

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 nm. It was shown that the lower-energy $A_{2u}(\text{LO})1$ sub-band around 819 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 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 MoS₂.** 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 (MoS₂) have been demonstrated by chemical vapor deposition (CVD) on polycrystalline catalytic copper substrates. These Cu foil substrates (25 μm 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 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°C for 5 hrs under H₂ 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 MoS₂. 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 O₂ bubbling at random nucleation sites on Cu surface, are mitigated by using additives, such as acetic acid and ethylene glycol, in the H₃PO₄ 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., MoS₂, 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 MoS₂ 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 (FR-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 MoS₂ films have been prepared from (η^5 -ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum and elemental sulfur. As-grown films are smooth and continuous with major MoS₂ 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 Yulav*, 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 cleanness 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 (μ LEED) of local crystal orientation at length scales down to ~1 μ 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: MoS₂ prepared by exfoliation (onto Si), MoSe₂ grown by molecular beam epitaxy (MBE) (on epitaxial graphene), and WSe₂ 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 μ m, the MBE-grown MoSe₂ forms a nearly continuous film, and the CVD-grown WSe₂ forms triangular islands several mm in extent. μ LEED studies of the MBE-grown MoSe₂ and CVD-grown WSe₂ 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 WSe₂ 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 CaGe₂. 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 CaGe₂ 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

Nanometer-scale Science and Technology
Room: 212B - Session NS+AS+SP-MoA

Optical Spectroscopy at the Nanoscale

Moderator: Craig Prater, Anasys Instruments

2:20pm **NS+AS+SP-MoA1 Nanoscale Infrared Spectroscopy Characterization of Amyloid Aggregates Structure**, *Francesco Simone Ruggeri*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *T. Muller*, University of Cambridge, UK, *D. Galante*, CNR, Italy, *T.P.J. Knowles*, University of Cambridge, UK, *H. Lashuel*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *C. D'Arrigo*, CNR, Italy, *G. Dieterl*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
INVITED

Aging of world population has increased the onset of several neurodegenerative disorders (ND). These diseases are connected with insoluble fibrillar proteins aggregates, termed Amyloid. During their aggregation, starting monomeric proteins undergo internal structural rearrangement bringing to fibrils with a final universal cross β -sheet quaternary structure. This structure is independent by the monomeric initial one and it is the fingerprint of amyloid and related diseases. Previously, the final fibrillar cross- β sheet structures were considered the cause of the illnesses. Nowadays, there is strong evidence that the intermediate oligomeric stages of fibrillation could be the cytotoxic one and most of the research groups are investigating the early stages of fibrillation and the inter-conversion of monomers into fibrils. Infrared spectroscopy is a key method for studying conformational properties of proteins and their structural conversion during amyloid fibrillation. Unfortunately, this and others bulk techniques are just able to give average information of the heterogeneous aggregating amyloid solution. To study the chemical structure of amyloid species at the nanoscale, we utilized a thermomechanical detection technique based on atomic force microscopy (nanoIR). If an IR pulse is absorbed by a sample, the local temperature rises and leads to a local thermal expansion. This deformation excites mechanical resonances of the AFM cantilever, in contact with the sample, allowing simultaneously acquiring topography, nanoscale chemical IR maps and/or spectra. We focused on the study of different amyloidogenic proteins, as α -synuclein, lysozyme and $\alpha\beta$ 2. We measured chemical spectra and IR maps of monomeric and fibrillar aggregates. For the first time, we distinguished chemically different amyloid structures at the single aggregate nanometer scale. Nanoscale chemical characterization of amyloidogenic structures as oligomers, protofibrils and fibrils is central to understand how proteins misfold and aggregate, to unravel the structural rearrangement of monomers inside amyloid fibrils and to target pharmacological approach to ND.

3:00pm **NS+AS+SP-MoA3 Recent Progress in Tip-Enhanced Mid-Infrared Photoexpansion Nanospectroscopy**, *M. Jin*, *F. Lu*, *Mikhail Belkin*, The University of Texas at Austin
INVITED

Mid-infrared absorption spectroscopy in the molecular fingerprint region ($1/\lambda \sim 600\text{--}4000\text{ cm}^{-1}$) is widely used for chemical identification and quantitative analysis. The ability to perform mid-infrared spectroscopy with nanometer spatial resolution is highly desired for applications in chemical, materials, and life sciences. Nanoscale mid-infrared spectra can be obtained by detecting mechanical forces exerted by sample on an atomic force microscope (AFM) tip upon sample light absorption and photoexpansion. The first demonstration that photoexpansion of bulk polymers can be detected by AFM and used for mid-infrared nanospectroscopy was by Alexander Dazzi and co-workers [1]. However, only relatively thick polymer samples (approximately 50-nm-thick or thicker) produced detectable cantilever deflections in these experiments, even when mid-infrared optical intensity was close to sample damage. We demonstrated that the sensitivity of mid-infrared photoexpansion nanospectroscopy, also known as AFM-IR, may be improved by several orders of magnitude if we send low-power laser pulses at a repetition frequency that is tuned in resonance with the mechanical vibrational frequency of an AFM cantilever and if we further employ tip-enhancement of the optical field below a sharp gold-coated AFM tip. As a result, monolayer sensitivity and 25 nanometer spatial resolution was achieved for molecular imaging in air [2]. We will discuss details of these experiments and recent progress of this technique, including development of background suppression methods that may lead to further enhancement in sensitivity and progress towards achieving photoexpansion nanospectroscopy of samples in aqueous environment that requires mitigation of liquid damping of cantilever vibration and strong infrared absorption.

[1] A. Dazzi, R. Prazeres, F. Glotin and J.M. Ortega, Opt. Lett. 30, 2388 (2005).

[2] F. Lu, M. Jin and M.A. Belkin, Nature Photonics 8, 307 (2014).

3:40pm **NS+AS+SP-MoA5 Nano-photonic Phenomena in van der Waals Heterostructures**, *Dmitri Basov*, University of California San Diego
INVITED

Layered van der Waals (vdW) crystals consist of individual atomic planes weakly coupled by vdW interaction, similar to graphene monolayers in bulk graphite. These materials can harbor superconductivity and ferromagnetism with high transition temperatures, emit light and exhibit topologically protected surface states. An ambitious practical goal is to exploit atomic planes of vdW crystals as building blocks of more complex artificially stacked heterostructures where each such block will deliver layer-specific attributes for the purpose of their combined functionality. We investigated van der Waals heterostructures assembled from atomically thin layers of graphene and hexagonal boron nitride (Hbn). We observed a rich variety of optical effects due to surface plasmons in graphene and hyperbolic phonon polaritons in Hbn. We launched, detected and imaged plasmonic, phonon polaritonic and hybrid plasmon-phonon polariton waves in a setting of an antenna based nano-infrared apparatus. Peculiar properties of hyperbolic phonon polaritons in Hbn enabled sub-diffractive focusing in infrared frequencies. Because electronic, plasmonic and phonon polaritonic properties in van der Waals heterostructures are intertwined, gate voltage and/or details of layer assembly enable efficient control of nano-photonic effects. I will also discuss an ability to manipulate plasmonic response of in these structures at femto second time scales that we have demonstrated using a novel technique of pump-probe nano-infrared spectroscopy.

