene via sublimation of silicon and graphitization of carbon atoms from silicon carbide (SiC) is ideal for large scale manufacturing of plasmonic devices but due to partially covalent bonding between the SiC (0001) substrate and the first carbon layer ( $6\sqrt{3}$  buffer layer), the high room temperature mobility necessary for THz plasmonics is reduced significantly compared to exfoliated graphene. The objective of this work is to improve THz response of EG by increasing the mobility and carrier concentration of graphene through hydrogen intercalation where the Si atoms covalently bound to the buffer layer are satisfied by hydrogen atoms and create quasi free standing graphene.

Epitaxial graphene was grown from 6H-SiC (0001) in an Aixtron/Epigress VP508 horizontal hot-wall reactor, etching in  $H_2$  during temperature ramp to  $1570^\circ\text{C}$  and growing graphene in Ar ambient at  $1580^\circ\text{C}$ . H-intercalation of EG was carried out in the same reactor at  $1050^\circ\text{C}$  with a flow of 80slm of  $H_2$  and chamber pressure of 900mbar for 15-75 minutes. Morphology of the quasi-free standing graphene was observed by AFM and SEM. Raman spectroscopy using a 532nm laser (9.6mW) and spot size of  $0.3\mu\text{m}$  were used to take  $80\times 10\mu\text{m}$  maps of each sample where release of the buffer layer is observed, with broadening of the 2D peak full-width-half-max (FWHM) before and after H-intercalation is observed on the graphene terraces and step edges. Number of monolayers before and after H-intercalation was determined by XPS.

From SEM, AFM, Raman and Hall we observe changes in degree of hydrogen intercalation with respect to time. Large areas of partially intercalated EG is observed at 15 minutes which confirmed by a mix of charge carriers and reduced carrier mobility at  $\sim 250\text{cm}^2/\text{Vs}$ . At 30 minutes some graphene terraces remain coupled to the SiC substrate with carrier mobility  $\sim 2250\text{cm}^2/\text{Vs}$ . From 45, 60 and 75 minutes the buffer layer becomes mostly quasi free standing with small spots possibly coupled to the substrate as observed in the SEM with mobilities of  $\sim 3900$ ,  $\sim 4000$  and  $\sim 3700\text{cm}^2/\text{Vs}$  respectively. Measurements of the resulting THz transmission spectra are currently underway to determine if the increase in mobility and carrier concentration results in narrower THz response.

11:20am **2D+EM+NS+SS+TF-TuM11 Determining the Optical Properties of Exfoliated 2D Molybdenum Disulfide on Various Substrates with Imaging Spectroscopic Ellipsometry, Peter H. Thiesen,** Accurion GmbH, Germany, *S. Funke*, HAWK, Germany, *B. Miller, E. Parzinger*, TU München, Germany, *G. Hearn*, Accurion Inc., *A.W. Holleitner, U. Wurstbauer*, TU München, Germany

Ellipsometry is a non-destructive optical method for determining film thickness and optical properties. It measures the change in the state of polarization of the light reflected from the film interfaces. Imaging ellipsometry, which combines the power of ellipsometry with microscopy, has overcome the limitation of poor sample lateral resolution found in conventional non-imaging ellipsometers. The enhanced spatial resolution of imaging ellipsometers potentially expands ellipsometry into new areas of microanalysis, microelectronics, and bio analytics.

Molybdenum disulfide is a layered transition metal dichalcogenide. From the point of current research, 2D-nano materials based on  $\text{MoS}_2$  are very promising because of the special semiconducting properties. The bulk material has an indirect 1.2 eV electronic bandgap, but single layer  $\text{MoS}_2$  has a direct 1.8 eV bandgap. The monolayer can be used in prospective electronic devices like transistors (MOSFETs) or photo detectors.

Wavelength spectra of ellipsometric parameters Delta and Psi of the  $\text{MoS}_2$  monolayers and multilayers were recorded as well as microscopic maps. In case of Sapphire, The psi maps at wavelength of higher energies than the bandgap show a clear contrast between the monolayer and the substrate and at lower energies there is no contrast between the monolayer and the substrate, but the multilayer areas still show a clear contrast-making the unique properties of  $\text{MoS}_2$  monolayers directly visible. The advantage of imaging ellipsometry is the visualisation of the shape of the monolayer and the opportunity to classify the homogeneity of the optical properties of the microcrystallite. To quantify the optical properties, different approaches of optical modelling will be discussed.

11:40am **2D+EM+NS+SS+TF-TuM12 Nonlinear Optical Spectroscopy of 2D Semiconductor Monolayers, Xiaobo Yin,** University of Colorado Boulder

**INVITED**

Transition metal dichalcogenide (TMDC) monolayers have recently emerged as an important class of two-dimensional semiconductors with

potential for electronic and optoelectronic devices. Unlike semi-metallic graphene, layered TMDCs have a sizeable bandgap. More interestingly, when thinned down to a monolayer, TMDCs transform from indirect-bandgap to direct-bandgap semiconductors, exhibiting a number of intriguing optical phenomena such as valley-selective circular dichroism, doping-dependent charged excitons and strong photocurrent responses. Using nonlinear optical spectroscopy, we probe experimentally the evidence of a series of excitonic dark states as well as structural symmetry in single-layer  $\text{WS}_2$  and  $\text{MoS}_2$ .

# Tuesday Afternoon, October 20, 2015

## 2D Materials Focus Topic

Room: 212C - Session

2D+EM+MC+MI+NS+SP+SS+TF-TuA

## Electronic and Magnetic Properties of 2D Materials

**Moderator:** Thomas Mueller, Vienna University of Technology, Austria, Xiaobo Yin, University of Colorado Boulder

2:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA1 Direct Capacitive Probe of Isospin Order in Graphene Bilayers, Andrea Young**, University of California at Santa Barbara **INVITED**

Bilayer graphene is a highly tunable electronic system in which electric fields can be used to control both the carrier density as well as the electronic structure. Like its monolayer cousin, the bilayer graphene Landau levels are characterized by approximate spin and valley degeneracy; unlike monolayer, however, the three dimensional structure of the bilayer allows control of the sublattice splitting with a perpendicular electric field. This feature has been used extensively to probe the phase diagram of interacting electrons, particularly within the zero energy Landau level, revealing a number of interacting states characterized by spin and/or valley order. Typically, however, the spin or valley order is inferred indirectly by varying conjugate fields and inferring the order from the resulting changes in conductivity. Here I will describe a technique capable of resolving layer-polarization directly through high sensitivity capacitance measurements. The measurements confirm the known features of the bilayer graphene phase diagram, while revealing several new phases and a series of sharp features associated with phase transitions between states of different layer polarization. These features suggest a new mechanism for inversion symmetry breaking in Bernal stacked bilayer graphene.

3:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA3 Patterning Hydrogenated Graphene via Electron Beam Irradiation, Woo-Kyung Lee, K.E. Whitener, J.T. Robinson, P.E. Sheehan**, Naval Research Laboratory

We demonstrate that electron-beam irradiation selectively removes hydrogen atoms from hydrogenated graphene (HG) prepared by the Birch reduction.<sup>1</sup> Hydrogen removal can pattern the surface with two different functionalities. First, we show that partially-hydrogenated graphene (Phg) on a SiO<sub>2</sub> substrate is ferromagnetic, and that the local magnetic strength can be tuned using e-beam irradiation. An e-beam lithography system enables us to modulate or eliminate the permanent magnetization over a large area to produce a patterned magnetic array. Secondly, since removal of the hydrogens converts the highly electrically insulating HG back into conductive graphene, we can write chemically isolated, dehydrogenated graphene nanoribbons (GNR) as narrow as 100 nm. These GNRs have a low sheet resistance ( $\geq 31.5 \text{ K}\Omega/\square$ ), only 10x that of the pristine graphene, and their Dirac points before and after e-beam irradiation appear at comparable gate voltages.

1. W.K. Lee et al., *Advanced Materials*, 27, 1774 (2015).

3:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA4 Large-Area Low-Pressure Synthesis of Single-Layer MoS<sub>2</sub> Films and Schottky-Barrier Formation upon Metal Deposition, Michael Gomez, J. Martinez, M. Valentin, L. Bartels**, UC Riverside

Using a high vacuum CVD process we are able to synthesize large area monolayer MoS<sub>2</sub> films. Organic chalcogen precursors are released into the growth chamber and react with a Mo filament creating films up to 2cm<sup>2</sup> in size that are uniform and free of oxides. The films have pronounced photoluminescence intensity and are in Raman spectroscopy indistinguishable from exfoliated material. Metal contact formation to these films was investigated under UHV conditions utilizing X-Ray Photoelectron Spectroscopy. These measurements permit us to follow the formation of a Schottky Barrier with increasing metal film thickness on the Angstrom scale. We utilize core level spectroscopy to indicate the evolution of the MoS<sub>2</sub> valence band under metal deposition.

4:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA7 Accelerating the Discovery of Alternative Fuel Catalysts through Intelligent Computational Framework, Altaf Karim**, COMSATS Institute of Information Technology, Pakistan **INVITED**

In today's modern world of high performance computing, properties of materials can be predicted with high accuracy before these materials are

ever made. In this scenario my focus has been on the development of state of the art computational framework based on intelligent/ smart self-learning algorithms for the design and discovery of catalytic materials. By giving some examples, I will describe how this enterprise of the predictive multi-scale modeling/simulation has been passing through the stages of its evolution and how these complex algorithmic species integrated themselves into an intelligent python, which is helping scientists design & discover new materials for alternative fuel catalysis. In practice, our computational framework develops databases of candidate catalysts. Further this framework enables a set of algorithms to screen across a broad range of multi metallic catalytic materials with variable reactivity, selectivity, and stability while searching for materials with desired combination of properties required for the optimal catalytic performance for alternative fuel production. I would also explain that how our computational tools in catalyst design deal with the multi-component microstructures of catalysts composed of multi-element nano chunks. In order to tune up the rate limiting processes we can take advantage of the multi-element nano chunks. For example, on many catalytic surfaces the diffusion is rate limiting process for larger organic molecules. To enhance the diffusion such molecules on such surfaces, nano chunks of other materials (on which the diffusion of the organic molecules is comparatively higher) can be integrated in the catalyst's surface, which improves the overall performance of the catalyst in terms of overall reactivity and also selectivity. In addition to that our tools also help us to filter out, from the databases, stable multi-component microstructures of artificially engineered catalysts.

5:00pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA9 Probing Massive Dirac Electrons in Bilayer Graphene, Feng Wang**, University of California at Berkeley **INVITED**

Electrons in monolayer graphene are described by massless Dirac electrons, which exhibit unique quantum phenomena due to the pseudospin and Berry phase of the massless electrons. In this talk, I will discuss our effort in probing massive Dirac electrons in gapped bilayer graphene. In particular, I will discuss the topologically protected 1D conducting channel at the domain boundary of AB-BA bilayers, which can be attributed to the quantum valley Hall edge states in gapped bilayer graphene.

5:40pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA11 Combining Photoemission and Photoluminescence Microscopy to Study Substrate Transfer Process Effects in Chemical Vapor Deposited MoS<sub>2</sub> Monolayers, Olivier Renault, M. Frégnaux**, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, J. Bleuse, Univ. Grenoble-Alpes & CEA-INAC, France, H. Kim, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, D. Voiry, M. Chhowalla, Rutgers University

Within the perspective of integrating two-dimensional transition metal dichalcogenides (2D TMDs) such as molybdenum disulfide (MoS<sub>2</sub>), into devices, it becomes of utmost importance to assess the influence of each step of the device fabrication process on the optical and transport properties of the MoS<sub>2</sub> single layer (1L) domains. Particularly at the deposition stage the properties may be influenced by substrate effects [1], and later, transfer processes may further alter the desired properties of TMDs. This requires effective microscopic characterization techniques.

We present a characterization method combining photoemission microscopy (XPEEM and Kpeem) and photoluminescence microscopy to compare the structural, optical and electronic properties of both as-deposited and transferred MoS<sub>2</sub> 1L domains onto different substrates. XPEEM is used with laboratory sources in both direct space imaging for work function and core-level mapping [2] and particularly in the momentum microscopy mode (k-PEEM) to perform parallel angular imaging and retrieve the band structure in a one shot experiment [3]. Micro-photoluminescence spectroscopy at low (5K) and room temperature is used to detect the specific radiative recombination that occurs in MoS<sub>2</sub> 1L (direct band gap semiconductor behavior) and to evidence the eventual presence of midgap states caused by process-induced defects. The results of both characterization techniques will be presented for MoS<sub>2</sub> 1L domains transferred onto silica and gold substrates highlighting the roles of substrate nature (metal or insulant), surface roughness, and the presence of structural defects whether induced by the preparation process or intrinsic such as grain boundaries.

[1] Jin et al. *Phys. Rev. Lett.* 111 (2013), 106801.

[2] Kim, Renault, et al. *Appl. Phys. Lett.* 105 (2014) 011605.

[3] Mathieu et al., *PRB* 83 (2011) 235436.

# Wednesday Morning, October 21, 2015

## 2D Materials Focus Topic

Room: 212C - Session 2D+MN+NS+SP+SS+TF-WeM

### Mechanical and Thermal Properties of 2D Materials

**Moderator:** Oleg Yazev, Ecole Polytechnique Fédérale de Lausanne (EPFL), Petra Reinke, University of Virginia

8:00am **2D+MN+NS+SP+SS+TF-WeM1 Mechanical Properties of Polycrystalline Graphene, Joseph Gonzales**, University of South Florida, R. Perriot, Los Alamos National Laboratory, I.I. Oleynik, University of South Florida

Experimental investigation of mechanical properties indicates that the polycrystalline graphene grown by chemical vapor deposition is as strong as pristine. The microscopic characterization of graphene samples using Atomic Force microscopy (AFM) nano-indentation is limited in the sense that the detailed mechanical characteristics such as stress and strain distributions under the indenter, elastic moduli and breaking strength are not available directly from experiment. Using accurate description of interatomic interactions provided by novel screened environment-dependent bond order, (SED-REBO) potential, we performed large-scale molecular dynamics investigations of mechanical properties of polycrystalline graphene under conditions mimicking nano-indentation AFM experiments. The atomically resolved characterization of the stress and strain distributions under indenter are used to understand detailed mechanisms of graphene strength and failure. The breaking strength, the crack initiation and propagation are investigated as a function of the grain boundary structure and the grain size distribution as well as the position of the indenter – at the center of the grain, at the a single grain boundary and at the junction of three or more grain boundaries.

8:40am **2D+MN+NS+SP+SS+TF-WeM3 Lévy Flights Found in Freestanding Graphene, Paul Thibado**, 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 the 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 introduce a new theoretical approach using fractional-stochastic calculus.

Acknowledgements:

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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).

9:00am **2D+MN+NS+SP+SS+TF-WeM4 Multilayer Graphene Strength Characterization, Joseph Rowley**, N. Boyer, K. Berry, R.C. Davis, Brigham Young University, R. Creighton, J. Abbott, S. Cornaby, M. Harker, Moxtek Inc., R. Vanfleet, Brigham Young University

Although there are many examples in the literature of multilayer graphene fabrication and electrical characterization, there is a lack of data on the mechanical properties of multilayer graphene, especially many layer. Conversely there is data about the mechanical properties of single layer graphene, and limited information about bilayer and few layer, but little about many layer. Multilayer Graphene was fabricated using chemical vapor deposition on a Nickel catalyst. Different flow rates and cooling rates were investigated to produce many layer films. Due to the high strength in graphene, these films were able to be suspended over millimeter size openings and have a differential pressure applied. This allowed for the characterization of the strength of these membranes using bulge testing.

9:20am **2D+MN+NS+SP+SS+TF-WeM5 Nanoelectromechanical Systems Based on 2D Materials beyond Graphene -- Effects from Geometry, Nonlinearity, and Anisotropy, Zenghui Wang**, Case Western Reserve University **INVITED**

Investigating and manipulating the mechanical degree of freedom in two-dimensional (2D) nanostructures present unique challenges and opportunities: such effort demands advanced fabrication and measurement schemes, and offers new insight into the physical properties of 2D materials. I will present our explorations and findings in mechanical processes at the nanoscale, through studying resonant nanoelectromechanical systems (NEMS) based on 2D materials beyond graphene (e.g., molybdenum disulfide, black phosphorus, etc.). I will discuss the implications of geometrical irregularities on the nanomechanical responses of 2D-material-based resonators; impacts of device and material parameters on the mechanical nonlinearity and motional noise in 2D resonant transducers; and effects of material anisotropy in nanomechanical resonators based on new types of highly anisotropic 2D materials. These findings open new pathways towards nanomechanical coupling and tuning of the physical properties in 2D nanomaterials, and offer opportunities for building novel devices with new multimode functions.

11:00am **2D+MN+NS+SP+SS+TF-WeM10 Phonon Spectroscopy of Graphene Field Effect Devices with the STM, Fabian Natterer, Y. Zhao, J. Wyrick**, NIST/CNST, W.Y. Ruan, Y.-H.C. Chan, M.-Y.C. Chou, Georgia Institute of Technology, N.B. Zhitenev, J.A. Stroscio, NIST/CNST

Phonon spectroscopy of graphene by inelastic electron tunneling spectroscopy with the STM has been elusive in previous measurements [1–3]. The difficulty lies within the weak phonon signatures that are buried by other dominant spectral features that inhibit a clear distinction between phonons and miscellaneous excitations. Utilizing a back gated graphene device that permits continuous adjustment of the global charge carrier density, we employ an averaging method where individual tunneling spectra at varying charge carrier density are condensed into one representative spectrum [4]. This method improves the signal for inelastic transitions that appear at constant threshold, while it broadens and thereby suppresses dispersive spectral features. We use this method to demonstrate the mapping of the total graphene phonon density of states, in good agreement with density functional calculations. Using the knowledge about the phonons thusly obtained, we closely examine our gate resolved spectra and observe a surprising and abrupt change in the phonon intensity when the graphene charge carrier type is switched through a variation of the back gate electrode potential. This sudden variation in phonon intensity is asymmetric in carrier type, depending on the sign of the tunneling bias. We invoke a resonance mediated tunneling process that relies on the presence of tip-induced quasi-bound state resonances in graphene, resembling whispering gallery modes for electrons and holes [5]. Our tip-sample system thereby mimics a giant molecular state and shares analogies with resonant enhanced excitations of molecular vibrational or rotational modes [6–9].

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11:20am **2D+MN+NS+SP+SS+TF-WeM11 Edge-state-induced Stabilization of Dopants in Graphene, Yuuki Uchida, A. Akaiishi, J. Nakamura**, The University of Electro-Communications (UEC-Tokyo) and JST CREST, Japan

Impurity doping is an efficient way to modify electronic properties of graphene. Several groups have reported the stability of dopants in graphene, especially near edges of graphene: Impurity atoms prefer to locate at the zigzag edge of graphene rather than the armchair one[1]. It has also been

reported that the electronic properties are strongly dependent upon the location of dopants, which is derived from the non-equivalence of the two sublattice[2]. It is well-known that the edge-localized state emerges at the zigzag edge[3], which is specific for the so-called bipartite lattice. However, it has not been clarified yet how the edge-state affects the dopant stability depending on the sublattice. In this study, we investigate the role of the sublattice-dependent edge-state on the stabilization of impurities. We evaluate the dependence of the structural stability on the distance of impurity atoms from the zigzag edge using first-principles calculations within the density-functional theory. We have employed two types of graphene nanoribbons (GNRs) with the armchair- (AGNR) or the zigzag- (ZGNR) edge.

For AGNR, the formation energy of dopants does not change neither systematically nor monotonically as a function of the distance from the edge. On the other hand, for ZGNR, the formation energy is lower than that for AGNR and decreases with decreasing distance from the edge. In addition, two types of tendencies are confirmed for odd- and even-numbered sites from the zigzag edge, corresponding to the different sublattices of the bipartite lattice.