4:20pm **NS+AS+SP-MoA7 Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy and Fluorescence of a Self-Assembled Porphyrin Monolayer**, *Naihao Chiang**, *N. Jiang*, Northwestern University, *D. Chulhai*, Pennsylvania State University, *E. Pozzi*, *M.C. Hersam*, Northwestern University, *L. Jensen*, Pennsylvania State University, *T. Seideman*, *R.P. Van Duyne*, Northwestern University

The study of ultrahigh vacuum tip-enhanced Raman and fluorescence spectroscopy (UHV-TERS/TEF) has been raised to an unprecedented level. UHV-TER and TEF spectra for a self-assembled meso-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) on Ag(111) have been observed with five different laser excitations in the Q-band region. The observed TERS spectra are complemented by the time-dependent density functional theory (TDDFT) simulations. Chemical information of different vibronic excited states is revealed. The observed TEF spectra suggest a weak coupling of H_2TBPP to the surface due to the t-butyl groups. Therefore, the strong tip-enhancement is sufficient to overcome the quenching effect of the metal substrate. This study demonstrates the potential of combining TERS and TEF for studying surface-mounted porphyrins, thus setting the stage for future investigation into porphyrin-based photovoltaics and photocatalysis.

4:40pm **NS+AS+SP-MoA8 Nano-Optical Spectroscopic Imaging of Monolayer MoS_2** , *Wei Bao**, UC Berkeley, *N. Borys*, Lawrence Berkeley National Lab, *C. Ko*, *J. Suh*, *W. Fan*, UC Berkeley, *A. Thron*, Lawrence Berkeley National Lab, *Y. Zhang*, *A. Buyanin*, UC Berkeley, *J. Zhang*, *S. Cabrini*, *P. Ashby*, *A. Weber-Bargioni*, Lawrence Berkeley National Lab, *S. Tongay*, Arizona State University, *S. Aloni*, *D. Ogletree*, Lawrence Berkeley National Lab, *J. Wu*, UC Berkeley, *M.B. Salmeron*, Lawrence Berkeley Lab, UC Berkeley, *P. Schuck*, Lawrence Berkeley National Lab

With their remarkable electrical and optical properties, two dimensional (2D) monolayer transition metal dichalcogenide (ML-TMDC) semiconductors are ideal building blocks for atomically thin, flexible optoelectronic devices. Yet their performance falls far below theoretical expectations, particularly for critical factors such as carrier mobility and quantum yield. Overcoming these problems requires a fundamental understanding of the optoelectronic properties of these materials at the nanoscale, which is best obtained with optical microscopy and spectroscopy tools with spatial resolution below the diffraction limit. Here, we use the recently-developed "Campanile" nano-optical probe to spectroscopically image for the first time key optoelectronic properties in ML- MoS_2 with deeply sub-wavelength resolution – i.e., at a resolution commensurate with characteristic distances such as the exciton diffusion length. We find that synthetic ML- MoS_2 is composed of two distinct optoelectronic regions: a locally-ordered but mesoscopically heterogeneous interior, where photoluminescence (PL) intensity correlates with the local ratio of the exciton and trion populations, and an unexpected edge region ~ 300 nm wide

* NSTD Student Award Finalist

of energetically disordered states. In addition, we directly visualize the spatially-varying optical properties of inter- and intra- flake grain boundaries and quantify the characteristic length over which they quench excitons. Complimentary Nano-Auger elemental analysis reveals that the optically “defective” grain boundary and edge regions are sulfur-deficient. The nanoscale structure-property relationships established here have broad implications for the development of atomically thin transistors, quantum optical components, photodetectors and light-emitting devices based on high-quality ML-TMDCs.

1 Bao, W. Mapping local charge recombination heterogeneity by multidimensional nanospectroscopic imaging. , 1317-1321 (2012).

5:00pm **NS+AS+SP-MoA9 Hybrid Peak-force Tapping/near-field s-SNOM Microscope for Nano-chemical and Nano-mechanical Imaging of Proteins and Other Nanoscale Systems**, *Martin Wagner*, Bruker Nano Surfaces, *K. Carneiro*, *S. Habelitz*, University of California, *T. Mueller*, Bruker Nano Surfaces

Infrared spectroscopy can give valuable information on chemical composition, but far-field techniques such as FTIR spectroscopy are limited in spatial resolution. S-SNOM is a well-established near-field technique [1] that can overcome this diffraction limit, allowing an improvement in spatial resolution down to 10 nm.

Our s-SNOM instrument is based on an atomic force microscope whose tip is illuminated with a quantum cascade laser. Field-resolved detection of the scattered light measures absorption [2]. We have combined the instrument with peak-force tapping, a technique that allows Pn-level force control between tip and sample. Besides being able to image fragile material systems, one can extract valuable nano-mechanical information such as adhesion or modulus with molecular resolution [3].

Here, amongst other brief examples, we study an amelogenin sample. Amelogenin is a protein that is critical to dental enamel formation [4,5]. In the presence of calcium and phosphate ions it self-assembles into ordered, self-aligned nanoribbon bundles. Since the ordering is similar to the one observed in phosphate-based apatite crystals that comprise dental enamel, it is likely that the bundles form a template for these crystals. To help clarify that open question, we map the distributions of phosphate and hydroxyapatite nanocrystals within the bundles consisting of <30 nm narrow nanoribbons that have only a height of a few nm down to 1nm.

We present correlated topography, near-field and nano-mechanical data. While the presence of phosphate could be identified using s-SNOM absorption maps, no apatite nanocrystals with higher modulus than the ribbons were observed in peak-force tapping. This indicates that for these in vitro preparation conditions apatite crystals have not formed yet, but also highlights the high chemical sensitivity of the instrument.

In summary, using a novel combination of near-field imaging and peak-force tapping we study the phosphate distribution and crystallization in protein samples. Our findings help to understand the formation processes of dental enamel and the role of amelogenin protein.

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[3] F. Rico, C. Su, S. Scheuring, Nano Lett. 11, 3983 (2011)

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[5] B. Sani et al., J Dent Res 93 (9), 918 (2014)

Tuesday Morning, October 20, 2015

Nanometer-scale Science and Technology

Room: 212B - Session NS+SP-TuM

Nanoscale Imaging and Materials Characterization

Moderator: Mehmet Z. Baykara, Bilkent University

8:00am **NS+SP-TuM1 Influence of Focused Electron Beam on Electrical Characterization of Advanced MOSFETs**, *Jonghyuk Kang, S.H. Lee*, Samsung Electronics Co., LTD., South Korea, *B.D. Choi*, Sungkyunkwan University, Republic of Korea

The focused electron beam based inspection instruments such as Scanning Electron Microscope (SEM) have become widespread in the semiconductor manufacturing and failure analysis of scaled devices. Also, nano-probing systems with SEM guidance have become important in the failure analysis area to evaluate the localized device in the actual LSI [1]. However, electron beam leads to device degradation [2] and its damage are increasing with the scaling. As CMOS scaling is going to be sub-10nm regime [3], electron beam damages are becoming critical issue in performing electrical characterization at the contact level in integrated devices using nano-probe technique. To avoid the electron damage, the acceleration voltage should be lower. However, the lower acceleration voltage of electron beam leads to lower resolution of image created by SEM guidance.

In this work, we evaluated NMOS FinFET in SRAM cells manufactured in a 10nm CMOS process with Atomic Force Microscopy (AFM) based nano-probing system. AFM based nano-probing system has no electron beam damage because it uses topography image created by AFM instead of SEM for guidance at contact level [4]. After deprocessing the samples to the contact level, we irradiated electron beams to samples to investigate a dependency of the device characteristics on electron beam acceleration voltage. Compared to a non-exposed reference transistor, the exposure of electron beam on the target transistor lead to significant changes on device characteristics such as saturation current (I_{DS}), sub-threshold voltage (V_{TH}) and sub-threshold swing (S). This might be due to trapped charges in the gate oxide and interface state [5]. Our studies show that it is critical to avoid electron beam exposure before electrical device characterizations are carried out at the contact level using nano-probe system since electron beam induced device parameter changes are not negligible in the failure analysis of sub-10nm devices.

References

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8:20am **NS+SP-TuM2 In Situ Synthesis and Characterization of Core-Shell Nanoparticle Arrays Using Dynamic Transmission Electron Microscopy**, *Joseph McKeown*, Lawrence Livermore National Laboratory, *Y. Wu*, University of Tennessee, *J.D. Fowlkes*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee, *G.H. Campbell*, Lawrence Livermore National Laboratory

Core-shell nanoparticles have attracted much attention due to their unique and tunable properties relative to bulk structures of the same materials, making them candidates for a variety of energy- and catalysis-related applications. Intriguing magnetic behavior can be tailored by variation of size, interface, crystal orientation, and composition, and core-shell nanoparticles with noble-metal shells yield novel optical responses and enhanced electrocatalytic activity. The immiscible Co-Cu alloy system is of particular interest, because it combines a strong magnet (Co) with an effective conductor (Cu) that also has a tunable plasmonic resonance. The ability to monitor and characterize these dewetting processes in situ while the system is evolving can potentially lead to increased control and directed self-assembly. However, in situ characterization of the dynamics of self-assembly processes has proven extremely challenging, particularly in materials systems that utilize metallic nanoparticles as the dynamics of

these processes evolve extremely fast over very small spatial scales. Here, we present a method to synthesize Co@Cu nanoparticles via pulsed-laser-induced dewetting of Co-Cu alloy thin films. We show that this technique effectively synthesizes Co@Cu core-shell particles with controllable sizes ranging from tens to several hundred nanometers. The assembly dynamics during pulsed-laser-induced dewetting of Co-Cu alloy films were revealed using the high spatiotemporal resolution of the dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory.

Work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering for FWP SCW0974 under Contract DE-AC52-07NA27344. Work at the University of Tennessee was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Research conducted at the Center for Nanophase Materials Sciences is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division of the U.S. Department of Energy, Office of Science, Office of Basic Energy Science.

8:40am **NS+SP-TuM3 Investigation of Nickel-assisted Growth of Silicon Carbide Nanowires**, *Lunet E. Luna, R. Maboudian, C. Carraro*, University of California at Berkeley

Silicon carbide (SiC) based electronics hold promise for pushing past the limits of current technology to achieve small, durable devices that can function in high-temperature, high-voltage, corrosive, and biological environments. SiC is an ideal material for such conditions due to its high mechanical strength, excellent chemical stability, and its biocompatibility. Consequently, SiC nanowires have attracted interest in applications such as biological sensors, field emission cathodes, and energy storage devices. To realize SiC nanowire based devices for large-scale use, the growth mechanism must be further understood to enable strict control of nanowire crystal structure and orientation. Here we report on recent studies to understand the growth mechanism of Ni-assisted silicon carbide nanowires using single-source precursor methyltrichlorosilane. The effects of growth parameters, such as temperature and precursor flow rate, on the structure and morphology of the resulting nanowires will be presented. This study identifies the key parameters that may be varied to tailor nanowire growth for various applications.

9:00am **NS+SP-TuM4 Homogeneous Nucleation and Characterization of Nanodiamonds Synthesized in an Atmospheric-Pressure Microplasma**, *Jonathan Cole, R.M. Sankaran*, Case Western Reserve University

Nanodiamonds possess striking properties such as exceptional mechanical and chemical stability, low cytotoxicity, tunable active surface chemistry, and tunable photoluminescence-inducing color centers, but their synthesis remains a challenge. At normal temperature and pressure, graphite is the thermodynamically stable phase of bulk carbon, while the diamond phase requires high temperatures and pressures. Nanodiamonds have thus been produced via high-pressure, high-temperature (HPHT) conversion of graphite in the presence of carbonaceous precursors and via detonation of carbon-containing explosives. Alternatively, nanocrystalline diamond films have been deposited at low pressure (~1 Torr) by chemical vapor deposition (CVD). Supporting theoretical predictions¹ have shown that at the nanoscale, hydrogenated forms of carbon prefer sp³ bonding, even at normal conditions, up to a certain size.

Here, we present a study of a plasma process for the synthesis of nanodiamonds at low temperature (<1000 °C) and atmospheric pressure. C-H-O-containing vapor precursors diluted in Argon are continuously fed into a DC hollow cathode plasma discharge. Nanoparticles nucleate from radical moieties such as C₂ and CH, whose radiative transitions (specifically, C₂ 516 nm vibrational band and CH 431 nm electronic band) are monitored by optical emission spectroscopy (OES). Particles are carried as an aerosol to either a filter for *ex situ* materials analysis or an *in situ* scanning mobility particle sizer system (SMPS). SMPS measurements confirm particle formation and allow us to correlate particle yield and size distribution with OES results. Specifically, we have compared results for ethanol and methanol precursors and find that C₂ formation is favored by ethanol, while CH formation is favored by methanol, and that an increase in both radical populations (measured as the aforementioned peak intensities normalized to Ar 750 nm intensity) increase with both particle number density and average diameter.

Analogous to CVD of diamond films², we find from TEM analysis that the selectivity of diamond phase is dependent on the C-H-O atomic ratio of the precursor. Specifically, methanol is found to produce a significant amount of sub-5 nm nanodiamonds, while ethanol mostly yields larger amorphous

and graphitic carbon. We suggest that the radical chemistry observed via OES (i.e., C₂ versus CH populations) plays an important role in such observations, and we demonstrate that addition of H₂ gas to ethanol vapor will recover the results given by methanol.

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9:20am NS+SP-TuM5 Chemically-specific Intramolecular Imaging with Atomic Force Microscopy, *Ozgur Sahin*, Columbia University **INVITED**

Atomic force microscopy (AFM) is a powerful tool for imaging and chemical characterization of biological samples at molecular resolution in physiologically relevant environments. However, the localized tip-sample interactions limit high-resolution images to the topmost layer of surfaces. Consequently, characterizing the three-dimensional (3-D) inner structures of molecules has been a challenge. Here we demonstrate three-dimensional localization of chemical groups within a protein complex using AFM. We employ short DNA sequences to label specific chemical groups inside the protein complex. T-shaped cantilevers functionalized with complementary probe DNAs allow locating each label with sequence specificity and sub-nanometer resolution. We measure pairwise distances between labels and reconstruct the 3-D loci of the target groups using simple geometric calculations. Experiments with the biotin-streptavidin complex showed that the 3-D loci of carboxylic acids of biotins are within 2-Angstroms of their respective 3-D loci in the corresponding crystal structure, suggesting AFM may complement existing structural biological techniques in solving structures that are difficult to study due to their size and complexity.