Such peculiar behavior as for of the formation energy can be explained as follows : The doped N atom donates its electron to the unoccupied-edge-state just above the Fermi level, resulting in the lowering of the one-electron energy of this state. The smaller the distance of N atoms from the zigzag edge is, the larger the electrostatic attraction between electrons of edge-localized states and positively-charged ion-shell at the N site becomes. Further, N atoms are much more stabilized at the odd-numbered site, because the edge-state has finite amplitude only at the odd-numbered sites.

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11:40am **2D+MN+NS+SP+SS+TF-WeM12 Exploring the Thermal Stability of Two-Dimensional Black Phosphorus**, *Xiaolong Liu, J.D. Wood, K.-S. Chen, E. Cho, M.C. Hersam*, Northwestern University

Two dimensional (2D) black phosphorus (BP) has attracted significant attention due to its superlative electronic and optical properties. Unlike graphene, its intrinsic and thickness-dependent band gap makes it feasible for direct application in electronic and optoelectronic devices.<sup>1</sup> However, before 2D BP can be effectively employed in such applications, it is necessary to establish the thermal stability of 2D BP since annealing is a key element in most device fabrication processes. Towards this end, we have utilized *in situ* scanning/transmission electron microscopy and spectroscopy methods to characterize the thermal decomposition process of mechanically exfoliated 2D BP.<sup>2</sup> The decomposition is observed to occur at ~400 °C in the form of sublimation, compared to the 550 °C of bulk BP. This decomposition initiates *via* eye-shaped cracks along the [001] direction and then continues until only a thin, amorphous red phosphorous-like skeleton remains. *In situ* electron energy loss spectroscopy, energy-dispersive X-ray spectroscopy, and energy-loss near-edge structure changes provide further quantitative insight into this chemical transformation process.

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12:00pm **2D+MN+NS+SP+SS+TF-WeM13 Gas Permeation Through 1 nm Thick Carbon Nanomembranes**, *A. Beyer, M. Ai, Bielefeld University, Germany, S. Shishatskiy, J. Wind, Helmholtz-Zentrum Geesthacht, Germany, X. Zhang, V. Chinaryan, Y. Yang, Armin Götzhäuser*, Bielefeld University, Germany

The gas permeation characteristics of 1 nm thick carbon nanomembranes (CNMs) from self-assembled monolayers are reported. The assembly of CNMs onto polydimethylsiloxane (PDMS) support membranes allows determination of gas permeation characteristics. Single layer and triple layer CNMs were investigated in respect to permeation of hydrogen, helium, carbon dioxide, oxygen, nitrogen, argon, methane and ethane. In addition, the CNM-PDMS composites were characterized by X-ray photoelectron spectroscopy, helium-ion microscopy as well as atomic force microscopy. A careful analysis about the contribution of the PDMS support membranes to the gas permeation allowed an estimate of the intrinsic CNM permeances. These values indicate a molecular sieve-like property of CNMs which is attributed to molecular-sized channels in CNMs. As an example, hydrogen and carbon dioxide gas molecules display an order of magnitude higher permeance values for single layer CNMs in comparison to oxygen and nitrogen, which possess larger kinetic diameters.

## Plasma Science and Technology

Room: 210B - Session PS+2D+SE-WeM

## Plasma Diagnostics, Sensors and Control II

Moderator: Colin Wolden, Colorado School of Mines

8:20am **PS+2D+SE-WeM2 Diagnostics for Ionized Physical Vapor Deposition Chambers**, *YuiLun Wu, P. Piotrowicz*, University of Illinois at Urbana-Champaign, *I.A. Shehelkanov*, National Nuclear Research University (MEPhI), *D.N. Ruzic*, University of Illinois at Urbana-Champaign

As the critical dimension of the semiconductor device continues to shrink and aspect ratio continues to rise, more diagnostics are needed to accurately predict the deposition profile of features on the wafer. Traditionally, the incident ion fluxes are considered to be perfectly normal to the wafer plane due to the electric field of the plasma sheath. However from simulation results [1] the ion flux from a magnetron discharge has a narrow angular distribution and this distribution is becoming more significant as the aspect ratio increases. In order to confirm and adjust this predicted distribution a sensor to measure angular distribution of ions in an industrial scale chamber is designed and developed. The sensor is a combined gridded energy analyzer (GEA) and a quartz crystal microbalance (QCM) [2], with a high aspect ratio collimator in place of the normal electron repeller grid for angular measurement distribution measurements. The collimator is made of 3D-printed plastic elements with 600µm nominal openings which provides 1 degree angular resolution. This combined QCM and GEA setup is capable to determine fluxes of metal ions, metal atoms and argon ions at 30kW DC magnetron nominal target power. The setup is able to tilt around 10 degrees about the wafer plane in 1 degree intervals and measure the angular distribution of the ion and neutral fluxes generated by the discharge. A time resolved triple Langmuir probe was also employed to measure the plasma parameters such as electron temperature and density and scanning in a three dimensional map.

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8:40am **PS+2D+SE-WeM3 Probing the Plasma Chemistry that Underpins Diamond Chemical Vapour Deposition**, *Michael Ashfold*, University of Bristol, United Kingdom of Great Britain and Northern Ireland, *M.W. Kelly, B.S. Truscott*, University of Bristol, UK, United Kingdom of Great Britain and Northern Ireland, *Y.A. Mankelevich*, Moscow State University, Russia, Russian Federation

Most diamond chemical vapour deposition (CVD) employs microwave (MW) activated C/H (typically CH<sub>4</sub>/H<sub>2</sub>) gas mixtures. Many previous studies have sought to explore (and optimise) radical formation in such activated gas mixture, and the ways in which these radicals add to, and are accommodated on and in, the growing diamond surface.

Our activities in this area employ an interrelated three-pronged approach, *i.e.*

i) electronic spectroscopy methods (cavity ring down absorption and optical emission spectroscopies) to determine the spatial distributions of selected species (*e.g.* H atoms, CH and C<sub>2</sub> radicals) as functions of process variables like the process gas mixing ratio, flow rate and total pressure, and MW power,

ii) complementary 2-dimensional (2-D) modelling of the plasma chemistry and composition with the aim not just of rationalising the spatial resolved column density data obtained in (i), but also enabling prediction of the concentrations of other key gas phase species (*e.g.* CH<sub>3</sub> radicals, which are generally regarded as the dominant growth species) that are not amenable to spectroscopic detection, as functions of process condition, and

iii) quantum mechanical (QM) and QM-molecular mechanics (MM) calculations of the energetics of the elementary steps involved in radical addition to, migration on, and eventual accommodation on, a growing diamond surface.

This invited presentation will summarise the current understanding of diamond CVD from traditional C/H gas mixtures and results of recent studies designed to explore and explain the significant growth rate enhancements that can be achieved by adding trace amounts of nitrogen to such gas mixtures.

9:20am **PS+2D+SE-WeM5 Ionization Zones and the Deposition of Thin Films in the Transition Region from Non-Reactive to Reactive Magnetron Sputtering including dc, HiPIMS, and Burst-HiPIMS Modes, Yuchen Yang, X. Zhou, A. Anders,** Lawrence Berkeley Lab, University of California, Berkeley

Research has been done for copper and chromium targets in conventional non-reactive HiPIMS, revealing the disappearance of localized ionization zones when operating at high power due to high metal neutral supply from the target. However, relatively little research has been done for reactive HiPIMS. In this work we investigate the existence of ionization zones in various forms of reactive magnetron sputtering: direct current (dc) and HiPIMS for conventional pulse patterns and in burst mode. Copper and chromium targets are selected with nitrogen as reactive gas because (i) in the non-reactive regime Cu and Cr can be operated with or without ionization zones, and (ii) these target materials form application-relevant compound films, e.g. of interest in wear and corrosion-resistant applications, medical implants, metallization layers, etc.

Work at LBNL is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

11:00am **PS+2D+SE-WeM10 Modelling of the Reactive High Power Impulse Magnetron Sputtering (HiPIMS) process, JonTomas Gudmundsson,** University of Iceland, D. Lundin, Université Paris-Sud, France, N. Brenning, KTH Royal Institute of Technology, Sweden, T. Minea, Université Paris-Sud, France

Reactive high power impulse magnetron sputtering (HiPIMS) [1] provides both a high ionization fraction of the sputtered material and a high dissociation fraction of the molecular gas. We demonstrate this through an ionization

region model (IRM) [2] of the reactive Ar/O<sub>2</sub> HiPIMS discharge with a titanium target that was developed to study the temporal behavior of the discharge plasma parameters. We explore the influence of oxygen dilution on the discharge properties such as electron density, the ionization fraction of the sputtered vapour, the oxygen dissociation fraction and the onset and role of self sputtering. We discuss the important processes and challenges for more detailed modeling of the reactive HiPIMS discharge. Furthermore, we discuss experimental observations during reactive high power impulse magnetron sputtering (HiPIMS) of Ti target in Ar/N<sub>2</sub> and Ar/O<sub>2</sub> atmosphere. The discharge current waveform is highly dependent on the reactive gas flow rate, pulse repetition frequency and discharge voltage. The discharge current increases with decreasing repetition frequency. This we attribute to an increase in the effective secondary electron emission yield during the self-sputtering phase of the pulse, as nitride [3] or oxide [4] forms on the target.

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11:20am **PS+2D+SE-WeM11 Pulsed Magnetron Sputtering Plasma Optimization for Large Area Growth of Two-dimensional MoS<sub>2</sub>, Andrey Voevodin,** Air Force Research Laboratory, C. Muratore, University of Dayton, A.R. Waite, J. Bultman, A. Safriet, J. Hu, Air Force Research Laboratory

Pulsed magnetron sputtering process provides an alternative scalable and reduced temperature growth pathway for the direct synthesis of two-dimensional (2D) materials for electronic device applications [1]. To avoid defect generation by excessive ion bombardment, while maintaining sufficient adatom mobility on the condensation surface at low substrate temperatures, the ion flux and kinetic energy must be modulated. In this study a variable intensity magnetic field was used to control chemistry, energy, and spatial density distribution characteristics of plasma produced by pulsed magnetron sputtering of MoS<sub>2</sub> in 15 mTorr argon. An electromagnetic coil positioned above the substrate generated a 5-15 G magnetic field near substrate surface, causing redirection of magnetron particle flux for tuning of electron and ion densities at the substrate surface. Both plasma emission and mass-spectroscopy analysis showed an abundance of excited and ionized Ar as well as Mo and S species with no evidence for MoS radicals. Wavelength specific plasma imaging and mass spectroscopy studies demonstrated that the applied magnetic field mostly affects excited and ionized Ar generated in background gas collisions with electrons trapped by the magnetic field lines, while the trajectories of Mo and S species generated from the target surfaces are influenced to a much lesser degree. The imposed magnetic field intensity

was adjusted to selectively filter Ar species from reaching the substrate and to find a balance between reducing unnecessary Ar bombardment and preventing shifting energy distributions of all arriving ions above 8 eV, where point defect generation is expected for hexagonal MoS<sub>2</sub>. Plasma studies were used to select optimum growth conditions for 2D MoS<sub>2</sub> synthesis on SiO<sub>2</sub> surfaces at 700 °C. Film thickness uniformity was verified by producing 2-3 monolayer layer thick hexagonal polycrystalline MoS<sub>2</sub> films over 25-50 mm scale area sizes as confirmed by in-situ Raman spectroscopy and TEM microscopy.

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11:40am **PS+2D+SE-WeM12 Molybdenum Nitride Formation by N<sub>2</sub> Plasma Exposure on Molybdenum Disulfide: In-situ Surface Study, Angelica Azcatl, X. Qin, Q. Wang, N. Lu, M.J. Kim, C.L. Hinkle, R.M. Wallace,** The University of Texas at Dallas

Two-dimensional molybdenum disulfide (MoS<sub>2</sub>) is currently considered as a potential channel material for CMOS applications. Electron mobilities on the order of 470 cm<sup>2</sup>/Vs [1] have been reported for few-layer MoS<sub>2</sub> based FETs. Such promising results have fueled the efforts on synthesis of large area and high quality mono and few-layer MoS<sub>2</sub>. Yet, the development of MoS<sub>2</sub> processing techniques of interest for device fabrication (i.e. doping, etching, functionalization) is still in an early stage.

Recently, it has been reported that when MoS<sub>2</sub> is exposed to SF<sub>6</sub>, CF<sub>4</sub> or CHF<sub>3</sub> plasma treatments, fluorine can be introduced in the MoS<sub>2</sub> structure as an acceptor dopant, resulting in p-type doping. In parallel, due to the weak van der Waals interlayer forces, layer etching occurred as a side effect after these fluorine-based plasma exposures. [2]

Following the exploration of the effect of plasma exposures on MoS<sub>2</sub>, in this study nitrogen plasma exposures on MoS<sub>2</sub> were performed, while the surface chemistry was monitored by in-situ by X-ray Photoelectron Spectroscopy. Theoretical studies have shown that substitution of sulfur with nitrogen in MoS<sub>2</sub> leads to p-type doping. [3,4] Here, the chemical analysis obtained by XPS indicates that nitrogen will covalently interact with molybdenum to generate molybdenum nitride. It was found that the nitrogen content in MoS<sub>2</sub> can be controlled with exposure time. The thermal stability of MoN<sub>x</sub> formed due to sulfur replacement with nitrogen will be discussed. Finally, Raman Spectroscopy studies and Scanning Transmission Electrons Microscopy imaging on the MoN<sub>x</sub>/MoS<sub>2</sub> structure will be presented to discuss the impact of the Mo-N bonding environment on the MoS<sub>2</sub> structure. This study will give an important insight for the understanding of the interaction of MoS<sub>2</sub> with a non-metal dopant atom, nitrogen, which has implications on the electrical properties of MoS<sub>2</sub>.

This work is supported in part the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST.

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12:00pm **PS+2D+SE-WeM13 Low Temperature Synthesis of AlYB<sub>14</sub> by High Power Pulsed Magnetron Sputtering, Oliver Hunold, Y.T. Chen, D. Music,** RWTH Aachen University, Germany, P.O.A. Persson, Linköping University, Sweden, J.M. Schneider, RWTH Aachen University, Germany

The influence of ion bombardment on the structure evolution of AlYB<sub>14</sub> was studied by using high power pulsed magnetron sputtering (HPPMS). The structure was analyzed by X-ray and electron diffraction. The diffraction data are consistent with the formation of crystalline AlYB<sub>14</sub> domains in an amorphous matrix. As the growth temperature was 675 °C synthesis was conducted at 725 °C below the bulk synthesis temperature. It is reasonable to assume that this decrease in the growth temperature is facilitated by bombardment of ions formed in the HPPMS discharge resulting in enhanced surface diffusion and hence higher adatom mobility. This work may be relevant for synthesizing other boron rich solids with low symmetry crystal structures at temperatures well below their bulk synthesis temperature.

# Wednesday Afternoon, October 21, 2015

## 2D Materials Focus Topic

Room: 212C - Session 2D+EM+IS+MC+NS+SP+SS-WeA

### Dopants and Defects in 2D Materials

**Moderator:** Daniel Gunlycke, Naval Research Laboratory, Zenghui Wang, Case Western Reserve University

2:20pm **2D+EM+IS+MC+NS+SP+SS-WeA1 The Effect of Defect Density on the Mechanical Properties of Graphene**, *Jonathan Willman, J.M. Gonzales*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory, *I.I. Oleynik*, University of South Florida

Recent experiments involving nanoindentation of graphene have demonstrated counterintuitive weakening of Young's modulus with increasing concentrations of point defects in graphene in contradiction to previous investigations. To fully resolve these inconsistencies we perform large-scale molecular dynamics simulations of nanoindentation under conditions of Atomic Force Microscopy (AFM) nanoindentation experiments. The reliable description of interatomic interactions is achieved by using recently developed screened environment-dependent bond order (SED-REBO) potential. The elastic properties of the defective graphene, the breaking strength and the mechanisms of fracture under indenter are investigated as a function of type of point defects as well as their concentration.

2:40pm **2D+EM+IS+MC+NS+SP+SS-WeA2 Investigation of Grain Boundaries in CVD Grown MoS<sub>2</sub>**, *Kolyo Marinov, D. Ovchinnikov, D. Dumcenco, A. Kis*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

We present the characterization of grain boundaries in polycrystalline CVD-grown MoS<sub>2</sub> films. Epitaxial growth on sapphire substrates is achieved leading to preferred orientation of the domains, which is confirmed by transmission electron microscopy experiments. Using Scanning Kelvin probe microscopy the local potential drop across the three predominant types of grain boundaries in field effect transistors is investigated. These measurements demonstrate that the interfaces between single grains do not degrade the electrical conductivity, which is due to the well aligned growth of the single domains. Furthermore, the relatively high mobility of electrons in the polycrystalline material stays constant even in devices with channels of 80  $\mu\text{m}$  containing multiple grains, separated by grain boundaries. Our approach is a step forward to fabrication of large-area, uniform and high quality single-layer CVD MoS<sub>2</sub>.

3:00pm **2D+EM+IS+MC+NS+SP+SS-WeA3 Polycrystalline 2D Materials: Atomic Structure and Electronic Transport Properties**, *Oleg Yazyev*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland  
**INVITED**

Grain boundaries and dislocations are intrinsic topological defects of polycrystalline materials, which inevitably affect their physical properties. In my talk, I will discuss the structure of topological defects in two-dimensional (2D) materials such as graphene and monolayer transition metal dichalcogenides (TMDCs) [1].

I will first introduce a general approach for constructing dislocations in graphene characterized by arbitrary Burgers vectors and grain boundaries covering the complete range of possible misorientation angles. By means of first-principles calculations we address the thermodynamic properties of grain boundaries revealing energetically favorable large-angle configurations as well as dramatic stabilization of small-angle configurations via the out-of-plane deformation, a remarkable feature of graphene as a two-dimensional material [2]. Both the presence of stable large-angle grain-boundary motifs and the out-of-plane deformation of small-angle configurations have recently been observed by scanning tunneling microscopy [3].

In the rest of my talk, I will focus on the electronic transport properties of polycrystalline 2D materials. Ballistic charge-carrier transmission across periodic grain boundaries is governed primarily by momentum conservation. Two distinct transport behaviors of such grain boundaries in graphene are predicted – either perfect reflection or high transparency with respect to low-energy charge carriers depending on the grain boundary periodicity [4]. It is also shown that certain periodic line defect structures can be engineered and offer opportunities for generating valley polarized charge carriers [5]. Beyond the momentum conservation picture we find that the transmission of low-energy charge carriers can be dramatically suppressed in the small-angle limit [6]. Unlike graphene, TMDCs combine a two-valley electronic band structure with strong spin-orbit effects. The

latter can be employed for creating spin-polarized currents and adds yet another conservation law in the electronic transport across regular defects such as the frequently observed inversion domain boundaries [7,8].

\* This work has been supported by the Swiss NSF, ERC and Graphene Flagship.

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4:20pm **2D+EM+IS+MC+NS+SP+SS-WeA7 Defects Compensation and Refining Optical Luminescence in Organic/Transition Metal Dichalcogenide Heterostructure**, *J.H. Park*, UC San Diego, *A.M. Sanne, H.C.P. Movva*, UT-Austin, *S. Vishwanath*, Cornell University, *Il Jo Kwak*, UC San Diego, *H. Xing*, Cornell University, *J. Robertson*, University of Cambridge, UK, *S.K. Banerjee*, UT-Austin, *A.C. Kummel*, UC San Diego

Since layered transition-metal dichalcogenides (TMD) have demonstrated novel electronic and optoelectronic property, intense research has focused synthesis and integration into future electronic devices. Unlike graphene, TMD materials have band gaps, and these band structures can be tuned by thickness. However, in many cases, unintentional defects can be observed on TMD giving rise to the degradation of performance in the devices. Even for mechanical exfoliated TMD, there is a high density of defects, such as vacancies. For successful integration of TMD into devices, proper passivation of defects on TMD requires high stability in ambient conditions. In this study, a TiOPc monolayer was employed for passivation of defects to improve electrical and optical properties in TMD devices. Multilayer MoS<sub>2</sub> flakes were cleaved in ambient condition and transferred into the UHV chamber; afterwards, TiOPc monolayers were deposited on the MoS<sub>2</sub> surfaces by organic molecular beam epitaxy. After deposition, TiOPc forms a monolayer with only few defects, and the TiOPc monolayer structure has square lattice in a 1.5x1.5 nm grid. This crystal structure indicates that each TiOPc in the monolayer is directed outward to vacuum. The deposited TiOPc layer has very high thermal stability on MoS<sub>2</sub>; the TiOPc layer on MoS<sub>2</sub> requires annealing above of 673K for desorption. This high thermal stability indicates there are strong interaction between TiOPc and MoS<sub>2</sub> surface. STS shows the band gap of the monolayer is 1.8 eV, while bulk MoS<sub>2</sub> has a 1.3eV band gap. Moreover, the Fermi level of TiOPc/bulk MoS<sub>2</sub> is shifted to the valence band, consistent with a P type shift. However, bulk MoS<sub>2</sub> surface, where less than monolayer of TiOPc was deposited, has Fermi level shifted towards the conduction band, consistent with N type doping. In the single layer MoS<sub>2</sub> deposited TiOPc monolayer, threshold bias is shifted from -30 V to near 0 V, indicating P-doping of MoS<sub>2</sub>. It can be hypothesized that the work function transition of MoS<sub>2</sub> is changed as a function of thickness. Before deposition of the TiOPc monolayer, the defects peak corresponded to S vacancy is displayed at 1.7 eV in photoluminescence. Conversely, the deposition of TiOPc monolayer almost completely suppresses S vacancy peak located 1.7 eV. Moreover, in the single layer MoS<sub>2</sub> FET, the on/off ratio is enhanced more than 2 orders magnitude. The similar charge transfer behavior also can be observed in TiOPc/WSe<sub>2</sub>; on the bilayer WSe<sub>2</sub>/HOPG, the TiOPc monolayer deposited on the first layer of WSe<sub>2</sub> shows the a conduction band shifted Fermi level, while a TiOPc monolayer deposited on the second layer of WSe<sub>2</sub> shows a valence band shifted Fermi level.

4:40pm **2D+EM+IS+MC+NS+SP+SS-WeA8 Reactivity and Wettability of PVD Metals on 2D Transition Metal Dichalcogenides**, *Christopher Smyth, S. McDonnell, R. Addou, H. Zhu, C.L. Hinkle, R.M. Wallace*, University of Texas at Dallas

Transition metal dichalcogenides (TMDs) have been studied for years due to their tribological properties, but recent discoveries have illuminated unique opportunities for the use of single or few layer TMDs in electronics, specifically tunnel field effect transistors (TFETs). The properties of TFETs fabricated with single and few layer TMDs have been investigated with some degree of success, but it has been shown via in-situ chemical analysis that interface interactions between certain contact metals and the underlying TMD are not fully understood<sup>1,2</sup>.

In this study, the wettability and reactivity of various metals with a number of bulk TMDs (MoS<sub>2</sub>, HfSe<sub>2</sub>, SnSe<sub>2</sub>, etc.) were investigated. Multiple samples were processed in parallel to ensure that all sample sets saw

identical metal depositions. The metal-TMD interface was monitored in-situ using X-ray photoelectron spectroscopy (XPS) and metal film topography was imaged using atomic force microscopy (AFM). For some low work function metals, noticeable differences in interface chemistry were found between samples that saw high vacuum rather than UHV metal e-beam depositions.

Significant variations in compatibility between contact metal and TMD were discovered. These variations were dependent upon the metal-TMD pair and the base pressure of the chamber prior to metal deposition. Au exhibits far superior wettability on MoSe<sub>2</sub>, where uniform thin films were achieved, compared to ReSe<sub>2</sub>, on which Au grows as clusters. Au wettability varies between that of thin films and clusters for the other TMDs studied. An Au thin film deposited on SnSe<sub>2</sub> results in the formation of reaction products such as Sn metal, as evidenced by the evolution of different chemical states in the Sn 3d spectrum after deposition. Reactions between MoS<sub>2</sub> and Sc producing Mo metal occur when Sc is deposited in UHV instead of HV. These results provide further understanding for the critical interface between Sc and TMD in high performance TFETs.

This work was supported in part by NSF Award No. 1407765, the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the Southwest Academy on Nanoelectronics (SWAN) sponsored by the Nanoelectronic Research Initiative and NIST.

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#### 5:00pm **2D+EM+IS+MC+NS+SP+SS-WeA9 Defects and Boundaries in 2D Materials: Correlating Electronic Properties to Atomic Structures, An-Ping Li**, Oak Ridge National Laboratory **INVITED**

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films, which provide us fascinating playground for exploring defects and boundaries in a variety of atomic layers. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries and changes in layer thickness, which divide graphene into grains and domains. These interfaces and boundaries can break the lattice symmetry and are believed to have a major impact on the electronic properties, especially the transport, in 2D materials.

Here, we report on the electronic and transport properties of two types of defects studied by STM and multi-probe scanning tunneling potentiometry with a focus on the correlations to their atomic structures. The first type of defect is the monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC. By measuring the transport spectroscopy across individual ML-BL graphene boundaries, a greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, displaying an asymmetric electron transport upon bias polarity reversal [1, 2]. Interestingly, this asymmetry is not from a typical nonlinear conductance due to electron transmission through an asymmetric potential. Rather, it indicates the opening of an energy gap at the Fermi energy. Another type of defect is 1D interface in hexagonal boron nitride (hBN) and graphene planar heterostructures, where a polar-on-nonpolar 1D boundary is expected to possess peculiar electronic states associated with edge states of graphene and the polarity of hBN [2]. By implementing the concept of epitaxy to 2D space, we grow monolayer hBN from fresh edges of monolayer graphene with lattice coherence, forming a 1D boundary [3]. STM/STS measurements reveal an abrupt 1D zigzag oriented boundary, with boundary states about 0.6 eV below or above the Fermi level depending on the termination of the hBN at the boundary [4]. The boundary states are extended along the boundary, and exponentially decay into the bulk of graphene and hBN. The origin of boundary states and the effect of the polarity discontinuity at the interface will be discussed.

This research was conducted at the Center for Nanophase Materials Sciences, which is DOE Office of Science User Facility.

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#### 5:40pm **2D+EM+IS+MC+NS+SP+SS-WeA11 Metal Ion Intercalated 2D Materials as Transparent Electrodes, Jiayu Wan\***, W. Bao, F. Gu, University of Maryland, College Park, M. Fuhrer, Monash University, Malaysia, L. Hu, University of Maryland, College Park

Transparent electrode materials are critical for optoelectronic devices such as touch screen and solar cells. Graphene has been widely studied as transparent electrodes for its unique physical properties. To further boost the performance of graphene based transparent electrodes, we novelized Li-ion intercalation in graphene, and achieved highest performance of carbon based transparent electrodes.[1] Transmission as high as 91.7% with a sheet resistance of 3.0 ohm/sq is achieved for 19-layer LiC<sub>6</sub>, which corresponds to a figure of merit ( $\sigma_{de}/\sigma_{opt}$ ) at 1,400, significantly higher than any other continuous transparent electrodes. The unconventional modification of ultrathin graphite optoelectronic properties is explained by the suppression of interband optical transitions and a small intraband Drude conductivity near the interband edge. To achieve low cost, large scale graphene-based transparent electrodes, we further developed Na-ion intercalated printed reduced graphene oxide (RGO) film[2]. Unlike pristine graphene that inhibits Na-ion intercalation, the larger layer-layer distance of RGO allows Na-ion intercalation, leading to simultaneously much higher DC conductivity and higher optical transmittance. The typical increase of transmittance from 36% to 79% and decrease of sheet resistance from 83 kohms/sq to 311 ohms/sq in the printed network was observed after Na-ion intercalation. Compared with Li-intercalated graphene, Na-ion intercalated RGO shows much better environmental stability, which is likely due to the self-terminating oxidation of Na ions on the RGO edges. This study demonstrated the great potential of metal-ion intercalation to improve the performance of graphene-based materials for transparent conductor applications.

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#### 6:00pm **2D+EM+IS+MC+NS+SP+SS-WeA12 Oxygen Reduction Reaction on Nitrogen-doped Graphene, Jun Nakamura**, The University of Electro-Communications (UEC-Tokyo), Japan, A. Ichikawa, H. Matsuyama, A. Akaishi, The University of Electro-Communications (UEC-Tokyo)

Recently, several groups have reported high oxygen reduction reaction (ORR) activities in nitrogen-doped carbon nanomaterials which are candidates of metal-free catalysts for ORR [1]. Lee et al. have successfully fabricated nitrogen-doped graphene with the high ORR activity in acid media [2]. It has been confirmed that local atomic configurations of dopants in nitrogen-doped graphene are classified into three functional groups (pyrrole-like, pyridine-like, and graphite-like configurations) [3,4]. However, the mechanism of the ORR on the nitrogen-doped graphene has not fully understood.

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway (2e-) that is reduced to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and the direct four-electron pathway (4e-) that reduces to water (H<sub>2</sub>O). Thermodynamic electrode potentials of each process at standard conditions are about 0.68V (2e-) and 1.23V (4e-), respectively. In case of the associative mechanism for the two- and four- electron reduction pathways, the electrocatalytic activity is governed by the stability of reaction intermediates like OOH\*, OH\*, and O\* (where "\*" refers to a surface site). Free energies of the reaction intermediates have been calculated based on the computational hydrogen electrode model suggested by Nørskov et al. [5]. We have taken account of effects of electrode potential, pH of a solution, a local electric field in double layer, and water environment.

We have constructed energy diagrams at several electrode potentials on the basis of the first-principles calculations. It has been shown that the 2e- and 4e- reduction processes proceed at potentials up to about 0.5V and 0.8V, respectively. This means that we can control the reduction pathway for the nitrogen-doped graphene with the graphite-like N. Proton-electron transfer to OOH\* (the 2e- pathway), and the formation of OOH\* (the 4e- pathway) are confirmed to be the rate-limiting steps, respectively. Density dependence of N on the ORR activity will also be discussed in the presentation.

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## Scanning Probe Microscopy Focus Topic

### Room: 212A - Session SP+2D+AS+NS+SS-WeA

#### Probing Electronic and Transport Properties

**Moderator:** Tae-Hwan Kim, Pohang University of Science and Technology, Jewook Park, Oak Ridge National Laboratory

2:20pm **SP+2D+AS+NS+SS-WeA1 Geometric and Electronic Structures of Epitaxially Grown Pnictide 122, 111 and  $\text{Cu}_x\text{Bi}_2\text{Se}_3$  Samples, Young Kuk**, Seoul National University, Republic of Korea  
**INVITED**

Order parameters were measured mainly on low-temperature cleaved, superconductor surfaces from their measured topographic images (constant current maps) and Fourier-transformed, measured density of states (energy dependent  $dI/dV$  map) in previous scanning tunneling microscopy (STM) studies. However, no direct evidence of coupling mechanisms has been given for these *high temperature* superconductors by these STM studies. We intend to study how homogeneity of a doped sample influences the superconducting property in an STM study. We were able to grow pnictide 111, 122, and  $\text{Cu}_x\text{Bi}_2\text{Se}_3$  samples by molecular beam epitaxy. We found that surfaces of these grown samples are often terminated by alkali or alkaline atomic plane or non-superconducting metallic planes. These surfaces reveal distorted superconducting or non-superconducting properties. We adopted various ways to expose the superconducting planes in these samples. At the same time, we tried to grow samples homogeneously doped over the coherence lengths. Nodal structures were observed on these samples in their quasiparticle interference patterns. In this talk we will discuss the properties of the  $s_{\pm}$ ,  $s$ ,  $d$  states as likely candidates pairing states for these materials.

3:00pm **SP+2D+AS+NS+SS-WeA3 Direct Measurement of Conductance from Topological Surface States in Topological Insulators, Corentin Durand, X. Zhang, S. Hus, M. McGuire, I. Vlassiouk, A.-P. Li**, Oak Ridge National Laboratory

Topological insulators (TI) with characteristic topological surface states (TSS) attract great interest for both fundamental physics and device applications. However, the unavoidable presence of defects in bulk single crystals usually dopes the material leading to a metallic behavior. Thus, the direct measurement of the TSS electronic transport properties is hard to achieve due to the dominant contribution from the bulk states. Here, we measure the transport properties of  $\text{Bi}_2\text{Se}_3$  crystals by Four Probe Scanning Tunneling Microscopy (4P-STM) technique at different temperatures on fresh surfaces obtained by cleavage in Ultra-High Vacuum (UHV) (base pressure =  $2 \times 10^{-10}$  Torr). In contrast to conventional models that assume two resistors in parallel to count for both the TSS and bulk conductance channels, we show that this technique can be used to differentiate the 2D contribution of TSS to the transport from the 3D contribution (bulk) by considering the potential profiles across the interface. Our method allows quantitative determination of conductivities from both channels. We also compare our results with samples exhibiting pure 2D and 3D transport behaviors. Our results shows that our approach enables direct distinguishing and accessing electronic transport of TI surfaces surface states, which can be applied to the studies of 2D to 3D crossover of conductance in other complex systems.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

3:20pm **SP+2D+AS+NS+SS-WeA4 Chiral Edge States of Topological Insulator in 1D, Tae-Hwan Kim**, Pohang University of Science and Technology, Republic of Korea, S. Cheon, S.-H. Lee, Institute for Basic Science, Republic of Korea, H.W. Yeom, Pohang University of Science and Technology and Institute for Basic Science, Republic of Korea

Chiral edge states are one of the most fascinating hallmark of topological insulators [1-4]. While chiral edge states are the vitally important feature of 2D and 3D topological insulators, no correspondence has yet been found in 1D. On the other hand, in 1D, a Peierls-distorted atomic chain such as polyacetylene has two topologically different ground states and a topological edge state or so-called a topological soliton connecting between them [5,6]. The topological edge states in 1D show many interesting properties such as charge-spin separation, fractional charge, and so on [7,8].

However, they do not exhibit chirality as 2D or 3D topological insulators do. In this talk, we report that the 1D topological edge states, solitons, of the charge-density wave (CDW) system of indium atomic wires self-assembled on a silicon surface have the chiral property [9,10]. Our system can be well described by a coupled double Peierls-distorted atomic chain with zigzag interchain coupling, which induces dynamical sublattice symmetry breaking. This subtle change ensures a dynamically generated topological structure with four-fold symmetric ground states and has topological edge states with a new degree of freedom, chirality, which is absent in the case of a single Peierls atomic chain. We have performed scanning tunneling microscopy and spectroscopy in order to obtain experimental evidences of the chiral edge states in the 1D CDW. Individual right- and left-chiral edge states are directly identified from non-chiral ones, which are similar to the topological solitons found in a single Peierls atomic chain. Furthermore, we found that chiral edge states can produce quantized charge pumping across the chain that is topologically protected and controllable by their chirality. Thus, these topological chiral edge states or solitons can be utilized for future single-electron-level data storage devices or logic circuits, which are topologically protected.

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4:20pm **SP+2D+AS+NS+SS-WeA7 Electronic Properties of Quasi-one-dimensional Defects in Monolayer h-BN, Chuanxu Ma, J. Park**, Oak Ridge National Laboratory, L. Liu, G. Gu, The University of Tennessee, A.P. Baddorf, A.-P. Li, Oak Ridge National Laboratory

Two-dimensional (2D) hexagonal boron nitride (h-BN) monolayers have wide promising applications in nanoelectronics. The presence of defects could greatly impact its electronic properties. Here, we present experimental results about two types of line defects in h-BN monolayers, prepared on Cu foils by chemical vapor deposition (CVD) method.

Using scanning tunneling microscopy/spectroscopy (STM/STS), the structural and electronic properties of two types of quasi-1D defects are characterized in monolayer h-BN. An energy gap  $\sim 4$  eV is observed for h-BN monolayers on Cu foils. The first type of quasi-1D defects is the worm-like defects with length 3~30 nm, and width  $\sim 1.5$  nm. Nano-ripples with modulation  $\lambda \sim 5.2$  Å, which is about double the size of h-BN lattice, are observed both from the topographic images and  $\text{Di}/\text{Dv}$  mappings along the worm-like defects. The modulation is in phase at negative bias and out of phase at positive bias between the topographic images and  $\text{Di}/\text{Dv}$  mappings. The defects also show higher tunneling conductance than the h-BN sheet in the  $\text{Di}/\text{Dv}$  mappings. The observed nano-ripples in the defects might indicate interesting electronic properties, such as charge density wave (CDW).

The other type of defects are the linear boundaries of h-BN. The tilting angle between the two domains at the both sides of the boundary is about  $90^\circ$ , which is well in line with our simulations. From the  $\text{Di}/\text{Dv}$  mapping, the boundary shows lower tunneling conductance than the h-BN sheet, which is different from the first type of quasi-1D defects.

Our experimental results demonstrate that the existence of quasi-1D defects tremendously affect the structure and electronic properties of h-BN, thus could be used to tune the transport properties in h-BN-based nanodevices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US DOE.

4:40pm **SP+2D+AS+NS+SS-WeA8 Real-Space Imaging of the Multiple Scattering in Single Layer Graphene: FT-STM/STS Studies, M. Jung, S.-D. Sohn, J. Park, K. Lee, Hyung-Joon Shin**, Ulsan National Institute of Science and Technology, Republic of Korea

The electrons in graphene exhibit unusual two-dimensional behaviors, which can be described by massless Dirac quasiparticles. In order to understand the fundamental electronic properties of graphene, extensive studies have been focused on graphene both experimentally and



theoretically. Undoubtedly, however, not only the electronic property of graphene itself but also that of graphene on metallic substrates is of great importance for the further applications. In this study we investigated the scattering behaviors of electrons in single layer graphene (SLG) on a Cu(111) substrate by means of low-temperature scanning tunneling microscopy (LT-STM) and scanning tunneling spectroscopy (STS). When there is a defect in graphene, we can observe the scattering of electrons in the form of interference pattern by STM. In previous STM studies, the energy level of Dirac point has been assigned by the position of a dip in  $dI/dV$  curve. It is very difficult, however, to determine the exact position of Dirac point from STS for the graphene on metallic substrates, because surface states of the substrate is too close to Dirac point of graphene in energy level. Here, we could successfully deconvolute and identify the electronic dispersion relations in graphene and in Cu(111) by applying Fourier transformation to one-dimensional and two-dimensional STS maps, which enables us to resolve surface states of Cu(111) and Dirac point of graphene respectively. We will also present our first observation of the defect-induced intravalley scattering, which has not been observed experimentally to date for SLG. Our results show that the careful examination of interference pattern can provide valuable information regarding intravalley, intervalley, and interband scatterings of electrons in graphene/Cu(111).

5:00pm **SP+2D+AS+NS+SS-WeA9 Tunability of Single-Atom Electron Spin Relaxation Times and Their Characterization by Pump-Probe STM**, *William Paul*, *S. Baumann*, IBM Research - Almaden, *K. Yang*, Chinese Academy of Sciences, *N. Romming*, University of Hamburg, Germany, *T. Choi*, *C.P. Lutz*, *A. Heinrich*, IBM Research - Almaden

A single atomic spin constitutes the ultimate limit to the miniaturization of magnetic bits. Can the state of such a spin be made stable against the quantum mechanical tunneling of magnetization? The energy relaxation time,  $T_1$ , of single spins on surfaces can be measured by spin-polarized pump-probe STM [1]. To date, the relaxation times reported for Fe-Cu dimers on  $\text{Cu}_2\text{N}$  insulating films have been of the order  $\sim 100$  ns [1]. A three-order-of-magnitude enhancement of lifetime, to  $\sim 200$   $\mu\text{s}$ , was recently demonstrated for Co on a single-monolayer of MgO [2]. This was accomplished by choosing a less conductive decoupling layer to electronically separate the atom from a metal substrate, along with the careful design of the symmetry of orbital states. Here, we report on the tailoring of the  $T_1$  lifetime of single Fe atoms on single- and multi-layer MgO films grown on Ag(001). We focus on the characterization of intrinsic lifetimes for the atom-substrate system which are independent of the STM tip used to probe them, that is, without influence of the nearby STM tip which can be a strong source of electronic de-excitation. We also report on new advances in pump-probe techniques which were necessary to carry out these measurements. These advances extend lifetime detection to the femto-ampere and many-millisecond regimes demanded by the Fe on MgO system.