11:00am NS+SP-TuM10 Time-Resolved Small-Angle X-ray Scattering of Detonating Composition B-3 at the Advanced Photon Source, *Rachel Huber*, *D. Podlesak*, Los Alamos National Laboratory (LANL), *M. Bagge-Hansen*, Lawrence Livermore National Laboratory (LLNL), *D. Dattelbaum*, *M. Firestone*, LANL, *T. Graber*, Washington State University, *R. Gustavsen*, LANL, *R. Hodgkin*, LLNL, *B.J. Jensen*, LANL, *L.M. Lauderbach*, LLNL, *P. Rigg*, Washington State University, *B. Ringstrand*, LANL, *S. Seifert*, Argonne National Laboratory, *N. Sinclair*, Washington State University, *E. Watkins*, LANL, *T.M. Willey*, *T. van Buuren*, LLNL

High explosive (HE) detonations drive chemical reactions under extreme conditions, in which explosive molecules are rapidly converted to small molecular products such as carbon, H₂O, CO₂ and N₂. Solid carbon products are known to be comprised of several allotropes including amorphous carbon, graphite, onion-like graphitic carbon, fullerenes, and nanodiamonds (NDs). The formation of different allotropes arises from the temperatures and pressures conditions on the nanocarbon phase diagram accessed during the detonation. Previously, only the starting explosive samples, and post-mortem soot were available for structural analysis. However, a fundamental understanding of how carbon particles form and evolve during a detonation must occur in real-time on the nanosecond timescale. New developments in *in-situ* time-resolved small angle X-ray scattering (TR-SAXS) has allowed for the measurement of multiple SAXS spectra of detonating Composition B-3 (60% TNT, 40% RDX) at the Dynamic Compression Sector (Sector 35-B) at the Advanced Photon Source (Argonne National Laboratory). The TR-SAXS measurements coupled to the detonation on the ns-timescale are the first of their kind in the United States. Through Guinier and Porod analysis of the TR-SAXS data, we are able to determine the size, morphology, and phase of the carbon allotropes at time delays behind the detonation front.^{1,2} In addition, electron microscopy, X-ray photoelectron spectroscopy, and static SAXS were used to study the carbon solids in the post-detonation soot. By understanding the formation of solid carbon behind the detonation front, an improved theoretical framework may be applied to modeling the products equation of state for explosives.

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2 Titov, V. M., Tolochko, B. P., Ten, K. A., Lukyanchikov, L. A. & Prueel, E. R. Where and when are nanodiamonds formed under explosion? *Diamond and Related Materials***16**, 2009-2013, doi:10.1016/j.diamond.2007.09.001 (2007).

11:20am NS+SP-TuM11 LEEM Imaging of Growth of Au on Ge(110), *Bret Stenger*, *A. Dorsett*, *M.S. van Zijll*, *C.A. Gabris*, *C.K.B. Paw U*, *S. Chiang*, University of California, Davis

The growth of Au on Ge(110) was observed with Low Energy Electron Microscopy (LEEM). The objectives of this study were to control the growth of low-dimensional nanostructures and understand the collective

diffusion behavior observed. Ge(110) was heated to 800°C and dosed with 0.5 ML of Au. During deposition, islands grew to ~1-2 microns in width and ~2-3 microns in length, all oriented along the same direction. The islands were observed to move and change shape over a short period of time (< 1s) indicating the rapid collective movement of ~4x10⁷ atoms. As the temperature decreased, the island behavior was also studied and revealed rapid island contractions which left traces on the Ge(110) surface. This island growth is similar to that previously observed for Ag on Ge(110), although the Ag islands are typically a factor of 10 narrower and often 3 to 5 times longer.

11:40am NS+SP-TuM12 Strength and Fracture of Graphene Oxide Nanosheets, *C. Cao*, University of Toronto, Canada, *M. Daly*, *B. Chen*, *C.V. Singh*, *Y. Sun*, University of Toronto, *Tobin Fillette*, University of Toronto, Canada

Graphene oxide (GO) is a layered material comprised of hierarchical features which possess vastly differing characteristic dimensions. GO has been applied as a good candidate for paper-like materials, robust fibers, and reinforcement elements in composites. The use of GO in these materials has been motivated in large part by the predicted high mechanical properties of individual GO monolayers. Recent experiments performed in our research group have measured the strength of GO monolayers to be ~25 GPa [1], which is in good agreement with previously theoretical predictions [2]. Macroscopic papers and fibers synthesized using GO, however, typically exhibit strengths on the order of 10-100's of MPa's. GO nanosheets represent the critical hierarchical structure that bridges the length-scale of these monolayer and bulk material architectures.

In this study, the strength and fracture behavior of GO nanosheets were examined *in situ* with a micro-tensile device operated inside scanning and transmission electron microscopes (SEM/TEM) [3]. The tensile strength of GO nanosheets was measured to be as high as 12 ± 4 GPa, approaching the intrinsic strength of monolayer GO, and orders of magnitude higher than bulk GO papers. During mechanical failure, the nanosheets were observed to undergo intraplanar brittle fracture in highly localized regions through the cross-section of nanosheets due to interlayer load transmission via a hydrogen bond networks as revealed by complimentary Molecular Dynamics simulations.

GO nanosheets were found to exhibit variations in strength that were strongly correlated with the effective volume. This is consistent with Weibull statistics, such that larger GO nanosheets are more likely to possess larger planar defects and adversely impact strength. Furthermore, the Young's modulus was inversely correlated to sample thickness, and approached that of monolayer GO (~380 GPa) for thin samples. These trends provide strong evidence of the scaling effects on the mechanical properties of GO materials, and help to bridge the understanding of the mechanical behavior of hierarchical GO materials which will ultimately guide application as GO papers and coatings.

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12:00pm NS+SP-TuM13 Low-Temperature Atomic Layer Deposition of Crystalline Platinum Nanoclusters on Graphene Nanoplatelets Using (Methylcyclopentadienyl)-Trimethylplatinum and Oxygen, *Hao Van Bui*, Delft University of Technology, Netherlands, *R. Bevaart*, *F. Grillo*, Delft University of Technology, *J.R. van Ommen*, Delft University of Technology, Netherlands

The thermal atomic layer deposition of platinum using (methylcyclopentadienyl)-trimethylplatinum (MeCpPtMe₃) and oxygen has been investigated for more than a decade and performed on various supports, including flat surfaces [1, 2], nanoparticles [3], nanowires [4] and carbon-based nanomaterials [5, 6, 7, 8]. It has been demonstrated and widely accepted that this ALD process has a lower limit of deposition temperature of 200 °C. Here, we demonstrate the thermal Pt ALD on graphene nanoplatelets using MeCpPtMe₃ and dry air (20% wt. O₂), and show that highly dispersed and crystalline Pt nanoparticles can be obtained at a temperature as low as 80 °C. The feasible low-temperature deposition is attributed to the role of the graphene support that can activate molecular oxygen to form O₂⁻ anions [9], which consequently enhances the oxidation reactions in ALD. Importantly, the low deposition temperatures (i.e., 80 °C and 100 °C) can prevent the ripening of nanoparticles and hinder the formation of new nuclei during the ALD, allowing for better control in particle size and distribution. In contrast, at higher temperatures (150-250

°C), the ripening occurs, and new nuclei are constantly formed during the deposition, resulting in a broader particle size distribution.

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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.¹ Hydrogen removal can pattern the surface with two different functionalities. First, we show that partially-hydrogenated graphene (Phg) on a SiO₂ 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 MoS₂ 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 MoS₂ films. Organic chalcogen precursors are released into the growth chamber and react with a Mo filament creating films up to 2cm² 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 MoS₂ 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 MoS₂ 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 (MoS₂), 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 MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ 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.

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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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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. Akashi*, *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.¹ 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.² 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.

Scanning Probe Microscopy Focus Topic Room: 212A - Session SP+AS+NS+SS-WeM

Advances in Scanning Probe Microscopy

Moderator: An-Ping Li, Oak Ridge National Lab, Saban Hus, Oak Ridge National Laboratory

8:00am **SP+AS+NS+SS-WeM1 Designer Electrons: Quantum Information and New Particles in Atomically Assembled Matter**, *Hari Manoharan*, Stanford University **INVITED**

The observation of massless Dirac fermions in monolayer graphene has propelled a new area of science and technology seeking to harness charge carriers that behave relativistically within solid-state materials. Using low-temperature scanning tunneling microscopy and spectroscopy, we show the emergence of Dirac fermions in a fully tunable condensed-matter system—molecular graphene—assembled via atomic manipulation of a conventional two-dimensional electron system in a surface state. We embed, image, and tune the symmetries underlying the two-dimensional Dirac equation into these electrons by sculpting the surface potential with manipulated molecules. By distorting the effective electron hopping parameters into a Kekulé pattern, we find that these natively massless Dirac particles can be endowed with a tunable mass engendered by the associated scalar gauge field, in analogy to the Higgs field. With altered symmetry and texturing of the assembled lattices, the Dirac fermions can be dressed with gauge electric or magnetic fields such that the carriers believe they are in real fields and condense into the corresponding ground state, as confirmed by tunneling spectroscopy. Using these techniques we ultimately fabricate a quantum Hall state without breaking time-reversal symmetry, in which electrons quantize in a gauge magnetic field ramped to 60 Tesla with zero applied laboratory field. We show that these and other chiral states now possible to realize have direct analogues in topological insulators, and can be used to guide or confine charge in nontrivial ways or to synthesize new particles [1,2].

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8:40am **SP+AS+NS+SS-WeM3 Scanning Quantum Dot Microscopy**, *Ruslan Temirov, C.W. Wagner, M.F.B.G. Green, P.L. Leinen*, Forschungszentrum Juelich GmbH, Germany, *T.D. Deilmann, P. Krueger, M.R. Rohlfing*, Muenster University, Germany, *F.S.T. Tautz*, Forschungszentrum Juelich GmbH, Germany

Interactions between atomic and molecular objects are to a large extent defined by the nanoscale electrostatic potentials which these objects produce. Consequently, a tool for nanometre scale imaging and quantification of

local electrostatic fields could help in many areas of nanoscience research. In this contribution we introduce a

scanning probe technique that for the first time enables truly three-dimensional imaging of local electrostatic

potential fields with sub-nanometre resolution. Registering single electron charging events of a molecular

quantum dot attached to the tip of a tuning fork atomic force microscope operated at 5 K, we image the

quadrupole field of a single molecule adsorbed on a metal surface. To demonstrate quantitative measurements,

we investigate the Smoluchowski dipole field created by a single metal adatom adsorbed on a metal surface. We

show that because of its high sensitivity the technique can probe electrostatic potentials at large distances from

their sources, which should allow for the imaging of samples with increased surface roughness.

Reference

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arXiv:1503.07738 (2015)

9:00am **SP+AS+NS+SS-WeM4 Local Probing of the Photo-carrier Lifetime by Kelvin Probe Force Microscopy**, *Nicolas Chevalier, S. Pouch, D. Mariolle*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *B. Grevin*, Univ. Grenoble Alpes/ CEA, INAC, SPram, LEMOH, France, *L. Borowik*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France

The photo-carrier lifetime plays a major role in the overall efficiency of a solar cell because it limits the proportion of photo-generated charges collected at the electrodes. This lifetime, which should be ideally as large as possible in an organic or inorganic solar cell, is rather difficult to measure in nanostructured materials or in more complex hybrid systems, indirect band-gap semiconductors, and ultra-thin layers. Identifying the losses mechanisms is one of the main objectives for increasing the performances of solar cells. Most of the experimental approaches developed so far consist in studying recombination by techniques such as transient photovoltage measurements or charge extraction. All these techniques average sample properties over macroscopic scales, making them unsuitable for directly assessing the impact of local heterogeneity on the recombination process. In this paper, we propose a steady method to measure the photo carrier lifetime by photo-modulated techniques based on Kelvin probe force microscopy (KPFM). [1] Additionally, KPFM technique provides a spatially resolved measurement, which is applicable on the overall of solar cells.

We will present the principle of this original method based on the measurement of the surface potential by KPFM under an illumination with a rectangular waveform light modulation. Photo-carrier lifetime down to μ s scale is reachable with our experimental setup. The modulation-dependent surface potential is plotted as a function of the frequency. Assuming an immediate generation time under illumination and an exponential decay of the surface potential during the dark condition, the averaged surface potential over a cycle can be fitted as a function of the frequency by simple equation where the only fit parameter is the photocarrier-lifetime. [2] Instrumental aspects as well as data treatment will be reviewed. Measurements obtained on silicon nanocrystals embedded in 30 nm film of silicon dioxide [3] and on organic donor-acceptor blend (PBTFB and PCBM) [4] will be presented to illustrate the potential of the technique.

This work was supported by the French "Recherche Technologique de Base" Program and performed in the frame of the trSPV Nanoscience project. The measurements were performed on the CEA Minatec Nanocharacterization Platform (PFNC).

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9:20am **SP+AS+NS+SS-WeM5 Nanoscale Capacitance-Voltage (C-V) Curves: Using Scanning Microwave Impedance Microscopy (sMIM) to Characterize Local Electrical Properties of Linear and Non-Linear Materials**, *Stuart Friedman, Y. Yang, O. Amster*, PrimeNano, Inc.

Understanding and optimizing advanced materials frequently requires detailed knowledge of nanoscale electrical properties. Scanning probe techniques such as scanning tunneling microscopy (STM), conductive AFM (cAFM), scanning capacitance microscopy (SCM), and Kelvin probe force microscopy (KPFM) provide such nano-electrical measurements, but are generally limited in the classes of materials they can characterize or the properties they can measure. Scanning microwave impedance microscopy (sMIM) uses GHz frequency microwaves and shielded AFM probes to directly measure the impedance (capacitance and conductance) of the tip sample interface. As such sMIM is sensitive to the permittivity and conductivity of a wide variety of samples including dielectrics, conductors, and semiconductors.

When sMIM is applied to non-linear materials, changing the tip sample bias changes the local electric field thereby changing the local electrical properties of the sample just under the AFM tip. The electric field induced changes in the sample create changes in the tip-sample impedance that can be measured by sMIM. For example, when imaging doped semiconductor samples, the tip sample interface forms either a metal-semiconductor junction or a metal-insulator-semiconductor junction. Plotting the sMIM measured capacitance as a function of the tip sample bias voltage produces the equivalent of a typical capacitance-voltage curve, but from nanoscale regions selected from an AFM image. C vs V results from doped silicon samples that closely match theoretical calculations will be discussed. The talk will also present results from advanced and novel materials and devices, such as III-V semiconductors, 2D materials and 1D structures where sMIM data has been used to assess non-linear behavior and characterize dopant type and distribution.