[1] Loth *et al.*, *Science* **329**, 1628 (2010)

[2] Rau *et al.*, *Science* **344**, 988 (2014).

5:20pm **SP+2D+AS+NS+SS-WeA10 Imaging and Spectroscopy of Graphene Heterostructures**, *Brian LeRoy*, University of Arizona  
**INVITED**

The ability to create arbitrary stacking configurations of layered two-dimensional materials opens the way to the creation of designer band structures in these materials. Graphene on hexagonal boron nitride is an example of such a van der Waals heterostructure where the electronic properties of the composite material can be different from either individual material [1]. These van der Waals heterostructures can be formed using a wide variety of layered materials including from transition metal dichalcogenides, graphene and topological insulators. This talk will focus on devices consisting of graphene coupled to other layered materials. The lattice mismatch and twist angle between the layers produces a moiré pattern and affects their electronic properties. In double layer graphene systems, we find a van Hove singularity whose energy depends on the rotation angle [2]. This singularity in the density of states leads to a strong enhancement of the absorption at a particular wavelength. In graphene on transition metal dichalcogenides, the interaction between the materials leads to the possibility of commensurate stackings and the presence of new states in graphene [3].

[1] M. Yankowitz *et al.*, *Nature Physics* **8**, 382 (2012).

[2] S. Huang *et al.*, arXiv:1504.08357 (2015).

[3] M. Yankowitz *et al.*, *Nano Letters* **15**, 1925 (2015).

6:00pm **SP+2D+AS+NS+SS-WeA12 Correlated STM and Electron Transport Study of Individual Nanowires down to Atomic Scale**, *Shengyong Qin*, University of Science and Technology of China, *T.H. Kim*, Oak Ridge National Laboratory, *Y. Zhang*, *R. Wu*, University of California, Irvine, *H.H. Weitering*, The University of Tennessee, Knoxville, *C.K. Shih*, The University of Texas at Austin, *A.-P. Li*, Oak Ridge National Laboratory  
The electronic conductance in quantum wires is often dictated by quantum instabilities and strong localization at the atomic scale. We present a novel nano-transport technique which combines local nano-contacts and four-probe STM. The approach allows for correlated study of electron transport and scanning tunneling spectroscopy in individual nanowires. We first apply it to the  $\text{GdSi}_2$  quantum wires, which show that isolated nanowires exhibit a metal-insulator transition upon cooling, driven by the defect-induced localizations, while wire bundles maintain a robust metallic state, stabilized by interwire electronic coupling. We then demonstrate applications of this transport technique with carbon nanotubes and copper wires in situ. The method bridges the gap between the transport and the local electronic and structural properties down to the atomic scale.

# Thursday Morning, October 22, 2015

## 2D Materials Focus Topic

Room: 212C - Session

2D+EM+MG+NS+SE+SM+SS+TF-ThM

## Emergent 2D Materials

Moderator: Paul Sheehan, Naval Research Laboratory

8:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM1 CVD Growth and Characterization of 2D MoS<sub>2</sub>, MoSe<sub>2</sub>, MoTe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>, and MoS<sub>2</sub>-xSe<sub>x</sub> Alloys**, David Barroso, T. Empante, A. Nguyen, V. Klee, I. Lu, E. Preciado, C. Lee, C. Huang, W. Coley, S. Naghibi, G. von Son, A. Brooks, J. Kim, L. Bartels, University of California, Riverside

Transition Metal Dichalcogenides (TMDs) have been of increasing interest over the past years due to their exciting semiconducting properties. In the bulk, TMDs possess a native indirect bandgap and transition to a direct bandgap as they approach the monolayer limit. The bandgaps range from 1.15 eV to 1.95 eV depending on composition. Using organic liquids and/or inorganic powders as precursors, CVD growth techniques have been realized for MX<sub>2</sub> TMDs (M = Mo, W; X = S, Se, Te) and their alloys at tunable compositions. We achieved consistent synthesis of these TMDs materials. The films can either be made homogeneous in bandgap or exhibiting a linear bandgap gradient. Characterization of the films include Raman and photoluminescence spectroscopy, as well as AFM. Device fabrication allows for transport measurements. Depending on the composition, the materials show n- or p-doping in a consistent fashion.

8:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM2 Investigation of Manganese Dioxide Nanosheets by STM and AFM**, Lorraine Vernisse, S. Afsari, S.L. Shumlas, A.C. Thenuwara, D.R. Strongin, E. Borguet, Temple University

Interest in ultrathin two-dimensional nanosheets has grown exponentially thanks to their unique and diverse electronic properties. As they possess atomic or molecular thickness and infinite planar dimension, they are expected to have different properties than the bulk of the material from which they originate. This offers opportunities for the development of devices in various areas, ranging from catalysis to electronics. Using the exfoliation approach, it is possible to investigate 2D nanosheets of different materials in search of new phenomena and applications. Bearing this mind, we focused on manganese dioxide (MnO<sub>2</sub>), and more specifically  $\delta$ -MnO<sub>2</sub> (Birnessite). This mineral has the advantage to present a low surface enthalpy[1], which results in weak water binding. Moreover, the presence of defects, e.g., oxygen vacancies has a dopant effect on water oxidation. These properties make MnO<sub>2</sub> a perfect candidate as a catalytic surface for water splitting and pave the way to the design of clean and renewable energy system. Furthermore, MnO<sub>2</sub> can be easily exfoliated into ultrathin nanosheets owing to the layered structure of the manganese oxide precursors.

Our goal is to investigate the catalytic activity of ultrathin MnO<sub>2</sub> nanosheets using scanning probe microscopy techniques, especially atomic force microscopy (tapping mode) and scanning tunneling microscopy (ambient and electrochemical conditions). In this perspective, we have first improved the deposition processes and find the imaging conditions to observe MnO<sub>2</sub> nanosheets with an average thickness of one or two layers. We have also showed that MnO<sub>2</sub> single layer nanosheets exhibit an expected hexagonal atomic pattern and present some defects. We will now resolve and identify the different defects and investigate the evolution of the conductivity as a function of the defect concentration and the number of layers.

This work was supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575.

[1] M. M. Najafpour, E. Amini, M. Khatamian, R. Carpentier, S. I. Allakhverdiev, Journal of Photochemistry and Photobiology B: Biology (2014), 133, 124.

8:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM3 Two-Dimensional Early Transition Metal Carbides and Carbonitrides "MXenes": Synthesis, Properties and Applications**, Michael Naguib, Oak Ridge National Laboratory

INVITED

Ternary layered carbides and nitrides with formula of M<sub>n+1</sub>AX<sub>n</sub> (M stands for early transition metal, A for group A element, X is carbon or nitrogen, and n=1, 2, or 3), so called MAX phases, are known for their unique combinations properties of ceramics and metals. It was found recently that etching atomically thin layers of aluminum from the MAX phases results in

forming weakly bonded stacks of two-dimensional (2D) layers of early transition, coined as MXenes. The etching was carried out in fluoride contained aqueous systems. Thus MXenes surfaces are terminated with a mixture of groups including OH, O, and F. Sonicating MXenes in water results in delaminating few layers of MXenes from each other. However, to achieve a large-scale delamination, intercalation of a large compound between the layers prior to delamination is needed. MXenes were found to be a very interesting family of 2D materials since they are electrically conductors and hydrophilic. They also showed an excellent performance as electrodes for electrochemical super capacitors and Li-ion batteries. Here the recent progress in MXenes research from the synthesis to properties and applications will be covered, and in more details, large-scale delamination of MXenes will be discussed. Also, light will be shed on the performance of MXenes as electrode materials for electrochemical energy storage systems.

9:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM5 Molecular Beam Epitaxy of Large area HfSe<sub>2</sub>(ZrSe<sub>2</sub>)/MoSe<sub>2</sub> van der Waals Heterostructures on AlN(0001)/Si substrates**, Athanasios Dimoulas, P. Tsipas, E. Xenogiannopoulou, D. Tsoutsou, K.E. Aretouli, J. Marquez-Velasco, S.A. Giamini, N. Kelaidis, NCSR DEMOKRITOS, Greece

Two dimensional (2D) semiconductor van der Waals heterostructures (HS) made of group IVB (Zr, Hf) and group VIB (Mo, W) metal dichalcogenides are predicted [1] to have type II or type III band alignments mainly because of a large difference in their workfunctions and band gaps, which makes them candidates for novel 2D staggered, or broken gap tunneling field effect transistors (TFET). We use molecular beam epitaxy (MBE) to grow high quality large area HfSe<sub>2</sub> [2,3], ZrSe<sub>2</sub> [4] and MoSe<sub>2</sub> [5] films directly on AlN(0001)/Si(111) substrates. We confirm by RHEED and HRTEM that atomically thin layers (1-6 ML) are grown in single crystal form with a well-defined in-plane orientation on AlN. The films are continuous with smooth surface morphology (0.6 nm RMS roughness) and abrupt interfaces with no detectable reaction as verified by in-situ XPS and HRTEM. Micro Raman mapping for all layers confirms their structural integrity down to one monolayer and reveals very good uniformity on a cm-scale wafer and excellent stability of MoSe<sub>2</sub> over a period of at least two weeks in air. Strong room temperature PL signal of 1 ML MoSe<sub>2</sub> indicate high quality direct gap semiconductor in agreement with valence band structure details imaged by our in-situ ARPES [3, 5]. In a second step, MoSe<sub>2</sub>/HfSe<sub>2</sub> [3] and MoSe<sub>2</sub>/ZrSe<sub>2</sub> [4] HS were grown. Despite the large lattice mismatch, all layers are grown epitaxially as evidenced by RHEED with no detectable defects at the interfaces as confirmed by HRTEM suggesting good quality VdW epitaxy [6]. Using UPS the workfunctions (WF) were estimated to be 5.2, 5.5 and 5.4 eV for MoSe<sub>2</sub>, HfSe<sub>2</sub> and ZrSe<sub>2</sub> respectively [3,4]. The last two differ substantially from theoretical values (~ 6 eV). Based on our STM and DFT calculations [3], we conclude that this difference is due to an ordered Se adlayer which lowers the HfSe<sub>2</sub> and ZrSe<sub>2</sub> WF bridging the WF gap between them and MoSe<sub>2</sub>. As a result, small valence band offsets of 0.13 and 0.58 eV were found for the HfSe<sub>2</sub>/MoSe<sub>2</sub> and ZrSe<sub>2</sub>/MoSe<sub>2</sub> HS, respectively leading to type II band alignments. The availability of low cost wide-gap-AlN/Si wafers in 300 mm wafer sizes defines a manufacturable route for single crystal 2D semiconductor technology.

We acknowledge financial support from ERC Advanced Grant SMARTGATE-291260. We thank IMEC for providing the AlN/Si substrates.

[1] C. Gong et al., *APL*, **103**, 053513 (2013)

[2] R. Yue et al., *ACS Nano*, **9**, 474 (2014)

[3] K. E. Aretouli et al., *APL*, **106**, 143105 (2015)

[4] P. Tsipas et al., *Microelectron. Eng.* (2015), <http://dx.doi.org/10.1016/j.mee.2015.04.113>

[5] E. Xenogiannopoulou et al, *Nanoscale* **7**, 7896 (2015)

[6] F.S. Ohuchi et al., *JAP*, **68**, 2168 (1990)

9:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM6 Surface Investigation of WSe<sub>2</sub> Atomically Thin Film and Bulk Crystal Surfaces**, Rafik Addou, H. Zhu, University of Texas at Dallas, Y.-C. Lin, S.M. Eichfeld, J.A. Robinson, Penn State University, R.M. Wallace, University of Texas at Dallas

Heterogeneous fabrication of semiconducting two-dimensional layered materials presents a promising opportunity to develop highly tunable electronic and optoelectronic materials. (1-2) An example of crystalline monolayer of WSe<sub>2</sub> grown by chemical vapor deposition on epitaxial graphene (EG) grown from silicon carbide had been investigated at nanoscale level. The WSe<sub>2</sub> surface was characterized using atomic force microscopy (AFM) scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS). (3,4) AFM and

large STM images show high-quality WSe<sub>2</sub> monolayers. The sharpness of the W 4f and Se 3d core levels confirms the absence of any measurable reaction at the interface and oxide formation. The photoemission measurements of WSe<sub>2</sub>-Graphene interface suggest p-type doping due to charge transfer (EG withdraws electrons from WSe<sub>2</sub>) at the interface and formation of Schottky-type contact,(5) suggesting possible applications of such heterostructures as diodes and photodetectors. High-resolution STM images reveal atomic-size imperfections induced by Se vacancies and impurities. Additionally, the investigation of bulk WSe<sub>2</sub>(0001) surface shows spatial variation attributed to the presence of two components in W 4f<sub>7/2</sub> core level attributed to the presence of both n- and p-type behavior. STM images exhibit also various types of defect induced by vacancies and dopants. The STS spectra reveal two main characteristics i) expected p-type conductivity where the Fermi level located at the valence band edge, and ii) zero conductivity at negative bias explained by defect-induced band bending as reported on geological MoS<sub>2</sub> crystal surfaces.(4) In conclusion, the spatial variation (topography and electronic structure) is more noticeable in bulk WSe<sub>2</sub> grown by chemical vapor transport than in CVD thin films.

This work was supported in part by the Southwest Academy on Nanoelectronics sponsored by the Nanoelectronic Research Initiative and NIST and the Center for Low Energy Systems Technology, one of six centers supported by the STARnet phase of the Focus Center Research Program, a Semiconductor Research Corporation program sponsored by MARCO and DARPA.

- (1) Yu-Chuan Lin et al., Nano Lett., **14** (2014) 6936-6941.
- (2) Yu-Chuan Lin et al., Nature Comm. arXiv:1503.05592v1.
- (3) Robert M. Wallace, ECS Trans., **64** (2014) 109-116.
- (4) Rafik Addou, Luigi Colombo, and Robert M. Wallace, ACS Appl. Mater. Interfaces (Accepted, 2015).
- (5) Horacio Coy Diaz, Rafik Addou, and Matthias Batzill, Nanoscale **6** (2014) 1071-1078.

11:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM10 A Kinetic Study on the Adsorption of Polar (Water) and Non-Polar (Benzene) Molecules on CVD Graphene, Nilushni Sivapragasam, U. Burghaus, North Dakota State University**

The adsorption kinetics of water and benzene at ultrahigh vacuum conditions were studied. Two different chemical vapor deposited graphene samples (graphene/SiO<sub>2</sub> and graphene/Cu) were utilized. Different surface analytical techniques (Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy) were used to characterize the surface. Subsequently, a kinetics study - to understand the adsorption of water and benzene- using thermal desorption spectroscopy (TDS) was conducted. The TDS results revealed the hydrophobicity of water on graphene. However, the adsorption kinetics of water on graphene did not mimic the bare substrate, i.e., graphene is non-transparent for water adsorption. In contrast, graphene was transparent for benzene adsorption. Furthermore, the adsorption kinetics of both, water and benzene were substrate dependent.

11:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM11 Epitaxial Ultrathin MoSe<sub>2</sub> Layers Grown by Molecular Beam Epitaxy, Ming-Wei Chen, M.B. Whitwick, O. Lopez-Sanchez, D. Dumcenco, A. Kis, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**

Two-dimensional transition metal dichalcogenides (TMDs) have attracted widespread attention recently, and the focus is specifically on ultrathin layers due to the strong spin-orbit coupling and direct band-gap transition of single-layers. The unique properties of various TMDs also enable the possibilities for future optoelectronic applications. However, the synthesis of TMDs with uniform large-area and high-quality still remains challenging. While chemical vapour deposition has been demonstrated as a promising technique, the complexity of chemical precursors and the lacking of *in-situ* observation technique strongly hinder the progress.

Here, We propose to use ultra-high vacuum molecular beam epitaxy (MBE) to grow MoSe<sub>2</sub> ultrathin layers, down to single-layer in a controllable way. Epitaxial MoSe<sub>2</sub> layers were successfully grown on different crystalline substrates via van der Waals epitaxy mechanism, benefited from the weak interlayer interaction and the lacking of dangling bonds. Reflection high energy electron diffraction (RHEED) was used to *in-situ* monitor the initial growth stage and revealed a clear transition of the streaks, demonstrating the formation of MoSe<sub>2</sub> layer. Sharp streaks were obtained in the growth end, with the streak spacing corresponding to MoSe<sub>2</sub> lattice constant, and no significant strain effect was observed. In order to demonstrate the validity of van der Waals epitaxy, different crystalline substrates with lattice mismatch up to 30 % have been tested. The epitaxial layers showed a smooth and uniform surface in atomic force microscopy, and the quality was further confirmed in Raman spectrum and transmission electron

microscopy. Furthermore, photoluminescence of the single-layer MoSe<sub>2</sub> showing a sharp peak of ~1.58 eV at room temperature demonstrates the direct band-gap feature and indicates the potentials of photovoltaic applications. In the end, the growth of two-dimensional van der Waals heterostructures has also been addressed and the results pave way for heterostructure studies.

In summary, molecular beam epitaxy has been proved to be a reliable route to grow large-area and high-crystalline transition metal chalcogenides, and is promising to facilitate the integration of other two-dimensional materials in the future.

11:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM12 A Two-Dimensional Oxide Quasicrystal, Stefan Förster, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J.I. Flege, Institute of Physics, University of Bremen, Germany, K. Meinel, R. Hammer, M. Trautmann, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J. Falta, Institute of Solid State Physics, University of Bremen, Germany, T. Greber, Physik-Institut, University of Zürich, Switzerland, W. Widdra, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany**

**INVITED**

With the recent discovery of the first oxide quasicrystal (QC) aperiodicity is entering the field of two-dimensional materials [1]. Aperiodicity means that the system exhibits long-range order as expressed by sharp diffraction spots but since the ordering follows an aperiodic function the system is lacking translational symmetry. We report here on the complex growth process of the oxide QC involving a high-temperature wetting process and periodic approximant structures.

The QC is derived from BaTiO<sub>3</sub> thin films on a hexagonal Pt(111) substrate and exhibits a sharp twelve-fold diffraction pattern [1]. Based on scanning tunneling microscopy the aperiodic atomic structure had been resolved [1]. It is formed by surface atoms arranged in forms of squares, triangles, and rhombi with a next-neighbour distance of 0.69 nm. In addition to this dodecagonal atomic arrangement, building blocks of squares, triangles, and rhombi are also found on (2+√3) and (2+√3)<sup>2</sup> larger scales indicating the characteristic self-similarity of an ordered QC [1]. The high-resolution STM measurements allow furthermore to identify atomic flips in the structure indicating lattice excitations in the quasicrystal called phasons. Using low-energy electron microscopy (LEEM) the preparation and the growth of the QC films on top of the hexagonal Pt(111) is monitored in all details from room temperature up to about 1200 K. LEEM shows that upon high-temperature annealing large 3DBaTiO<sub>3</sub> islands are formed with bare Pt(111)-(1x1) in between. At temperatures above 1020 K a wetting layer spreads on the free Pt area. This wetting process can be reversed by annealing in an oxygen atmosphere. In-situ LEEM measurements show that under these conditions the QC decays into small BaTiO<sub>3</sub> islands. The observed interface-driven formation of a 2D QC from a perovskite oxide in contact with a hexagonal substrate is expected to be a general phenomenon.