9:40am **SP+AS+NS+SS-WeM6 STM Study of the Correlation between Structural, Magnetic, and Electronic Properties of Co Nano-Islands on Cu(111)**, *Jewook Park, C. Park, M. Yoon, Z. Gai, A.P. Baddorf, A.-P. Li*, Oak Ridge National Laboratory

An epitaxially grown Co nano-island on Cu(111) surface is a model system to study the correlation between structural, magnetic, and electrical properties of nanophase materials. We carried out an extensive study on Co islands by using spin-polarized scanning tunneling microscopy and spectroscopy (SP-STM/S) at low temperatures (130 K and 38 K). Two structurally different island types are clearly distinguished, rotated by 180° about the surface normal due to a stacking fault in one type of the islands. The triangular Co islands are 5-20 nm wide and 4 Å high. Regardless of the structural asymmetry, both faulted and un-faulted Co islands possess two distinctive spin orientations. With Cr-coated W-tip as a spin-polarized probe, bias-dependent tunneling conductance maps are measured on Co islands. An antiparallel spin-orientation between magnetized tip and Co islands display higher conductance compared to a parallel relation at -400 meV and *vice versa* at around Fermi-level, which is verified by density functional theory calculations. Furthermore, by recording 23 hours of time-lapse images from the same Co islands, we demonstrate a time-dependent correlation between structural, magnetic, and electrical behaviors. We find that a contamination-induced structural change modifies the magnetic properties of Co islands and is confirmed by theoretical calculations.

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.

11:00am **SP+AS+NS+SS-WeM10 Probing Electrostatic Field Effect in Quantum Materials by Microwave Impedance Microscopy**, *Keji Lai*, University of Texas at Austin **INVITED**

The research of complex quantum materials, in which a dazzling number of emergent phenomena take place in the nanoscale, is a major theme in modern condensed matter physics. For real-space imaging of complex systems, electrical impedance microscopy fills an important void that is not well represented by the existing local probes. Using shielded cantilever probes and sensitive microwave electronics, we can now perform non-invasive electrical imaging with sub-100nm resolution and sub-aF sensitivity.

Combining the cryogenic microwave impedance microscopy (MIM) and a spin-coated thin ionic gel layer, we are able to visualize the metal-insulator transition of functional materials in electrolyte-gated electric double-layer transistors. The microwave images acquired at different gate voltages clearly show the spatial evolution of channel conductivity and its local fluctuations through the transition. By applying a large source-drain bias above the glass transition temperature of the gel, an uneven conductance profile is established across the EDLT channel, which can be visualized by the MIM and further investigated by transport measurements and numerical simulations. The combination of ultra-thin ion-gel gating and microwave microscopy paves the way for studying the microscopic evolution of phase transitions in complex materials induced by electrostatic field effects.

11:40am **SP+AS+NS+SS-WeM12 Subsurface Visualization of Soft Matrix using 3D-Spectroscopic Atomic Force Acoustic Microscopy**, *Kuniko Kimura, K. Kobayashi, A. Yao, H. Yamada*, Kyoto University, Japan

Nondestructive visualization of subsurface features of various materials with nanometer-scale spatial resolution is strongly demanded in a wide variety of scientific research fields such as nanoelectronics, nanomechanics and life science. Recently, many research groups have demonstrated the visualization of nanometer-scale subsurface features using various techniques based on atomic force microscopy (AFM) [1-4]. (All references and figures are given in Supplement.) We recently demonstrated the imaging of Au nanoparticles buried under 900 nm from the surface of a polymer matrix by atomic force acoustic microscopy (AFAM), as shown in Fig. 1 [5]. In AFAM, the amplitude and phase of the cantilever vibration at the contact resonance frequency induced by the sample excitation are measured, which allows us the quantitative evaluation of surface stiffness [6]. The AFAM images in Fig. 1 show that the surface viscoelasticity of the soft matrix is affected by subsurface hard objects such as the Au nanoparticles buried even roughly 1 micro-meter below the surface. However, only from AFAM images, it is difficult to determine which the dominant mechanism for the subsurface imaging is viscosity variation or elasticity variation, because AFAM images were taken at a single excitation frequency near contact resonance.

In this presentation, we discuss the origin of the visualization of subsurface features in soft matrix based on spectroscopy of AFAM [7]. We recorded the amplitude and phase spectra at every pixel of the AFAM image as represented in Fig. 2, which we call 3-dimensional spectroscopic atomic

force acoustic microscopy (3D-spectroscopic AFAM). A schematic diagram of the 3D-spectroscopic AFAM is shown in Fig. 3. After the tip was brought into contact with the surface, we first measured the contact resonance frequency (f_c). Then we recorded the amplitude and phase spectra measured by a lock-in amplifier, while the tip was raster-scanned with the contact mode. At each scanning pixel, the excitation frequency was swept with the span of 25 kHz which was centering around f_c , whose sweep time was 35 msec. The total acquisition time for 128 x 128 pixels took about 20 min.

Using this method, we can compare the frequency spectrum measured on the subsurface Au nanoparticle with that on another position having no subsurface particle, as shown in Fig. 4. We can also reconstruct AFAM images of arbitrary frequencies within the sweep frequency range, which is the meaning of “3-dimensional”. Moreover, the 3D-spectroscopic AFAM enables us to characterize the amplitude and phase spectra and to detect the variation that may be caused by the nonlinear tip-sample interactions.

12:00pm **SP+AS+NS+SS-WeM13 Quantifying the Effects of Cantilever Modes Shapes on Studies of the Liquid-Solid Interface, Aleks Labuda, M. Viani, D. Walters, R. Proksch**, Asylum Research, an Oxford Instruments company

At the core of most AFM measurements is the assumption that the motion of the cantilever probe can be well quantified. However, most AFM systems use a “beam bounce” optical beam deflection (OBD) method which, because it is fundamentally an angular measurement, only provides accurate tip position information when the mode shape of the cantilever matches the calibration conditions. For example, if the OBD sensitivity is calibrated with a force curve, the calibration holds true only for experiments where the mode shape is similar to an end-loaded cantilever. This assumption is quickly violated when the cantilever is oscillated at frequencies different from the calibration. This is especially true in liquids, where $Q \sim 1$ and the combination of significant base motion and hydrodynamic effects lead to a variety of different mode shapes that are strongly frequency dependent (see Figure). This clearly demonstrates that the sensitivity (nm/V) is actually a frequency dependent quantity. Worse, it may also drift with time. Another consequence is that the effective stiffness of the cantilever, which depends on mode shape, is also highly frequency dependent. Both of these effects cause quantitative misinterpretation of the tip-sample interaction and artifacts in imaging contrast. These problems affect both dynamic AFM modes (such as AM-AFM and FM-AFM) as well as sub-resonance modes such as fast force mapping and force modulation.

To quantify this effect, we present measurements based on Ref [1-2] using a modified commercial AFM that combines a standard OBD detector with an integrated laser Doppler vibrometer (LDV) system that directly measures displacement. As shown in the Figure, The OBD and LDV can be used simultaneously, such that the cantilever base motion or tip motion can be accurately monitored with the LDV during an AFM experiment – independent of the OBD and any feedback loops. In the Figure, the $\sim 2 \mu\text{m}$ LDV laser spot was scanned along the cantilever for high-resolution in situ mapping of its dynamics across a wide spectrum of frequencies and showing significant deviations from ideal mode shapes over the entire frequency range.

The effects of these frequency-dependent mode shapes are then quantified by appropriate modeling for a variety of experimental conditions, and demonstrated experimentally using stiff levers for AM-AFM at the calcite-water interface and soft levers for fast force mapping of polymeric materials.

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 MoS₂, 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 MoS₂ 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 μm 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 MoS₂.

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 MoS₂ flakes were cleaved in ambient condition and transferred into the UHV chamber; afterwards, TiOPc monolayers were deposited on the MoS₂ 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 MoS₂; the TiOPc layer on MoS₂ requires annealing above of 673K for desorption. This high thermal stability indicates there are strong interaction between TiOPc and MoS₂ surface. STS shows the band gap of the monolayer is 1.8 eV, while bulk MoS₂ has a 1.3eV band gap. Moreover, the Fermi level of TiOPc/bulk MoS₂ is shifted to the valence band, consistent with a P type shift. However, bulk MoS₂ 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 MoS₂ deposited TiOPc monolayer, threshold bias is shifted from -30 V to near 0 V, indicating P-doping of MoS₂. It can be hypothesized that the work function transition of MoS₂ 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 MoS₂ FET, the on/off ratio is enhanced more than 2 orders magnitude. The similar charge transfer behavior also can be observed in TiOPc/WSe₂; on the bilayer WSe₂/HOPG, the TiOPc monolayer deposited on the first layer of WSe₂ shows the a conduction band shifted Fermi level, while a TiOPc monolayer deposited on the second layer of WSe₂ 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^{1,2}.

In this study, the wettability and reactivity of various metals with a number of bulk TMDs (MoS₂, HfSe₂, SnSe₂, 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 MoSe₂, where uniform thin films were achieved, compared to ReSe₂, 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 SnSe₂ 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 MoS₂ 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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[2] Das, S.; Chen, H.Y.; Penumatcha, A. V.; Appenzeller, J. High Performance Multi-Layer MoS₂ Transistors with Scandium Contacts. *Nano Lett.* **2012**, *12*, 100-105.

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.

1 K. W. Clark, et al., *ACS Nano* **7**, 7956 (2013).

2 K. W. Clark, et al., *Phys. Rev. X* **4**, 011021 (2014).

3 L. Liu, et al., *Science* **343**, 163 (2014).

4 J. Park et al., *Nature Commun.* **5**, 5403 (2014).

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 LiC₆, which corresponds to a figure of merit (σ_{dc}/σ_{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.

Reference

1. Jiayu Wan^a, Wenzhong Bao^a, et al., *Nature communications*, 2014,5, 4224. (^a equally contribution)

2. Jiayu Wan, Feng Gu, Wenzhong Bao, et al. *Nano Letters*, 2015, DOI: 10.1021/acs.nanolett.5b00300.

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 (H₂O₂), and the direct four-electron pathway (4e-) that reduces to water (H₂O). 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 Norskov 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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[2] K. R. Lee et al., *Electrochem. Commun.* **12**, 1052 (2010).

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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. Vlasiouk, 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 Bi_2Se_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 = 2×10^{-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 ~ 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 ~ 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 Di/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 Di/Dv mappings. The defects also show higher tunneling conductance than the h-BN sheet in the Di/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° , which is well in line with our simulations. From the Di/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 Cu_2N insulating films have been of the order ~ 100 ns [1]. A three-order-of-magnitude enhancement of lifetime, to ~ 200 μs , 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.

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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).

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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 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

Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+AS+NS+SS-ThM

Probing Chemical Reactions at the Nanoscale

Moderator: Stephen Nonnenmann, University of Massachusetts - Amherst, Shengyong Qin, University of Science and Technology of China

8:40am **SP+AS+NS+SS-ThM3 Adsorption of Trimethyl Acetic Acid on (1x2) Reconstructed TiO₂(110)**, **Kenneth Park, K. Zhu, Y. Xia, Z. Zhang**, Baylor University

The adsorption of trimethyl acetic acid on (1x2) reconstructed TiO₂(110) is investigated using scanning tunneling microscopy (STM) with the same area analysis. After de-protonation, trimethyl acetate (TMA) molecules preferentially adsorb in the troughs between two adjacent 1x2 strands. The nearest neighbor distance between TMA molecules is about 5.9 Å, twice the lattice constant along [001], corresponding to the bridging bidentate configuration over two 5-coordinated Ti⁴⁺ sites. With increasing coverage, they form linear chains, separated by (1x2) strands leading up to the nominal saturation coverage of 0.25 ML. Upon further adsorption, the second-layer of TMA molecules start clustering on top of 1x2 strands. The coverage-dependent TMA adsorption structures on (1x2) reconstructed TiO₂(110) will be compared and discussed with the reported TMA adsorption on (1x1) TiO₂(110), and relative reactivity of TMA with other defect sites including cross-links will be presented.

9:00am **SP+AS+NS+SS-ThM4 Anticorrelation between Surface and Subsurface Point-Defects and Influence on Redox Chemistry at TiO₂(110)**, **Igor Lyubinetsky, Y. Yoon, Y. Du**, Pacific Northwest National Laboratory, **J.C. Garcia**, Worcester Polytechnic Institute, **Z. Zhu, Z.-T. Wang, N.G. Petrik, G.A. Kimmel, Z. Dohnalek, M.A. Henderson, R. Rousseau**, Pacific Northwest National Laboratory, **N.A. Deskins**, Worcester Polytechnic Institute

The atoms at the surface that constitute reactive sites clearly govern surface chemistry. But subsurface atoms, particularly substitutional and/or interstitial defects, can also influence surface chemistry, though a detailed understanding is still emerging. Here we report the interplay and relative impact of surface vs. subsurface defects on the surface chemistry of rutile TiO₂, a prototypical metal oxide. Importantly, it contains both surface and subsurface intrinsic point-defects in the reduced state (along with residual extrinsic defects). Our scanning tunneling microscopy results show that O vacancies (V_O 's), the dominant surface defects, are virtually absent in the vicinity of positively-charged subsurface point-defects. Such anticorrelation of defects is consistent with density functional theory (DFT) calculations of the impact of subsurface defect proximity on V_O formation energy, which narrows down the possible candidates to certain interstitial defects, of both intrinsic and extrinsic nature. To monitor the influence of such (electron-donor type) defects on surface redox chemistry, a test reaction of the electron-mediated dissociative adsorption of O₂ is employed, which is observed to be suppressed around these defects. DFT results attribute this to a perceived absence of the intrinsic (Ti) (and likely extrinsic) interstitials in the nearest subsurface layer beneath "inhibited" areas, while the underlying energetic driver is largely repulsive electrostatics. Finally, we postulate that the entire subsurface region up to several atomic layers deep could be voided of any charged point-defects, whereas such defects are proposed to exist beyond the subsurface region. Subsequently, prevalent V_O 's are largely responsible for both the surface/subsurface reduction and mediation of the redox chemistry at reduced TiO₂(110) surface. Overall, this work provides new fundamental insights into the relation between surface and subsurface defects. In a broader perspective, the uncovered effects may prove to be general for other reducible oxides, and thus have potential implications in such diverse research fields as environmental remediation or microelectronics.

9:20am **SP+AS+NS+SS-ThM5 Dissociation of Water on Oxygen Pre-Covered Cu(110) Observed with Scanning Tunneling Microscopy**, **Zongqiang Pang**, Lawrence Berkeley National Laboratory (LBNL)

The dissociation of water on the oxygen pre-covered Cu(110) surface has been studied with Scanning Tunneling Microscopy (STM). At low temperature (77K), water reacts with pre-covered oxygen to produce hydrogen atoms and hydroxyl groups. Non-dissociated water molecules and hydroxyl groups combine to form a hexagonal network on the top of Cu(110) where water donates one hydrogen to the hydroxyl, while uncoordinated hydroxyls bind to the second layer intact water molecules. Following excitation by tunneling electron or by heat, the water molecules

in the hexagonal network gradually dissociate. The oxygen atoms involved in the reaction of water dissociation return to its original position, leaving ordered Cu-O and hydroxyl dimer chains on the Cu(110) surface which both align along <001> direction. Our results demonstrate that the oxygen atoms pre-adsorbed on the Cu(110) surface lower the energy barrier for water dissociation on the Cu(110) surface.