1. S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Nature* **502**, (2013) 215.

## Plasma Science and Technology

**Room: 210A - Session PS+2D-ThM**

## Plasma Processing for 2D Materials

**Moderator: Eric Hudson, Lam Research Corporation**

8:00am **PS+2D-ThM1 Low Pressure Plasma Cleaning and Doping of CVD Graphene, Daniil Marinov, LPP-CNRS, Ecole Polytechnique, France, G. Cunge, LTM - CEA/LETI, France, D. Ferrah, CEA, LETI, MINATEC Campus, France, E.V. Johnson, LPICM-CNRS, Ecole Polytechnique, France, J.-P. Booth, LPP-CNRS, Ecole Polytechnique, France**

**INVITED**

The rising importance of graphene and other 2D materials presents interesting new challenges for plasma technology. Processing of atomically thin layers requires unprecedented control of plasma parameters such as the fluxes and energy distributions of both ions and neutrals at the substrate. With sophisticated control, plasma technology can offer solutions to the major technological bottlenecks associated with graphene applications. Polymer residues (originating from the transfer of CVD graphene or from photo-resist masks) uncontrollably alter the electronic and chemical properties of graphene, a major problem for graphene integration in sophisticated devices. Removal of these surface contaminants by selective hydrogen plasma etching can perform better than classical techniques (wet chemistry with annealing) in terms of efficiency, throughput and compatibility with device fabrication processes [1]. In order to avoid plasma induced damage during graphene cleaning, the ion energy must be kept low

(e.g. below 12 eV for H<sup>+</sup> ions [2]). Band gap opening in graphene is another major challenge that can be tackled by plasma doping, provided that the ion energies can be controlled to favor substitutional doping rather than sputtering [3].

We are evaluating two types of plasma reactors for controllable cleaning and doping of graphene – a low density capacitive discharge excited by non-sinusoidal tailored voltage waveforms (TVW) and a high density pulse-modulated inductive plasma source. Both systems are capable of generating hydrogen plasmas with sufficiently low ion energies for low damage residue cleaning. The polymer (PMMA) etch rate obtained in the high density ICP is two orders of magnitude higher, making this system more suitable for graphene cleaning. The TVW discharge is particularly interesting for graphene doping. By changing the excitation voltage waveform in nitrogen CCP one can control the ion bombardment energy and hence the binding configuration of N dopants in single layer graphene. Using an ion bombardment energy of about 40 eV nitrogen atoms can be incorporated with a total concentration of 5 at. %, with more than half of them in graphitic sites. When the ion energy is below 20 eV only pyridinic and pyrrolic N is observed.

The role of the substrate carrying the graphene was found to be very important. In the case of hydrogen plasma treatment, ions passing through the graphene layer may participate in catalytic reactions at the substrate or lead to blister formation.

[1] Cunge *et al.* submitted to *ACS Nano*

[2] Despia-Pujo *et al.* *J. Appl. Phys.* 2013, 113, 114302

[3] Zhao *et al.* *Phys. Rev. B* 2012, 86, 165428

**8:40am PS+2D-ThM3 Sensing Cleanliness of PMMA Transferred CVD Grown Graphene, Christian Teichert, M.C. Kratzer, Montanuniversität Leoben, Austria, B.C. Bayer, University of Cambridge, UK**

Crystalline films of small organic semiconductors offer attractive potential for optoelectronic applications on flexible substrates. However, these applications require a transparent and flexible electrode material; and here the novel material graphene (Gr) comes into play. Since small conjugated molecules like the rod-like oligophenylene molecule para-hexaphenyl (6P) fits well to the hexagonal structure of graphene, growth of 6P on Gr can be expected in a lying configuration.

As demonstrated by in situ by low-energy electron microscopy, 6P grows at 240 K indeed in a layer-by-layer mode with lying molecular orientation on Ir(111) supported graphene [1]. Islands nucleate at Gr wrinkles [2]. At higher temperatures, needle-like 6P crystallites – also composed of lying molecules are observed [3]. Also on exfoliated, wrinkle-free graphene, such needles develop with discrete orientations defined by the Gr lattice as was detected by atomic-force microscopy (AFM) [4,5]. Needles are never observed on contaminations or on the silicon oxide substrate. There, exclusively islands composed of upright standing molecules are observed. Since these islands are easily detected by AFM, growth of 6P can be used to sense the cleanliness of a variety of graphene substrates as we have demonstrated for PMMA transferred CVD grown graphene. On the as grown samples, PMMA remainders hinder the growth of extended needles. For increasing annealing temperature, the 6P needles grow in length because the PMMA residues decrease substantially [6].

[1] G. Hlawacek, *et al.*, *Nano Lett.* **11** (2011) 333. [2] G. Hlawacek, *et al.*, *IBM J. Res. Devel.* **55** (2011) 15. [3] F. Khokar, *et al.*, *Surf. Sci.* **606** (2012) 475. [4] M. Kratzer, *et al.*, *JVSTB* **31** (2013) 04D114. [5] M. Kratzer, *et al.*, *e-J. Surf. Sci. Nanotechn.* **12** (2014) 015303. [6] M. Kratzer, *et al.*, *Appl. Phys. Lett.* **106** (2015) 103101.

**9:00am PS+2D-ThM4 Plasma Processes of Graphene and Related 2d Materials for Energy Applications, L.C. Chen, Indrajit Shown, National Taiwan University, Taiwan, Republic of China**

**INVITED**

Plasma-assisted direct-growth of arrayed graphene and related hybrids will be presented. The main advantages of this type of nanostructures include high conductivity, high surface area and corrosion resistance, making them excellent candidates as electrocatalytic supports or electrodes for electrochemical (EC) energy applications, including fuel cells, supercapacitors and solar fuels. We will demonstrate the fabrication of integrated energy devices in an on-chip manner. Since the carrier transfer rate of electrode plays a crucial role in determining the energy-conversion performance, special emphases will be placed on the control of interfaces. Vertically aligned and edge-oriented graphene arrays were first synthesized by microwave plasma-enhanced chemical vapor deposition. Subsequent chemical doping can also be done in the same plasma reactor via either in-situ or ex-situ manners. Interestingly, for nitrogen doping in graphene, plasma process resulted in selective bond configuration. When applied as an EC electrode, the arrayed graphene exhibits nearly reversible redox characteristics. By varying the process parameters, samples can be produced

with controllable compressive or tensile strains, which in turn show strong effects on the resultant catalytic properties.

The hierarchical graphene nanowalls can be directly grown on a variety of substrates, including Si wafers, carbon cloth as well as flexible and ultralight carbon nanofibers. The latter substrate makes such electrode an ideal portable platform having high gravimetric, areal, and volumetric electrochemical characterizations. For instance, the carbon nanofibers supported graphene-based supercapacitors exhibit excellent specific capacitance of 352.53 F/g (220.33 mF/cm<sup>2</sup>) at a specific current of 13.33 A/g, which is among the highest reported to date. Meanwhile, 99 % of Coulomb efficiency and 98 % of the initial capacitance after 10,000 charge-discharge cycles were maintained. Finally, efficient and simple routes to further attach other heterogeneous nanostructures onto graphene nanowalls have also been developed. Cyclic voltammeter studies for electro-oxidation of methanol show a high ratio of forward anodic peak current to reverse peak current, suggesting an efficient oxidation of methanol to CO<sub>2</sub> on the graphene-based electrode. Our approach offers a promising route toward wafer-scale fabrication of graphene not only for fundamental research but also opens up various potential applications in sensing, catalysis, as well as energy storage and production.

**11:00am PS+2D-ThM10 Engineering Chemical Functionality in Graphene, Sandra Hernandez, P.E. Sheehan, S. Tsoi, P. Dev, J.T. Robinson, C. Junkermeier, K.E. Whitener, W.K. Lee, T.L. Reinecke, S.G. Walton, Naval Research Laboratory**

Graphene has attracted enormous attention due to its unique properties. Equally important is the ability to further tailor these properties through modification of select attributes such as surface chemistry, number of layers, sheet width, and edge structures. Manipulating the surface chemistry of graphene is important since the chemical composition strongly impacts the electronic properties as well as chemical reactivity both globally and locally. Precise control of the surface chemistry of graphene can also allow for subsequent surface procedures focused on band gap engineering, device fabrication and sensor applications. Given the strong impact of adsorbates, global chemical modification provides opportunities towards greater control over the properties of graphene films. Control over the spatial distribution of these groups provides an even greater functionality in that the local graphene reactivity can be manipulated, opening up a wealth of opportunities in biosensing, plasmonics, catalysis, smart surfaces, and heterojunction devices.

Using the unique attributes of electron beam generated plasmas to manipulate the chemistry of graphene and employing patterning techniques to regulate the spatial distribution of various functional groups on the surface, we demonstrate further abilities to govern surface properties. Spatial control over structural and chemical changes is characterized through micro (m-Raman and high-resolution x-ray photoelectron spectroscopy (XPS) mapping and electrical measurements are used to determine how local changes in chemistry influence the electronic properties. Lastly, we show that the resulting chemical moieties can be used to manipulate the local surface reactivity of graphene, enabling programmable, site-specific electrochemical deposition. These findings demonstrate the ability to tailor the locality of the surface chemistry on graphene surfaces opening up a wide range of reactivity studies and synthesis capabilities, such as programmable material deposition.

**11:20am PS+2D-ThM11 Formation of Aromatic Nitrogen Groups in Graphene Films by Post-Growth Treatment in Late-Afterglows of Nitrogen Microwave Plasmas, Luc Stafford, Université de Montréal, Canada**

Graphene films were exposed to the late afterglow of a reduced-pressure N<sub>2</sub> plasma sustained by microwave electromagnetic fields. X-ray photoelectron spectroscopy (XPS) shows that plasma-generated N atoms are incorporated into both pyridinic and pyrrolic groups, without excessive reduction of sp<sup>2</sup> bonding. Nitrogen incorporation was found to be preceded by N adsorption, where N adatom density increased linearly with treatment time while aromatic nitrogen saturated. This finding was confirmed by Raman spectra showing a linear increase of the D:G ratio attributed to constant surface flux of plasma generated species.

Combined Density Functional Theory calculations with a Nudged Elastic Band (DFT-NEB) approach indicate that incorporation reactions taking place at point vacancies in the graphene lattice requires an activation energy in the 2-6 eV range, but the energy required for the reverse reaction exceeds 8 eV. Stable nitrogen incorporation is therefore judged to be defect-localized and dependent on the energy transfer (6 eV) provided by N<sub>2</sub>(A)-to-N<sub>2</sub>(X) metastable-to-ground de-excitation reactions occurring at the late-afterglow-graphene interface.

# Thursday Afternoon, October 22, 2015

## 2D Materials Focus Topic

Room: 212C - Session 2D+EM+MG+NS+SS+TF-ThA

### Heterostructures of 2D Materials

**Moderator:** Stefan Förster, Martin-Luther-Universität Halle-Wittenberg, Michael Naguib, Oak Ridge National Laboratory

2:20pm **2D+EM+MG+NS+SS+TF-ThA1 Dielectrics Layer Deposition on 2D Materials by Functionalization with Polar Titanyl Phthalocyanine**, JunHong Park, UC San Diego, S. Fathipour, University of Notre Dame, I.J. Kwak, UC San Diego, H.C.P. Movva, UT-Austin, S. Vishwanath, H. Xing, Cornell University, S.K. Banerjee, UT-Austin, A.C. Seabaugh, University of Notre Dame, A.C. Kummel, University of California at San Diego

Several novel designs for beyond CMOS devices have emerged using two-dimensional semiconductors. These devices require deposition of thin insulators on 2D semiconductors or between two sheets of 2D semiconductors. However, 2D semiconductors are nearly inert surfaces thereby making uniform nucleation of oxide growth challenging preventing scaling of the insulator thickness. A new technique has been developed to employ a monolayer of ordered metal phthalocyanines (MPc) on 2D semiconductors directly as a nucleation layer for growth of ALD dielectric. TiOPc monolayers were deposited on HOPG surfaces and WSe<sub>2</sub> by organic molecular beam epitaxy. TiOPc forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.6 x 1.6 nm grid on both HOPG and WSe<sub>2</sub>. Observation of bright protrusions on each O-TiPc indicates that each O-TiPc in the monolayer is directed outward to vacuum. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H<sub>2</sub>O), insulating aluminum oxide was deposited uniformly on TiOPc/HOPG. After formation of AlO<sub>x</sub> on TiOPc/HOPG, the band gap of surface increases from 1.7 eV to 3.4 eV, while the conductance decreased. A metal-oxide-TiOPc-graphene capacitor has the lower thickness and the higher capacitance value than any reported graphene MOSCAPs. In the dual gated graphene FET with 40 cycles of AlO<sub>x</sub>, TiOPc assisted AlO<sub>x</sub> shows very low leakage current. Employing the TiOPc seeding layer also can be expanded to other TMD materials. The bottom gated WSe<sub>2</sub> FET was fabricated. On the bottom gated WSe<sub>2</sub> FET, the TiOPc monolayer was deposited, then 50 cycle of AlO<sub>x</sub> was deposited via ALD. In this dual gated WSe<sub>2</sub> FET, the leakage current of the AlO<sub>x</sub> is measured as ~0.05 pA/μm<sup>2</sup> at 0.5 VTG. As a control, 20 cycles of Al<sub>2</sub>O<sub>3</sub>, and 140 cycles of HfO<sub>2</sub> were deposited on bare WSe<sub>2</sub>. The leakage current of the TiOPc assisted 50 cycle Al<sub>2</sub>O<sub>3</sub> oxide is 3 orders of magnitude lower than HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/WSe<sub>2</sub>, consistent with a high nucleation.

2:40pm **2D+EM+MG+NS+SS+TF-ThA2 Direct Probing of the Electronic Structure of Bilayer Homo- and Hetero-Structures and Tracking their Evolution with Interlayer Twist-Angle**, Nader Zaki, P. Yeh, W. Jin, R.M. Osgood, Jr., Columbia University

2D atomic layer materials such as graphene and transition-metal dichalcogenides such as MoS<sub>2</sub> have garnered much interest over the last few years due to their surprising electronic properties. For example, graphene possesses an exceptionally high mobility while monolayer MoS<sub>2</sub> possesses a direct bandgap with an exceptionally high light-matter interaction. One of the directions the 2D materials community is now pursuing is one in which these materials are combined together by way of vertical stacking in order to fabricate custom layered structures with potentially rich physics and unique device properties. Naturally, determining the electronic structure of these custom assembled structures is a necessary task to understanding their electronic behavior. While the electronic structure of the constituent materials have already been studied for monolayer form, the electronic structure of the stacked structures has only recently started to be deciphered. This talk will report on the direct determination of the electronic structure of two bilayer systems: twisted bilayer MoS<sub>2</sub> and twisted graphene/MoS<sub>2</sub>. Using LEEM, μLEED, and μARPES, the stack quality, stack orientation, and stack electronic structure are directly probed and resolved with few μm and higher spatial resolution. To be discussed will be the evolution of the electronic structure with twist angle and its implications on the electronic properties of the respective homo- and hetero-structures.

3:00pm **2D+EM+MG+NS+SS+TF-ThA3 In Situ Microscopy on 2D Materials: Heterostructures, Nanostructures, Novel Materials Systems**, Peter Sutter, University of Nebraska - Lincoln **INVITED**

Two-dimensional (2D) materials, such as graphene, hexagonal boron nitride, and a family of metal dichalcogenides have fascinating properties

and show promise for applications. The broad exploration and use of these materials depends on the development of scalable synthesis methods, and of a fundamental understanding of their properties. I will discuss recent advances in understanding the synthesis, processing, and properties of 2D materials derived primarily from in-situ surface imaging.

In-situ microscopy provides the basis for creating complex heterostructures of different 2D materials, such as graphene and hexagonal boron nitride, and for studying atomically precise graphene nanostructures. Real-time imaging yields quantitative information on the growth and processing of new classes of 2D materials, such as metal dichalcogenide semiconductors. Finally, the combination of in-situ microscopy with synchrotron-based spectroscopy represents a unique approach for exploring the electronic band structure of 2D materials.

Our results illustrate that in-situ microscopy can be a powerful tool for realizing and probing the unique characteristics of two-dimensional materials.

4:00pm **2D+EM+MG+NS+SS+TF-ThA6 Direct Growth of Graphene/h-BN(0001) Multilayer Heterostructures for Novel Device Applications**, S. Driver, D. Beatty, B. Olanipekun, S. Reid, Jeffry Kelber, University of North Texas

We report the direct layer-by-layer growth of h-BN(0001) multilayers on Co(0001) by atomic layer epitaxy (ALE), and the direct growth of graphene multilayers on h-BN(0001) by molecular beam epitaxy (MBE). For the first time, this allows the growth of graphene/h-BN heterostructures with graphene and BN thicknesses controlled with atomic precision, and with all graphene and BN layers in azimuthal registry. Such control is a prerequisite for many proposed spintronic and electronic applications that emphasize charge or spin transport perpendicularly through the heterojunction. Further, the growth by direct, scalable methods without physical transfer, is essential for industrial development of such devices. h-BN(0001) multilayers have been deposited on Co(0001)/Al<sub>2</sub>O<sub>3</sub>(0001), using a BCl<sub>3</sub>/NH<sub>3</sub> ALE process at 600 K. X-ray photoelectron spectroscopy (XPS) indicates B:N atomic ratios of 1:1 with negligible Cl contamination or reaction with the metallic substrate. Low energy electron diffraction (LEED) data indicate BN domain sizes of ~300 Å or greater, with the lattice in registry with that of the Co(0001) substrate. LEED data also indicate BN domains larger than those of the Co substrate, suggesting BN overgrowth of Co domain boundaries. The XPS-derived average BN film thickness scales linearly with the number of BCl<sub>3</sub>/NH<sub>3</sub> cycles, and the lack of Co oxidation after ambient exposure of a BN bilayer indicates that these films are macroscopically continuous over the 1 cm x 1 cm sample size. Graphene formation on h-BN(0001) was achieved using MBE with a graphite rod source, with deposition carried out at 800 K. LEED data show the expected 6-fold LEED pattern in exact registry with that of the h-BN(0001)/Co(0001) substrate. XPS C 1s spectra indicate a C 1s binding energy near 284.5 eV and with the expected pi-to-pi\* transition. A heterojunction consisting of ~3 monolayers (ML) graphene/3 ML h-BN on Co(0001) proved stable in vacuum to at least 1000 K, indicating the adaptability of this growth process to a variety of industrial applications. Other recent results indicate the adaptability of this process to other substrates, such as Ru(0001) or CoSi<sub>2</sub>(111). These developments make possible a variety of spin filters, spin valves, and tunneling transistors proposed on the basis of close BN/graphene lattice matching, but not readily achievable with physically transferred films.

**Acknowledgements:** This work was supported by CSPIN, a MARCO/DARPA STARnet Center, under tasks 2381.001

and 2381.003, and by a UNT ROP grant. Peter Dowben and Jian-Ping Wang are acknowledged for stimulating and informative discussions.

4:20pm **2D+EM+MG+NS+SS+TF-ThA7 Al<sub>2</sub>O<sub>3</sub> on Black Phosphorus by Atomic Layer Deposition: An in situ Interface Study**, Hui Zhu, S. McDonnell, X. Qin, A. Azcatl, L. Cheng, R. Addou, J. Kim, UT-Dallas, P.D. Ye, Purdue University, R.M. Wallace, UT-Dallas

Black phosphorus ("black-P") is considered to be an appealing 2D material because of its novel properties and potential application in few-layer transistor structures.<sup>1,2,3</sup> However, a clear challenge in the implementation of black-P is the strong hydrophilic<sup>4</sup> and oxidation<sup>5</sup> reactions during device processing and thereafter. Thus, efficient isolation layers are necessary for black-P to preserve its electronic properties. Al<sub>2</sub>O<sub>3</sub><sup>2</sup> or HfO<sub>2</sub><sup>6</sup> dielectric layers deposited by atomic layer deposition (ALD) have been used as isolation layers in recent black-P transistors. In this work, three different samples oxidized by ambient air were investigated to understand the interfacial chemistry, and nucleation of atomic layer deposited Al<sub>2</sub>O<sub>3</sub> on black-P using *in situ* X-ray photoelectron spectroscopy (XPS). This work suggests that exposing a sample that is initially free of phosphorus oxide to the ALD precursors does not result in detectable oxidation. However, when

the phosphorus oxide is formed on the surface prior to deposition, the black-P can react with both the surface adventitious oxygen contamination and the H<sub>2</sub>O precursor at the deposition temperature of 200 °C. As a result, the concentration of the phosphorus oxide increases after both annealing and the atomic layer deposition process. The nucleation rate of Al<sub>2</sub>O<sub>3</sub> on black-P is correlated with the amount of oxygen on samples prior to the deposition. The growth of Al<sub>2</sub>O<sub>3</sub> follows a “substrate inhibited growth” behavior where an incubation period is required. *Ex situ* atomic force microscopy is also used to investigate the deposited Al<sub>2</sub>O<sub>3</sub> morphologies on black-P where the Al<sub>2</sub>O<sub>3</sub> tends to form islands on the exfoliated black-P samples.

This work was supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA, and the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765.

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#### 4:40pm **2D+EM+MG+NS+SS+TF-ThA8 Topological Winding Number Change and Broken Inversion Symmetry in a Hofstadter's Butterfly, Marc Bockrath,** UC Riverside

Recently several research groups have demonstrated accurate placement of graphene on hexagonal BN (hBN) with crystallographic alignment. Due to the resulting superlattice formed in the graphene/hBN heterostructures, an energy gap, secondary Dirac Points, and Hofstadter quantization in a magnetic field have been observed. Using aligned layer transfer we are able to produce graphene/hBN heterostructures with ~1 degree alignment accuracy, and measure the transport properties of the resulting systems. We observe an additional  $\pi$  Berry's phase shift in the magneto-oscillations when tuning the Fermi level past the secondary Dirac points, originating from a change in topological winding number from odd to even when the Fermi-surface electron orbit begins to enclose the secondary Dirac points. At large hole doping inversion symmetry breaking generates a distinct hexagonal pattern in the longitudinal resistivity versus magnetic field and charge density. This results from a systematic pattern of replica Dirac points and gaps, reflecting the fractal spectrum of the Hofstadter butterfly.

#### 5:00pm **2D+EM+MG+NS+SS+TF-ThA9 Compliant Substrate Epitaxy: Au on MoS<sub>2</sub>, Yuzhi Zhou, C. Daryl,** UC Berkeley

The heteroepitaxial growth of Au on MoS<sub>2</sub>, a layered van der Waals bonded dichalcogenide, is analyzed. It is argued that the weak coupling between the layers in the dichalcogenides enables the first substrate layer to deform elastically almost independently from the substrate layers below, and hence enables epitaxial growth for a larger mismatch than might otherwise be expected. Linear, continuum elasticity theory and density functional theory are used to show that a {111} oriented Au film is the preferred over an {001} oriented Au film, despite the fact that the {111} orientation leads to a much higher elastic strain. During the initial stages of growth, the {111} orientation is favored over the {001} orientation due to its lower surface and interfacial energies. As the Au film grows thicker, the elastic relaxation of the first layer of the substrate leads to a reduction in the elastic energy of the growing film. This reduces the elastic energy difference between the {001} and {111} orientations enabling the {111} orientation to remain stable for all film thicknesses. This work is supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

#### 5:20pm **2D+EM+MG+NS+SS+TF-ThA10 Direct Synthesis of 2D van der Waals Heterostructures, Judy Cha,** Yale University **INVITED**

Two-dimensional (2D) chalcogenides have gained renewed interest due to their interesting electrical properties such as topological insulator surface states in Bi<sub>2</sub>Se<sub>3</sub> and hydrogen evolution catalytic activities in MoS<sub>2</sub>. Our ability to thin them down to a single layer and their anisotropic bonding nature opens up possibilities for novel heterostructures where we can tailor

their electronic properties. I will present one-step, scalable heterostructure synthesis method to synthesize these chalcogenide nanostructures and examine their electronic transport properties. Intercalation into 2D materials will be considered as a novel way to design 2D heterostructures, in which the optical and electrical properties of the host 2D materials can drastically change. I will also discuss ways to control the alignment of molecular layers in these 2D chalcogenides, which exploits stress and strain built in the film during the growth. Electron tomography will be used to reconstruct the 3D structure of vertically oriented molecular layers in MoS<sub>2</sub> thin films. In the second part of the talk, I will present synthesis and electronic properties of SnTe topological crystalline insulator nanoplates. Although SnTe is cubic and not a layered material, large SnTe nanoplates expanding hundreds of microns in lateral dimension with ~100 nm in thickness are possible. I will discuss effects of substrates and growth conditions to promote thin film growth of non-layered materials.

# Thursday Evening Poster Sessions

## 2D Materials Focus Topic

Room: Hall 3 - Session 2D-ThP

## 2D Materials Focus Topic Poster Session

**2D-ThP1 Spin-Orbit Coupling in the Band Structure of Monolayer WSe<sub>2</sub>(0001), Iori Tanabe**, University of Nebraska - Lincoln, D. Le, University of Central Florida, A.V. Barinov, Sincrotrone Trieste, Italy, E. Preciado, M. Isarraraz, University of California - Riverside, T. Komesu, University of Nebraska - Lincoln, L. Bartels, University of California - Riverside, T.S. Rahman, University of Central Florida, P.A. Dowben, University of Nebraska - Lincoln

WSe<sub>2</sub> and the related metal dichalcogenides MX<sub>2</sub> (with M = V, Mo, W, Ta and X = S, Se, Te) are layered structures that in each plane consist of a hexagonal honeycomb lattice reminiscent of graphene or graphite. WSe<sub>2</sub> is a semiconductor, rather than a gapless semiconductor (like graphene) or semimetal, and is expected to have applications for new spintronic devices where spin-orbit coupling might play a valuable role. Here, we used high-resolution angle resolved photoemission spectroscopy (ARPES) and inverse photoemission spectroscopy (IPES) to map out the electronic band structure of single-layer WSe<sub>2</sub>. The splitting of the top of the valence band due to spin-orbit coupling was found to be 513±10 meV, far larger than that for MoS<sub>2</sub>. As expected the top of the valence band is at K. Overall, density functional theory (DFT) calculations were in excellent agreement with the ARPES results, and we have verified that the few discrepancies between theory and experiment were not due to the effect of strain. Cobalt on WSe<sub>2</sub> is seen to have a very complex interface, with strong interactions, as seen in the changes to the experimental electronic structure. Without the complexity of a metal adlayer, WSe<sub>2</sub> is seen to be routinely Se rich and should thus be reliably p-type.

**2D-ThP2 Ferroelectric Control of Monolayer MoS<sub>2</sub> via Direct Single-Layer Growth on LiNbO<sub>3</sub>, Ariana Nguyen, E. Preciado, V. Klee, D. Sun, I. Lu, D. Barroso, L. Bartels**, UC Riverside

We present the direct chemical vapor deposition (CVD) growth of monolayer molybdenum disulfide (MoS<sub>2</sub>) onto periodically poled lithium niobate. Single-layer MoS<sub>2</sub> displays a preference for the ferroelectric domains polarized “up” with respect to the surface. This may offer the possibilities of templated growth of TMD films using the substrate ferroelectric polarization as a pattern. Piezoresponse force microscopy reveals that the MoS<sub>2</sub> film maintains the substrate polarization on the “up” domains while partially quenching it on the “down” domains. Electrical transport measurements suggest the ability to invert the single-layer CVD MoS<sub>2</sub> majority charge carrier via gating depending on the domain orientation of the periodically poled lithium niobate substrate.

**2D-ThP4 Thermally Conductive Graphene-Polymer Composites, Michael Shtein, O. Regev**, Ben Gurion University, Israel

The rapidly increasing device densities in electronics dictate the need for efficient thermal management. If successfully exploited, graphene, which possesses extraordinary thermal properties, can be commercially utilized in polymer composites with ultrahigh thermal conductivity (TC). The total potential of graphene to enhance TC, however, is restricted by the large interfacial thermal resistance between the polymer mediated graphene boundaries. We report a facile and scalable dispersion of commercially available graphene nano platelets (GnPs) in a polymer matrix, which formed composite with an ultra-high TC of 12.4 W/mK (vs. 0.2 W/mK for neat polymer).[1] This ultra-high TC was achieved by applying high compression forces during the dispersion resulting in gap closure between adjacent GnPs with large lateral dimensions and low defect densities. We also found strong evidences for the existence of a *thermal percolation threshold*. Finally, the addition of electrically insulating nano-boron nitride to the thermally conductive GnP-polymer composite significantly reduces its electrical conductivity (to avoid short circuit) and synergistically increases the TC. The efficient dispersion of commercially available GnPs in polymer matrix provides an ideal framework for substantial progress toward large-scale production and commercialization of GnP-based thermally conductive composites.

**Reference:** Shtein M., Nadiv R., Buzaglo M., Kahil K. and Regev O., Thermally conductive graphene-polymer composites: size, percolation and synergy effects, *Chemistry of Materials*, 2015, 27, 2100–2106.

**2D-ThP5 Low Temperature Raman and Photoluminescence Measurements of MoS<sub>2</sub> Layer Grown by Chemical Vapor Deposition, Barbara Nichols**, U.S. Army Research Laboratory, R. Ghosh, S.K. Banerjee, University of Texas at Austin

The temperature-dependent Raman spectroscopy and photoluminescence mapping measurements of molybdenum disulfide (MoS<sub>2</sub>) layers grown on silicon oxide (SiO<sub>2</sub>) by chemical vapor deposition were performed. As grown, the MoS<sub>2</sub> monolayers are shaped as either hexagons or triangles with smaller dendritic adlayers randomly distributed throughout the layer. Specifically, Raman and PL mapping of a 20 micron wide hexagon was performed at room temperature in air and in vacuum. In both air and vacuum, the Raman A<sub>1g</sub> – E<sub>2g</sub> separation was wider for the dendritic adlayers than for the monolayer MoS<sub>2</sub> as well as a decreased PL intensity was observed for the dendrites when compared to the monolayer. Raman and PL mapping of the MoS<sub>2</sub> hexagon revealed these trends remained as the temperature was decreased from room temperature to 4 K. At 4 K, differences between the dendrites and the monolayer MoS<sub>2</sub> were mainly observed by the PL measurements. PL peak position shifts as much as 15 meV and peak shapes were observed for the A and B exciton transitions.

**2D-ThP6 CVD Growth of Single-Layer TMD Films Onto Pre-Fabricated Substrate Structures, B. Davis, E. Preciado, V. Klee, A. Nguyen, I. Lu, D. Barroso, S. Naghibi, I. Liao, G. von Son, D. Martinez-Ta, Ludwig Bartels**, UC Riverside

We demonstrate the growth of transition metal dichalcogenides (TMD) single-layer films through chemical vapor deposition (CVD) onto pre-fabricated patterns on SiO<sub>2</sub>/Si surfaces. For an ultimate technological application of single-layer TMD films, they need to be integrated into lithographic structures on SiO<sub>2</sub>/Si substrates; exfoliation and/or transfer are not suitable or scalable techniques. The comparatively low growth temperatures of TMD films (about 700°C) compared to graphene (about 1000°C) is a crucial advantage of the former, as SiO<sub>2</sub>/Si features can sustain the growth temperature. Here we offer examples of how pre-fabricated patterns can control the growth of TMD films, and how the latter arrange themselves into former to offer features (e.g., natively suspended material) that is typically not available directly from growth onto conventional flat substrates. We explore the electrical and optical properties of single-layer growth on substrates with holes, pillars, and trenches.

**2D-ThP7 MoS<sub>2</sub> Thin Films Deposited by Chemical Bath Deposition on Si and Glass Substrates, D.E. Perez-Barragan**, Escuela Superior de Ingeniería Química e Industrias Extractivas-IPN, Mexico, A. Garcia-Sotelo, E. Campos, Cinvestav-IPN, Mexico, Orlando Zelaya-Angel, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, M. Melendez-Lira, Cinvestav-IPN, Mexico

Even when the increasing interest in MoS<sub>2</sub> is driven by their properties as a 2D material, the deposit of MoS<sub>2</sub> films using low cost techniques is interesting and allows to explore the feasibility to find routes to produce low cost materials capable to improve photovoltaic structures, etc. The results of the deposit by chemical bath deposition of MoS<sub>2</sub> films employing Si and glass substrates are presented. Two precursor were employed: Ammonium molybdate (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> and Ammonium molybdate tetrahydrate (NH<sub>4</sub>)<sub>6</sub>MoO<sub>24</sub> · 4H<sub>2</sub>O. It was found that the first precursor is adequate to obtain amorphous MoS<sub>2</sub> films on glass while the second allows to obtain amorphous films on silicon.

The samples crystallized after a thermal annealing process carried out at 300 °C. UV-Vis spectroscopy indicated a blue-shift in the absorption edge from the MoS<sub>2</sub> bulk value, probably related to the film thickness. Samples were characterized also by XPS, Raman and AFM. The results are discussed in terms of the structural characteristic of the films and the interaction with the substrate.

\*: Partially funded by CONACyT-Mexico

**2D-ThP8 Development of Arrays of Field Effect Transistors Based on CVD Graphene and TaN as Metal Electrode, Aline Pascon**, UNICAMP, Brazil, C.C. Silva, University of Campinas, Brazil, J.F. Souza, UNICAMP, Brazil, L.T. Kubota, University of Campinas, Brazil, L.R.C. Fonseca, J.A. Diniz, UNICAMP, Brazil

Since graphene was successfully isolated for the first time by microcleaving of graphite [1], this material has attracting a significant attention of all scientific community, mainly due to its outstanding electronic properties, making it an ideal material to replace the silicon in the traditional FETs. However, the implementation of graphene in the development of FETs has two major issues that should be overcome. The first is that graphene obtained from microcleaving or exfoliation of graphite, does not feature like

a scalability technique to be employed in the fabrication of arrays of FETs. The second issue is related with the high contact resistance that appears in the interface metal/graphene. In order to replace the silicon by the graphene as a channel material, a suitable contact with electrodes is required. Aiming to overcome the related issues, herein we have addressed the implementation into arrays of FETs by large area of monolayer graphene produced by the CVD process. Furthermore, we evaluated the effects of the replacement of the conventional, non-refractory metallic electrodes such as Ti/Au or Ti/Pd for the refractory metallic electrodes, such as tantalum nitride (TaN) that has a work function similar to graphene reducing the barrier between metal and graphene.

The CVD graphene was grown based on the procedure proposed by Ruoff and coworkers [2]. This graphene film was transferred on FETs where 22 nm TaO<sub>x</sub> was used as gate dielectric, in just one step, homogenous and free from PMMA residues or other contamination. The Raman spectra obtained from different areas of the graphene displays a typical G peak at 1587 cm<sup>-1</sup>, free of defects and a 2D peak at 2684 cm<sup>-1</sup>, indicating a monolayer of graphene [3].

After the transferring process, the graphene was isolated between the source and drain TaN electrodes due to the photolithography step followed by the oxygen plasma etching, to remove the graphene in the outside area, creating a contact with the electrodes, similar to the dielectric gate. All this process was carried out directly on a die of 2.5 cm<sup>2</sup> containing four arrays with 300 FETs each. The latter two processes define the active region of the device, where the electronic transport will occur through the graphene monolayer.

Measurements of electrical properties, with transconductance of 3 mS and contact resistance of 3 kΩ indicate that our devices can achieve high performance, while allows fabricating a massive number of FET-Graphene devices through a simple, fast and scalable approach.

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**2D-ThP11 Conductance-Based Structural Characterization of Hybrid, 2-Dimensional, Molecule-Nanoparticle Arrays, Joshua Hihath, C.E. McCold, Q. Fu,** University of California, Davis, *J.Y. Howe*, Hitachi High-Technologies Corporation

Molecule-nanoparticle hybrid systems have emerged as promising materials for applications ranging from chemical sensing to nanoscale electronics. However, creating reproducible and repeatable 2-dimensional composite materials with precise electronic properties has remained an important challenge to the implementation of these meta-materials. Understanding the sources of variation that dominate the charge transport properties of these systems is essential for the advancement of nanoparticle-array based devices. In this work, we use a combination of charge-transport measurements, electron microscopy, optical characterization, and chemical ligand exchange to determine the role of morphology, structure, and array interconnection on the charge transport properties of 2-dimensional, monolayer arrays of molecularly-interlinked gold nanoparticles. Using these techniques we are able to determine the role of assembly-dependent, particle dependent, and molecule dependent defects on the conductivities of the monolayer films. These results demonstrate that micron-scale assembly processes dominate the dispersion of the conductance values, and result in order-of-magnitude differences in the conductance values, while nanoscale properties related to the nanoparticle and ligand features dictate the mean value of the conductance. By performing a systematic study of the conductance of these arrays as a function of nanoparticle size we are able to extract the carrier mobility for specific molecular ligands. We show that nanoparticle dispersion correlates with the void density in the array, and that because of this correlation it is possible to accurately determine the void density within the array directly from conductance measurements. These results demonstrate that conductance-based measurements can be used to accurately and non-destructively determine the morphological and structural properties of these hybrid arrays, and thus provide a characterization platform that helps move 2-dimensional nanoparticle arrays toward robust and reproducible electronic systems. Based upon this understanding, it is then possible to control the conductance values of the hybrid arrays by tuning both the distance between nanoparticles, and the conjugation of the molecules interlinking the nanoparticles. This control allows the conductance of the 2D films to be tuned over a range of ~7 orders of magnitude.



## 2D Materials Focus Topic

Room: 212C - Session 2D+EM+IS+NS+PS+SP+SS-FrM

## Surface Chemistry of 2D Materials: Functionalization, Membranes, Sensors

**Moderator:** Peter Sutter, University of Nebraska - Lincoln, Judy Cha, Yale University

8:20am **2D+EM+IS+NS+PS+SP+SS-FrM1 Chemically Modifying Graphene for Surface Functionality**, Paul Sheehan, S. Tsoi, S.C. Hernández, S.G. Walton, T.L. Reinecke, K.E. Whitener, J.T. Robinson, Naval Research Laboratory, R. Stine, Nova Research

Graphene has many superlative properties that may be tailored for specific applications, or even enhanced, through chemical functionalization. Chemical functionalization dramatically changes almost every critical property of graphene, changing it from opaque to transparent, from diamagnetic to ferromagnetic, from electron rich or electron poor, from electrically conducting to insulating (and back again!). This extensive control suggests that chemically modified graphene may aid applications from flexible sensors to surface engineering. I will discuss how stacks of 2D materials can control the dominant surface forces—van der Waals,<sup>1</sup> acid-base interactions, electrostatic interactions, etc.—and so surpass conventional methods of preparing surfaces with, for example, self-assembled monolayers. I will also briefly address goals as diverse as biosensing<sup>2</sup> or sloughing off chemical warfare agents.<sup>3</sup>

<sup>1</sup> ACS Nano, **2014**, 8 (12), pp 12410–12417

<sup>2</sup> BioTechniques, Vol. 57, No. 1, July 2014, pp. 21–30

<sup>3</sup> ACS Nano. 2013 Jun 25;7(6):4746–55.

8:40am **2D+EM+IS+NS+PS+SP+SS-FrM2 Structural Phase Stability Control of Monolayer MoTe<sub>2</sub> with Adsorbed Atoms and Molecules**, Yao Zhou, E.J. Reed, Stanford University

Of the Mo- and W- dichalcogenide monolayers, MoTe<sub>2</sub> is particularly interesting because it exhibits a small energy difference (approximately 31 meV per MoTe<sub>2</sub>) between its semiconducting 2H phase and metallic 1T' crystal structures. This feature makes it particularly interesting for potential phase change applications.

We study the adsorption of some common atoms and molecules onto monolayer MoTe<sub>2</sub> and the potential for adsorption to induce a phase change between the semiconducting 2H and metallic 1T' crystal structures of the monolayer. Using density functional theory with spin orbit and van der Waals energy contributions, we determined the most energetically favorable adsorption positions and orientations on the two phases of monolayer MoTe<sub>2</sub>. We then obtained the formation energies for these adsorption reactions and found that atomic adsorption generally favors 1T' metallic phases while molecular adsorption favors semiconducting 2H phases. A possible application of this work may be the chemical stabilization of a preferred phase during the growth process.

Further, we consider the Mo<sub>x</sub>W<sub>1-x</sub>Te<sub>2</sub> alloy monolayers that exhibit even smaller energy difference between phases. Our calculations indicate that it may be possible to engineer an alloy (0 < x < 0.5) such that specific molecules will induce a phase change to 1T' while other molecules studied stabilize the 2H phase, which suggests that alloying may provide some molecular selectivity. This potentially provides the basis for molecular sensing applications due to the large electronic contrast between 2H and 1T' phases.

9:00am **2D+EM+IS+NS+PS+SP+SS-FrM3 Selective Nanochemistry on Graphene/Silicon Carbide: Substrate Functionalization and Polycyclic Aromatic Hydrocarbons Formation**, Patrick Soukiassian, CEA, France

INVITED

Graphene & silicon carbide (SiC) are advanced semiconductors having figures of merit scaling well above those of well-established ones [1,2]. Understanding/mediating SiC and graphene surfaces & interfaces properties are of central importance toward functionalization and applications. As a 2D material, graphene is a single atomic layer of carbon atoms in a sp<sup>2</sup> bonding configuration. Therefore, functionalization remains challenging since interacting too strongly with the graphene atomic layer may change its bonding configuration and properties. Instead, interacting with the SiC substrate offers an alternative approach. The 1<sup>st</sup> case of hydrogen-induced metallization of a semiconductor surface has been shown for a 3C-SiC(001) surface [3]. Here, combining investigations using advanced experimental techniques such as STM/STS, vibrational & 3rd generation synchrotron radiation-based photoelectron spectroscopies together with state-of-art

calculations will be presented and discussed. It includes: i) the 1<sup>st</sup> evidence of H/D-induced nanotunnel opening at a semiconductor sub-surface shown here for SiC [4]. Depending on H coverage, these nanotunnels could either be metallic or semiconducting. Dangling bonds generated inside the nanotunnels offer a promising template to capture atoms or molecules. These features open nano-tailoring capabilities towards advanced applications in electronics, chemistry, storage, sensors or biotechnology. Understanding & controlling such a mechanism open routes towards selective surface/interface functionalization of epitaxial graphene [4]. ii) The role of H interaction with graphene on SiC dust grains in polycyclic aromatic hydrocarbons (PAH) formation in the interstellar space with a possible route toward prebiotic roots of life in the universe [5].

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9:40am **2D+EM+IS+NS+PS+SP+SS-FrM5 Intrinsic Wettability of Graphene**, Haitao Liu, Department of Chemistry, University of Pittsburgh

Graphene and graphite are long believed to be hydrophobic. Here we show that a clean graphitic surface is in fact mildly hydrophilic [1]. We find that an as-prepared graphene sample is hydrophilic with a water contact angle of ca. 40°. Upon exposure to ambient air, the water contact angle gradually increased to ca. 60° within 20 min and plateaued at ca. 80° after 1 day. Infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that airborne hydrocarbon adsorbed onto the graphene surface during this process. Both thermal annealing and controlled UV/O<sub>3</sub> treatment removed the hydrocarbon contaminants, which was accompanied by a concurrent decrease in the water contact angle. Our findings show that graphene is more hydrophilic than previously believed and suggest that the reported hydrophobic nature of graphene is due to unintentional hydrocarbon contamination from ambient air.

Reference

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10:00am **2D+EM+IS+NS+PS+SP+SS-FrM6 Au-doped Graphene As a Promising Electrocatalyst for the Oxygen Reduction Reaction in Hydrogen Fuel Cells: Prediction from First Principles**, Sergey Stolbov, University of Central Florida, M. Alcantara Ortigoza, Tuskegee University

One of the main obstacles hindering large scale practical application of hydrogen fuel cells is a prohibited cost of the Pt (or Pt-based) catalysts for the oxygen reduction reaction (ORR) on the fuel cell cathode. In this work, we consider Au-doped graphene as an alternative to Pt for facilitating ORR. Our first-principles calculations show that Au atoms incorporated into graphene di-vacancies form a thermodynamically and electrochemically stable structure. Furthermore, calculation of the binding energies of the ORR intermediates reveals that Au-C bonding makes the C atoms neighboring to Au optimally reactive for ORR. The calculated ORR free energy diagrams suggest that the Au-graphene structures have an ORR onset potential as high as that of Pt. We also demonstrate that the linear relation among the binding energy of the reaction intermediates assumed in a number of works on computational high-throughput material screening does not hold, at least for this none purely transition-metal material.

10:20am **2D+EM+IS+NS+PS+SP+SS-FrM7 Spontaneous Deposition of Palladium Nanoparticles on Graphene through Redox Reaction**, Xiaorui Zhang, W. Ooki, Y.R. Kosaka, T. Kondo, J. Nakamura, University of Tsukuba, Japan

Due to its unique properties such as huge surface area and excellent conductivity, graphene becomes great interesting for supporting noble metal catalysts. Some noble metals such as palladium, platinum, gold nanoparticles was reported to be able to spontaneous deposition on as-synthesized reduced graphene oxide with external reducing agent-free

recently. Yet the mechanism of spontaneous deposition of metals on graphene has not been clarified until now. In the present research, we spontaneously deposited palladium nanoparticles on as-synthesized reduced graphene oxide in H<sub>2</sub>O medium without external reducing agent. It was found that the deposited amount of palladium varied with pH, meanwhile, the bivalent Pd<sup>2+</sup> precursor was reduced to metallic palladium, and graphene was oxidized simultaneously with an increasing of its oxygen functional groups. The atomic ratio of the deposited Pd and the increased O in rGO located in a range from 1 to 2. As reducing agent-free, the mechanism on spontaneous redox deposition of metal nanoparticles on graphene was proposed, firstly, an efficient adsorption of metal precursor on graphene is a prerequisite which is determined by their electrical charges and adjusted by pH. Secondly, a positive galvanic potential between metal precursor and graphene is necessary for metal spontaneous deposition.

10:40am **2D+EM+IS+NS+PS+SP+SS-FrM8 Gradient Electrochemical Response of Template Synthesized Thickness Sorted MoS<sub>2</sub> Nanosheets for Cellular Level Free Radical Detection**, *Ankur Gupta, T. Selvan, S. Das, S. Seal*, University of Central Florida

The human body is a complex system capable of defending in adverse conditions. A classic example of such complex process is balanced equilibrium production between pro-oxidant and antioxidant in cells. However, when this equilibrium is disturbed, production of free radicals such as superoxide and nitric oxide strengthen, and causes serious cellular damages. Furthermore, myeloperoxidase (MPO) is released during the oxidative burst. This MPO combines with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and Cl<sup>-</sup> and generate hypochlorous acid (HOCl). This is a short-lived and powerful diffusible oxidant strong oxidizer and could react with O<sup>2-</sup> to produce OH<sup>-</sup>. Therefore, in physiological condition HOCl has a major role as a potent microbicidal agent in the immune defense; however, during the oxidative burst HOCl not only damage healthy tissue and generate radicals that are extremely reactive. Therefore, monitoring of the production of free radicals at the cellular level is important for diagnostic purpose. Over past years, several material have been used to develop sensors for free radical detection such as cerium oxide nanoparticles, MoS<sub>2</sub> nanosheets and nanoparticles. However, detection of free radicals at cellular level is still a challenge.

In this attempt, layered molybdenum disulfide (MoS<sub>2</sub>) were synthesized via hydrothermal method. SBA-15 polymer template were utilized during hydrothermal process to grow MoS<sub>2</sub> around it to develop porosity. After the hydrothermal synthesis and washing, polymer template was removed by dissolving it in isopropanol which leaves high surface area layered MoS<sub>2</sub> crystal. Wet chemical exfoliation of MoS<sub>2</sub> were carried out in aqueous solution of Pluronic<sup>®</sup> F-127 having hydrophobic and hydrophilic chains. Pluronic<sup>®</sup> F-127 was used to bring down the buoyant density of MoS<sub>2</sub>. Non-templated nanosheets were synthesized as control. The exfoliated solution were centrifuged at 3000 rpm to remove large particle and supernatant was collected for density gradient ultracentrifugation (DGU). Separation of different thickness layers is carried out by DGU. Thickness sort MoS<sub>2</sub> nanosheets were characterized using AFM, XPS, HRTEM, Raman and UV-Vis spectroscopy for structural and chemical analysis. XPS, HETEM and EFTEM analysis of nanosheets have illustrate the sulfur deficiency at the edges of the nanosheets. MoS<sub>2</sub> nanosheets were deposited on glassy carbon electrode for cyclic-voltammetry and chronoamperometry measurements. Higher sensitivity and repeatability were demonstrated by nanosheets prepared via template method as compared to control for reactive oxygen and nitrogen species, and HOCl.

11:00am **2D+EM+IS+NS+PS+SP+SS-FrM9 Methanol Synthesis on Defect-Laden Single-Layer MoS<sub>2</sub> Supported on Cu(111): Results of a First Principles Study**, *D. Le, Takat B. Rawal, T.S. Rahman*, University of Central Florida

Despite being found to be the preferred structure in single layer MoS<sub>2</sub>, the sulfur vacancy row does not facilitate alcohol synthesis from syngas [1] because its narrow size limits adsorption, diffusion, and formation of possible intermediates. On the Cu(111) surface, strong interactions between MoS<sub>2</sub> and Cu are expected to reduce the corrugations caused by sulfur vacancy rows, resulting in a larger exposure of vacancies to adsorbates which could enhance the catalytic activity of the row towards alcohol synthesis from syngas. Based on the results of our density functional theory (DFT) simulations utilizing the DFT-D3 correction for accounting the van der Waals interactions, we show that: (1) there is a significant charge transfer from the Cu(111) surface to MoS<sub>2</sub>, enhancing its catalytic properties, (2) the binding energies of CO and dissociated H<sub>2</sub> increase by 0.3 eV in comparison to that on unsupported MoS<sub>2</sub>, indicating stronger interactions, and (3) the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS<sub>2</sub>. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syn gas on single-layer MoS<sub>2</sub> with a vacancy row. We will also present the energetic pathways for the

formations of other reaction products such as methane, formaldehyde, and water, as well as that of (the reverse) water gas-shift reaction.

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\*This work is supported in part by the U.S. Department of Energy under grant DE-FG02-07ER15842

11:20am **2D+EM+IS+NS+PS+SP+SS-FrM10 The Happy Marriage of Graphene and Germanium: Graphene Achieves Exceptional Conductivity and Protects Germanium from Oxidizing**, *Richard Rojas Delgado*, University of Wisconsin-Madison, *F. Cavallo*, University of New Mexico, *R.M. Jacobberger, J.R. Sanchez Perez, D. Schroeder, M.A. Eriksson, M.S. Arnold, M.G. Lagally*, University of Wisconsin-Madison

The properties of graphene (G) make it an outstanding candidate for electronic-device applications, especially those that require no band gap but a high conductance. The conductance, involving both carrier mobility and carrier concentration, will depend critically on the substrate to which G is transferred. We demonstrate an exceptionally high conductance for G transferred to Ge(001) and provide an understanding of the mechanism.[1] Essential in this understanding is an interfacial chemistry consisting of Ge oxide and suboxide layers that provide the necessary charges to dope the graphene sheet, and whose chemical behavior is such that one can obtain long-term stability in the conductance. In contrast, when high-quality G is grown directly on Ge (100), (111), or (110), the conductance is unexceptional, but oxidation of the surface is significantly delayed and slowed, relative to both clean Ge and Ge with G transferred to its surface. [2,3] We fabricate Hall bars in G transferred to Ge and G grown using atmospheric-pressure CVD with methane precursors. X-ray photoelectron spectroscopy (XPS) is used to investigate the oxide in all stages of the measurements. The sheet resistance and Hall effect are measured from 300K to 10K for transferred and grown samples. Values of mobility and carrier concentration are extracted. It appears we have reached the highest combination of mobility and carrier concentration in graphene (suspended or supported) for temperatures from 10 to 300K. The implication is that the primary mechanisms for scattering charge in the G, roughness and a non-uniform electrostatic potential due to fixed charges, have limited effect when the substrate is oxidized Ge. Finally the subsequent oxidation kinetics of Ge (001) are compared for graphene directly grown on Ge and for graphene transferred to Ge. XPS shows that for graphene grown on Ge(001) the interface is oxide-free and remains so over long periods of time. For graphene transferred to Ge(001) the interface contains stoichiometric and substoichiometric oxides. The thickness of these oxides increases with time, but quite slowly. Using spatially resolved XPS, we propose a model of diffusion limited oxidation initiated at edges of the graphene.

Research supported by DOE.

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 2D+EM+IS+NS+PS+SP+SS-FrM10, 26  
 Everitt, H.O.: TF+2D+MG+NS-MoA1, 5

## — F —

Falta, J.:  
 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 19  
 Fathipour, S.: 2D+EM+MG+NS+SS+TF-ThA1, 21  
 Feenstra, R.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2  
 Feigelson, B.N.:  
 2D+EM+NS+PS+SP+SS+TF-MoM1, **1**;  
 2D+EM+NS+PS+SP+SS+TF-MoM3, 1  
 Ferrah, D.: PS+2D-ThM1, 19  
 Fiori, G.: 2D+EM+MC+MS+NS-MoA6, 4  
 Flege, J.I.:  
 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 19  
 Florea, I.: TF+2D+MG+NS-MoA10, 7  
 Fonseca, L.R.C.: 2D-ThP8, 23  
 Förster, S.:  
 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, **19**  
 Frégnaux, M.:  
 2D+EM+MC+MI+NS+SP+SS+TF-TuA11, 10  
 Fu, Q.: 2D-ThP11, 24  
 Fuhrer, M.: 2D+EM+IS+MC+NS+SP+SS-WeA11, 15;  
 2D+EM+NS+PS+SP+SS+TF-MoM3, 1  
 Funke, S.: 2D+EM+NS+SS+TF-TuM11, 9;  
 2D+EM+NS+SS+TF-TuM6, **8**  
 Furdyna, J.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2

## — G —

Garcia-Sotelo, A.: 2D-ThP7, 23  
 Gaskill, D.K.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1; 2D+EM+NS+SS+TF-TuM10, 9; TF+2D+MG+NS-MoA5, 6  
 Ghosh, R.: 2D-ThP5, 23  
 Giamini, S.A.:  
 2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 18  
 Giugliano, M.: 2D+EM+NS+SS+TF-TuM2, 8

- Goldberger, J.: 2D+EM+NS+PS+SP+SS+TF-MoM10, **2**
- Göhlhäuser, A.: 2D+MN+NS+SP+SS+TF-WeM13, **12**
- Gomez, M.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA4, **10**
- Gonzales, J.M.: 2D+EM+IS+MC+NS+SP+SS-WeA1, **14**; 2D+MN+NS+SP+SS+TF-WeM1, **11**
- Goovaerts, E.: 2D+EM+NS+SS+TF-TuM2, **8**
- Greber, T.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, **19**
- Greg Hearn, G.: 2D+EM+NS+SS+TF-TuM6, **8**
- Gu, F.: 2D+EM+IS+MC+NS+SP+SS-WeA11, **15**
- Gu, G.: SP+2D+AS+NS+SS-WeA7, **16**
- Gudmundsson, J.T.: PS+2D+SE-WeM10, **13**
- Gunlycke, D.: 2D+EM+NS+SS+TF-TuM1, **8**
- Gupta, A.: 2D+EM+IS+NS+PS+SP+SS-FrM8, **26**
- **H** —
- Hammer, R.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, **19**
- Harker, M.: 2D+MN+NS+SP+SS+TF-WeM4, **11**
- Hearn, G.: 2D+EM+NS+SS+TF-TuM11, **9**
- Heinrich, A.: SP+2D+AS+NS+SS-WeA9, **17**
- Hernandez, S.: PS+2D-ThM10, **20**
- Hernández, S.C.: 2D+EM+IS+NS+PS+SP+SS-FrM1, **25**; 2D+EM+NS+PS+SP+SS+TF-MoM1, **1**
- Hersam, M.C.: 2D+EM+MC+MS+NS-MoA9, **4**; 2D+MN+NS+SP+SS+TF-WeM12, **12**
- Hight Walker, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, **2**
- Hihath, J.: 2D-ThP11, **24**
- Hinkle, C.L.: 2D+EM+IS+MC+NS+SP+SS-WeA8, **14**; PS+2D+SE-WeM12, **13**
- Hite, J.K.: 2D+EM+NS+PS+SP+SS+TF-MoM1, **1**; 2D+EM+NS+PS+SP+SS+TF-MoM3, **1**; TF+2D+MG+NS-MoA5, **6**
- Holleitner, A.W.: 2D+EM+NS+SS+TF-TuM11, **9**
- Howe, J.Y.: 2D-ThP11, **24**
- Hu, J.: PS+2D+SE-WeM11, **13**
- Hu, L.: 2D+EM+IS+MC+NS+SP+SS-WeA11, **15**
- Huang, C.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **18**
- Hunold, O.: PS+2D+SE-WeM13, **13**
- Hus, S.: SP+2D+AS+NS+SS-WeA3, **16**
- **I** —
- Iannaccone, G.: 2D+EM+MC+MS+NS-MoA6, **4**
- Ichikawa, A.: 2D+EM+IS+MC+NS+SP+SS-WeA12, **15**
- Isarraraz, M.: 2D+EM+MC+MS+NS-MoA10, **4**; 2D-ThP1, **23**
- **J** —
- Jacobberger, R.M.: 2D+EM+IS+NS+PS+SP+SS-FrM10, **26**
- Jariwala, D.: 2D+EM+MC+MS+NS-MoA9, **4**
- Jasiuk, I.: MG+2D+MI+NS+TF-MoA5, **5**
- Jena, D.: 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
- Jin, W.: 2D+EM+MG+NS+SS+TF-ThA2, **21**
- Johnson, E.V.: PS+2D-ThM1, **19**; TF+2D+MG+NS-MoA10, **7**
- Jung, M.: SP+2D+AS+NS+SS-WeA8, **16**
- Junkermeier, C.: PS+2D-ThM10, **20**
- Jur, J.S.: TF+2D+MG+NS-MoA1, **5**
- **K** —
- Kalanyan, B.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
- Karim, A.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA7, **10**
- Kelaidis, N.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM5, **18**
- Kelber, A.: 2D+EM+MG+NS+SS+TF-ThA6, **21**
- Kelly, M.W.: PS+2D+SE-WeM3, **12**
- Kim, H.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA11, **10**
- Kim, J.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **18**; 2D+EM+MG+NS+SS+TF-ThA7, **21**
- Kim, M.J.: PS+2D+SE-WeM12, **13**
- Kim, T.H.: SP+2D+AS+NS+SS-WeA12, **17**
- Kim, T.-H.: SP+2D+AS+NS+SS-WeA4, **16**
- Kimes, W.A.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
- Kis, A.: 2D+EM+IS+MC+NS+SP+SS-WeA2, **14**; 2D+EM+MG+NS+SE+SM+SS+TF-ThM11, **19**
- Klee, V.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **18**; 2D-ThP2, **23**; 2D-ThP6, **23**
- Koehler, A.D.: TF+2D+MG+NS-MoA5, **6**
- Kolmakov, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, **2**
- Komesu, T.: 2D-ThP1, **23**
- Kondo, T.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **25**
- Kosaka, Y.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **25**
- Kratzer, M.C.: PS+2D-ThM3, **20**
- Krenner, H.: 2D+EM+MC+MS+NS-MoA10, **4**
- Kubota, L.T.: 2D-ThP8, **23**
- Kuk, Y.: SP+2D+AS+NS+SS-WeA1, **16**
- Kummel, A.C.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**; 2D+EM+MG+NS+SS+TF-ThA1, **21**
- Kwak, I.J.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**; 2D+EM+MG+NS+SS+TF-ThA1, **21**
- **L** —
- Lagally, M.G.: 2D+EM+IS+NS+PS+SP+SS-FrM10, **26**
- Lauhon, L.: 2D+EM+MC+MS+NS-MoA9, **4**
- Le, D.: 2D+EM+IS+NS+PS+SP+SS-FrM9, **26**; 2D-ThP1, **23**
- Lee, C.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **18**
- Lee, K.: SP+2D+AS+NS+SS-WeA8, **16**
- Lee, S.-H.: SP+2D+AS+NS+SS-WeA4, **16**
- Lee, W.K.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA3, **10**; PS+2D-ThM10, **20**
- Leite, M.: 2D+EM+NS+PS+SP+SS+TF-MoM8, **2**
- LeRoy, B.J.: SP+2D+AS+NS+SS-WeA10, **17**
- Li, A.-P.: 2D+EM+IS+MC+NS+SP+SS-WeA9, **15**; SP+2D+AS+NS+SS-WeA12, **17**; SP+2D+AS+NS+SS-WeA3, **16**; SP+2D+AS+NS+SS-WeA7, **16**
- Li, Y.: 2D+EM+MC+MS+NS-MoA3, **4**
- Liao, I.: 2D-ThP6, **23**
- Lin, Y.-C.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM6, **18**; 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
- Linford, M.R.: MG+2D+MI+NS+TF-MoA6, **5**
- Liu, H.: 2D+EM+IS+NS+PS+SP+SS-FrM5, **25**
- Liu, L.: SP+2D+AS+NS+SS-WeA7, **16**
- Liu, X.: 2D+EM+MC+MS+NS-MoA9, **4**; 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**; 2D+MN+NS+SP+SS+TF-WeM12, **12**
- López Sánchez, O.: 2D+EM+MC+MS+NS-MoA6, **4**
- Lopez-Sanchez, O.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM11, **19**
- Lu, I.: 2D+EM+MC+MS+NS-MoA10, **4**; 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **18**; 2D-ThP2, **23**; 2D-ThP6, **23**
- Lu, N.: PS+2D+SE-WeM12, **13**
- Luna-López, J.A.: TF+2D+MG+NS-MoA7, **6**
- Lundin, D.: PS+2D+SE-WeM10, **13**
- Lutz, C.P.: SP+2D+AS+NS+SS-WeA9, **17**
- **M** —
- Ma, C.: SP+2D+AS+NS+SS-WeA7, **16**
- Mankelevich, Y.A.: PS+2D+SE-WeM3, **12**
- Marinov, D.: PS+2D-ThM1, **19**
- Marinov, K.M.: 2D+EM+IS+MC+NS+SP+SS-WeA2, **14**
- Marks, T.J.: 2D+EM+MC+MS+NS-MoA9, **4**
- Marquez-Velasco, J.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM5, **18**
- Martinez, J.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA4, **10**
- Martinez-Ta, D.: 2D-ThP6, **23**
- Maslar, J.E.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
- Mastro, M.A.: TF+2D+MG+NS-MoA5, **6**
- Matsuyama, H.: 2D+EM+IS+MC+NS+SP+SS-WeA12, **15**
- Maurice, J.L.: TF+2D+MG+NS-MoA10, **7**
- McCold, C.E.: 2D-ThP11, **24**
- McDonnell, S.: 2D+EM+IS+MC+NS+SP+SS-WeA8, **14**; 2D+EM+MG+NS+SS+TF-ThA7, **21**
- McGuire, M.: SP+2D+AS+NS+SS-WeA3, **16**
- Meinel, K.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM12, **19**
- Melendez-Lira, M.: 2D-ThP7, **23**
- Mende, P.: 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
- Miller, B.: 2D+EM+NS+SS+TF-TuM11, **9**
- Minea, T.: PS+2D+SE-WeM10, **13**
- Monfil-Leyva, K.: TF+2D+MG+NS-MoA7, **6**
- Movva, H.C.P.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**; 2D+EM+MG+NS+SS+TF-ThA1, **21**
- Mowll, T.R.: 2D+EM+NS+PS+SP+SS+TF-MoM2, **1**
- Mueller, T.: 2D+EM+NS+SS+TF-TuM3, **8**
- Muñoz-Zurita, A.L.: TF+2D+MG+NS-MoA7, **6**
- Muratore, C.: PS+2D+SE-WeM11, **13**
- Music, D.: PS+2D+SE-WeM13, **13**
- Myers-Ward, R.L.: 2D+EM+NS+SS+TF-TuM10, **9**; TF+2D+MG+NS-MoA5, **6**
- **N** —
- Naghibi, S.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, **18**; 2D-ThP6, **23**
- Naguib, M.: 2D+EM+MG+NS+SE+SM+SS+TF-ThM3, **18**
- Nakamura, J.: 2D+EM+IS+MC+NS+SP+SS-WeA12, **15**;

- 2D+EM+IS+NS+PS+SP+SS-FrM7, 25;  
2D+MN+NS+SP+SS+TF-WeM11, 11
- Nath, A.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1; TF+2D+MG+NS-MoA5, 6
- Natterer, F.D.: 2D+MN+NS+SP+SS+TF-WeM10, **11**
- Neek-Amal, M.: 2D+MN+NS+SP+SS+TF-WeM3, 11
- Nepal, N.: TF+2D+MG+NS-MoA5, 6
- Nesladek, M.: 2D+EM+NS+SS+TF-TuM2, 8
- Nguyen, A.: 2D+EM+MC+MS+NS-MoA10, 4; 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 18; 2D-ThP2, **23**; 2D-ThP6, 23
- Nichols, B.: 2D-ThP5, **23**
- Nyakiti, L.O.: 2D+EM+NS+PS+SP+SS+TF-MoM3, 1
- **O** —
- Ojeda-Durán, E.: TF+2D+MG+NS-MoA7, 6
- Olanipekun, B.: 2D+EM+MG+NS+SS+TF-ThA6, 21
- Oleynik, I.I.: 2D+EM+IS+MC+NS+SP+SS-WeA1, 14; 2D+MN+NS+SP+SS+TF-WeM1, 11
- Ong, E.W.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- Ooki, W.: 2D+EM+IS+NS+PS+SP+SS-FrM7, 25
- Orzali, T.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Osgood, Jr., R.M.:  
2D+EM+MG+NS+SS+TF-ThA2, 21
- Ovchinnikov, D.:  
2D+EM+IS+MC+NS+SP+SS-WeA2, 14
- **P** —
- Park, J.: SP+2D+AS+NS+SS-WeA7, 16;  
SP+2D+AS+NS+SS-WeA8, 16
- Park, J.H.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 14; 2D+EM+MG+NS+SS+TF-ThA1, **21**
- Parzinger, E.: 2D+EM+NS+SS+TF-TuM11, 9
- Pascon, A.M.: 2D-ThP8, **23**
- Paul, W.: SP+2D+AS+NS+SS-WeA9, **17**
- Peeters, F.: 2D+MN+NS+SP+SS+TF-WeM3, 11
- Perez-Barragan, D.E.: 2D-ThP7, 23
- Perriot, R.: 2D+EM+IS+MC+NS+SP+SS-WeA1, 14; 2D+MN+NS+SP+SS+TF-WeM1, 11
- Persson, P.O.A.: PS+2D+SE-WeM13, 13
- Pham, C.: TF+2D+MG+NS-MoA9, 6
- Pintauro, P.: TF+2D+MG+NS-MoA5, 6
- Piotrowicz, P.: PS+2D+SE-WeM2, 12
- Preciado, E.: 2D+EM+MC+MS+NS-MoA10, **4**;  
2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 18; 2D-ThP1, 23; 2D-ThP2, 23;  
2D-ThP6, 23
- **Q** —
- Qin, S.: SP+2D+AS+NS+SS-WeA12, **17**
- Qin, X.: 2D+EM+MG+NS+SS+TF-ThA7, 21; PS+2D+SE-WeM12, 13
- **R** —
- Rahman, T.S.: 2D+EM+IS+NS+PS+SP+SS-FrM9, 26; 2D+EM+NS+SS+TF-TuM5, 8; 2D-ThP1, 23
- Ramprasad, R.: MG+2D+MI+NS+TF-MoA3, **5**
- Rawal, T.B.: 2D+EM+IS+NS+PS+SP+SS-FrM9, **26**
- Reed, E.J.: 2D+EM+IS+NS+PS+SP+SS-FrM2, 25; 2D+EM+MC+MS+NS-MoA3, 4
- Regev, O.: 2D-ThP4, 23
- Reid, S.: 2D+EM+MG+NS+SS+TF-ThA6, 21
- Reinecke, T.L.:  
2D+EM+IS+NS+PS+SP+SS-FrM1, 25;  
PS+2D-ThM10, 20
- Renault, O.J.:  
2D+EM+MC+MI+NS+SP+SS+TF-TuA11, **10**
- Robertson, J.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 14
- Robinson, J.A.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 18; 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Robinson, J.T.:  
2D+EM+IS+NS+PS+SP+SS-FrM1, 25;  
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 10; PS+2D-ThM10, 20
- Robinson, Z.R.:  
2D+EM+NS+PS+SP+SS+TF-MoM1, 1;  
2D+EM+NS+PS+SP+SS+TF-MoM2, 1;  
TF+2D+MG+NS-MoA5, 6
- Rojas Delgado, R.:  
2D+EM+IS+NS+PS+SP+SS-FrM10, **26**
- Romming, N.: SP+2D+AS+NS+SS-WeA9, 17
- Rowley, J.T.: 2D+MN+NS+SP+SS+TF-WeM4, **11**
- Ruan, W.Y.: 2D+MN+NS+SP+SS+TF-WeM10, 11
- Ruzic, D.N.: MG+2D+MI+NS+TF-MoA5, 5;  
PS+2D+SE-WeM2, 12
- **S** —
- Safriet, A.: PS+2D+SE-WeM11, 13
- Sanchez Perez, J.R.:  
2D+EM+IS+NS+PS+SP+SS-FrM10, 26
- Sangwan, V.: 2D+EM+MC+MS+NS-MoA9, 4
- Sanne, A.M.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 14
- Satpathy, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Schneider, J.M.: PS+2D+SE-WeM13, 13
- Schroeder, D.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 26
- Schüle, F.J.R.: 2D+EM+MC+MS+NS-MoA10, 4
- Seabough, A.C.: 2D+EM+MG+NS+SS+TF-ThA1, 21
- Seal, S.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 26
- Self, E.: TF+2D+MG+NS-MoA5, 6
- Selvan, T.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 26
- Shchelkanov, I.A.: MG+2D+MI+NS+TF-MoA5, **5**
- Sheehan, P.E.: 2D+EM+IS+NS+PS+SP+SS-FrM1, **25**;  
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 10; PS+2D-ThM10, 20
- Shehelkanov, I.A.: PS+2D+SE-WeM2, 12
- Shih, C.K.: SP+2D+AS+NS+SS-WeA12, 17
- Shin, H.-J.: SP+2D+AS+NS+SS-WeA8, **16**
- Shishatskiy, S.: 2D+MN+NS+SP+SS+TF-WeM13, 12
- Shown, I.: PS+2D-ThM4, **20**
- Shtein, M.: 2D-ThP4, **23**
- Shumlas, S.L.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 18
- Silva, C.C.: 2D-ThP8, 23
- Simmons, J.G.: TF+2D+MG+NS-MoA1, 5
- Simsek, E.: 2D+EM+NS+SS+TF-TuM1, 8
- Singam, S.K.R.: 2D+EM+NS+SS+TF-TuM2, 8
- Singh, B.: MG+2D+MI+NS+TF-MoA6, 5
- Sivapragasam, N.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM10, **19**
- Smyth, C.M.: 2D+EM+IS+MC+NS+SP+SS-WeA8, **14**
- Sohn, S.-D.: SP+2D+AS+NS+SS-WeA8, 16
- Soukiasian, G.:  
2D+EM+IS+NS+PS+SP+SS-FrM3, **25**
- Souza, J.F.: 2D-ThP8, 23
- Sperling, B.A.:  
2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Sridhara, K.: 2D+EM+NS+PS+SP+SS+TF-MoM1, 1
- Sridhara, K.S.: 2D+EM+NS+PS+SP+SS+TF-MoM3, **1**
- Stafford, L.: PS+2D-ThM11, **20**
- Stiff-Roberts, A.D.: TF+2D+MG+NS-MoA2, **5**
- Stine, R.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 25
- Stolbov, S.: 2D+EM+IS+NS+PS+SP+SS-FrM6, **25**
- Stranick, S.J.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Strongin, D.R.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 18
- Stroschio, J.A.: 2D+MN+NS+SP+SS+TF-WeM10, 11
- Sun, D.: 2D-ThP2, 23
- Sutter, P.W.: 2D+EM+MG+NS+SS+TF-ThA3, **21**
- Suzer, S.: 2D+EM+MC+MS+NS-MoA4, **4**
- **T** —
- Tanabe, I.: 2D-ThP1, **23**
- Teichert, C.K.: PS+2D-ThM3, **20**
- Thenuwara, A.C.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM2, 18
- Thibado, P.: 2D+MN+NS+SP+SS+TF-WeM3, **11**
- Thiesen, P.H.: 2D+EM+NS+SS+TF-TuM11, **9**; 2D+EM+NS+SS+TF-TuM6, 8
- Tieckelmann, R.:  
2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Trautmann, M.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 19
- Truscott, B.S.: PS+2D+SE-WeM3, 12
- Tseng, F.: 2D+EM+NS+SS+TF-TuM1, 8
- Tsipas, P.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 18
- Tsoi, S.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 25; PS+2D-ThM10, 20
- Tsoutsou, D.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 18
- Turkowski, V.: 2D+EM+NS+SS+TF-TuM5, **8**
- Tyagi, P.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- **U** —
- Uchida, Y.: 2D+MN+NS+SP+SS+TF-WeM11, **11**
- **V** —
- Valentin, M.:  
2D+EM+MC+MI+NS+SP+SS+TF-TuA4, 10
- van der Zande, A.M.:  
2D+EM+NS+PS+SP+SS+TF-MoM5, **2**
- Vanfleet, R.: 2D+MN+NS+SP+SS+TF-WeM4, 11
- Ventrice, Jr., C.A.:  
2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- Vernisse, L.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM2, **18**
- Vishwanath, S.:  
2D+EM+IS+MC+NS+SP+SS-WeA7, 14;  
2D+EM+MG+NS+SS+TF-ThA1, 21;  
2D+EM+NS+PS+SP+SS+TF-MoM9, 2

- Vlassiounk, I.: SP+2D+AS+NS+SS-WeA3, 16  
Voevodin, A.A.: PS+2D+SE-WeM11, **13**  
Voiry, D.:  
2D+EM+MC+MI+NS+SP+SS+TF-TuA11, 10  
von Son, G.: 2D+EM+MC+MS+NS-MoA10, 4; 2D+EM+MG+NS+SE+SM+SS+TF-ThM1, 18; 2D-ThP6, 23  
— **W** —  
Waite, A.R.: PS+2D+SE-WeM11, 13  
Wallace, R.M.:  
2D+EM+IS+MC+NS+SP+SS-WeA8, 14;  
2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 18; 2D+EM+MG+NS+SS+TF-ThA7, 21; PS+2D+SE-WeM12, 13  
Walton, S.G.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 25; PS+2D-ThM10, 20  
Wan, J.: 2D+EM+IS+MC+NS+SP+SS-WeA11, **15**  
Wang, F.:  
2D+EM+MC+MI+NS+SP+SS+TF-TuA9, **10**  
Wang, J.K.: TF+2D+MG+NS-MoA10, 7  
Wang, Q.: PS+2D+SE-WeM12, 13  
Wang, Z.: 2D+MN+NS+SP+SS+TF-WeM5, **11**  
Weitering, H.H.: SP+2D+AS+NS+SS-WeA12, 17  
Wells, S.: 2D+EM+MC+MS+NS-MoA9, 4  
Wheeler, V.D.:  
2D+EM+NS+PS+SP+SS+TF-MoM1, 1;  
TF+2D+MG+NS-MoA5, **6**  
Whitener, K.E.:  
2D+EM+IS+NS+PS+SP+SS-FrM1, 25;  
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 10; PS+2D-ThM10, 20  
Whitwick, M.B.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM11, 19  
Widdra, W.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM12, 19  
Willman, J.T.:  
2D+EM+IS+MC+NS+SP+SS-WeA1, **14**  
Wind, J.: 2D+MN+NS+SP+SS+TF-WeM13, 12  
Wixforth, A.: 2D+EM+MC+MS+NS-MoA10, 4  
Wood, J.D.: 2D+EM+MC+MS+NS-MoA9, 4; 2D+MN+NS+SP+SS+TF-WeM12, 12  
Wu, R.: SP+2D+AS+NS+SS-WeA12, 17  
Wu, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2  
Wu, Y.L.: PS+2D+SE-WeM2, **12**  
Wurstbauer, U.: 2D+EM+NS+SS+TF-TuM11, 9  
Wyrick, J.: 2D+MN+NS+SP+SS+TF-WeM10, 11  
— **X** —  
Xenogiannopoulou, E.:  
2D+EM+MG+NS+SE+SM+SS+TF-ThM5, 18  
Xing, H.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 14; 2D+EM+MG+NS+SS+TF-ThA1, 21; 2D+EM+NS+PS+SP+SS+TF-MoM9, 2  
Xu, X.D.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2  
— **Y** —  
Yang, K.: SP+2D+AS+NS+SS-WeA9, 17  
Yang, Y.: 2D+MN+NS+SP+SS+TF-WeM13, 12; PS+2D+SE-WeM5, **13**  
Yazyev, O.V.:  
2D+EM+IS+MC+NS+SP+SS-WeA3, **14**  
Ye, P.D.: 2D+EM+MC+MS+NS-MoA7, **4**;  
2D+EM+MG+NS+SS+TF-ThA7, 21  
Yeh, P.: 2D+EM+MG+NS+SS+TF-ThA2, 21  
Yeom, H.W.: SP+2D+AS+NS+SS-WeA4, 16  
Yin, X.: 2D+EM+NS+SS+TF-TuM12, **9**  
Young, A.F.:  
2D+EM+MC+MI+NS+SP+SS+TF-TuA1, **10**  
Yulaev, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, **2**  
— **Z** —  
Zaki, N.: 2D+EM+MG+NS+SS+TF-ThA2, **21**  
Zelaya-Angel, O.: 2D-ThP7, **23**  
Zhang, X.: 2D+MN+NS+SP+SS+TF-WeM13, 12; SP+2D+AS+NS+SS-WeA3, 16  
Zhang, X.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **25**  
Zhang, Y.: SP+2D+AS+NS+SS-WeA12, 17  
Zhao, Y.: 2D+MN+NS+SP+SS+TF-WeM10, 11  
Zhitenev, N.B.: 2D+MN+NS+SP+SS+TF-WeM10, 11  
Zhou, X.: PS+2D+SE-WeM5, 13  
Zhou, Y.: 2D+EM+IS+NS+PS+SP+SS-FrM2, **25**; 2D+EM+MG+NS+SS+TF-ThA9, **22**  
Zhu, H.: 2D+EM+IS+MC+NS+SP+SS-WeA8, 14;  
2D+EM+MG+NS+SE+SM+SS+TF-ThM6, 18; 2D+EM+MG+NS+SS+TF-ThA7, **21**