9:40am **SP+AS+NS+SS-ThM6 Probing Local Electrochemical Activity within Yttria-Stabilized-Zirconia via In Situ High-Temperature Atomic Force Microscopy**, **Jiaxin Zhu**, University of Massachusetts - Amherst, **C. Perez, T. Oh, R. Kungas, J. Vohs, D. Bonnell**, University of Pennsylvania, **S.S. Nonnenmann**, University of Massachusetts - Amherst

Considerable interest in understanding interfacial phenomena occurring across nanostructured solid oxide fuel cell (SOFC) membrane electrode assemblies has increased demand for *in situ* characterization techniques with higher resolution. We briefly outline recent advancements in atomic force microscopy (AFM) instrumentation and sub-systems in realizing real time imaging at high temperatures and ambient pressures, and the use of these *in situ*, multi-stimuli probes in collecting local information related to physical and fundamental processes. Here we demonstrate direct probing of local surface potential gradients related to the ionic conductivity of yttria-stabilized zirconia (YSZ) within symmetric SOFCs under intermediate operating temperatures (500 °C – 600 °C) via variable temperature scanning surface potential microscopy (VT-SSPM). The conductivity values obtained at different temperatures are then used to estimate the activation energy. These locally collected conductivity and activation energy values are subsequently compared to macroscopic electrochemical impedance results and bulk literature values, thus supporting the validity of the approach.

Thursday Afternoon, October 22, 2015

Scanning Probe Microscopy Focus Topic

Room: 212A - Session SP+BI+NS+SS+TF-ThA

Probing Material Growth on the Surface

Moderator: Chuanxu Ma, Oak Ridge National Laboratory

2:20pm **SP+BI+NS+SS+TF-ThA1 Tailoring the Growth of Organic Thin Films via Chemical Reactions at the Molecular Scale, Pengpeng Zhang**, Michigan State University **INVITED**

Control of highly ordered organic molecular thin films with extended π systems is currently of intense interest for integrating molecules into modern electronics due to their tunable nature. Selection of molecules and substrates can lead to desired transport properties such as charge transfer, charge injection, exciton diffusion, etc., at the heterointerface, which is crucial to the development of organic and molecular electronics. However, achieving large-scale molecular ordering remains a significant challenge that requires a thorough understanding of the growth mechanism. I will discuss our recent discovery of the anisotropic crystalline step-flow growth of the prototypical metal phthalocyanine molecules on the deactivated Si(111)-B surface. I will then address the growth mechanism and show that the molecular ordering and molecular orientation can be effectively controlled through selective orbital coupling between the molecule and substrate. Finally, I will illustrate an abnormal temperature dependent growth evolution and discuss the associated mechanism.

This research is funded by the U.S. Department of Energy (DOE) Office of Science Early Career Research Program (DE-SC0006400) through the Office of Basic Energy Sciences.

3:00pm **SP+BI+NS+SS+TF-ThA3 Investigation of Initial Stages of Oxidation of Ni-Cr and Ni-Cr-Mo alloys by Scanning Tunneling Microscopy and Spectroscopy, Gopalakrishnan Ramalingam***, P. Reinke, University of Virginia

Ni-Cr alloys are excellent candidates for use in highly corrosive environments due to the formation of a protective Cr_2O_3 layer. Molybdenum is a common alloying addition as it improves the resistance to localized corrosion and prevents the breakdown of the oxide layer. While the effect of Mo addition on corrosion resistance is well known, the underlying mechanisms at the atomic scale and the role of electronic structure changes due to Mo addition are poorly understood. In the current work, we have used STM/STS to investigate the initial stages of oxidation of Ni, Cr and Ni-Cr (10-25wt.% Cr) alloy thin films and subsequently, the effect of Mo addition (2-10 wt.%) on the oxidation behavior. The alloy thin films are grown on MgO(001) substrates using two recipes that yielded smooth films: (a) deposition at 100 °C and subsequent anneal at 300 °C for 2 hours, and (b) deposition at 400 °C with no post-growth annealing. While recipe (a) yielded smooth Ni films, co-deposition of Ni and Cr resulted in the formation of secondary Ni_2Cr phases. Alloy films grown using recipe (b) did not result in secondary phases and are optimal for oxidation studies of alloy films. STM/STS data of the oxidation (30 L of O_2) of a pure Ni thin film at 200 °C reveal preferential oxidation of some terraces compared to others and indicates a dependence of oxidation rate on the crystallographic orientation of the terrace. dI/dV maps of a Cr surface after 10 L oxidation at 200 °C shows the presence of a bandgap (1.32 eV) throughout the surface and indicates the growth of a uniform oxide layer. In the case of Ni-13wt.%Cr binary alloy, a 25 L exposure (at 1×10^{-8} mbar) at 300 °C results in a complete loss of step structure with a fully formed oxide layer as shown by STS spectra. A bandgap of 1.42 eV is observed throughout the surface and this value is less than the bulk bandgap of all possible oxide species (NiO , Cr_2O_3 or mixed). We will present the results of the initial stages of oxidation (<3 L) of the pure Ni thin films and discuss the differences in the oxidation processes due to the addition of 8-25 wt.% Cr. The progression from chemisorption regime (at low temperatures) to the oxide nucleation regime will be shown for different alloys by performing room temperature O_2 exposures and post-exposure annealing cycles and the effect of alloying additions on this transition will be discussed. Preliminary data on the changes in the atomic and electronic structure of the thin film and oxidation behavior due to the addition of Mo will be presented.

4:00pm **SP+BI+NS+SS+TF-ThA6 Growth and Properties of Skyrmionic Nanowires and Thin Film, Zheng Gai**, Oak Ridge National Laboratory, J. Yi, S. Tang, University of Tennessee, Oak Ridge National Laboratory, D. Mandrus, University of Tennessee **INVITED**

Magnetic skyrmion lattice, a vortex-like spin texture recently observed in chiral magnets, is of great interest to future spin-electronic data storage and other information technology applications. The combined effect of a large ferromagnetic exchange and a weak DM interaction is to twist the magnetization into a long-period spiral that can be tens to hundreds of nanometers in length. As these spirals are only weakly bound to the underlying lattice in cubic systems, they can be readily manipulated with modest applied fields. The skyrmion lattice in MnSi appears in a small region (known as the A phase) of the H-T phase diagram in bulk samples, but in 2D samples like thin films the skyrmion phase is much more robust. If skyrmion ordering can persist in one-dimensional MnSi nanowires and 2D films, then these systems are very promising for spintronics applications as the magnetic domains and individual skyrmions could be manipulated with small currents. We have systematically explored the synthesis of single crystal MnSi nanowires via controlled oxide-assisted chemical vapor deposition and observed a characteristic signature of skyrmion magnetic ordering in MnSi nanowires. The SiO_2 layer plays a key role for the high yield, correct stoichiometric and crystalline growth of the B20 MnSi nanowires. A growth phase diagram was constructed. For the thin films, a unique growth receipt was developed for the growth of high quality of thin films. The structure and magnetic properties of the films at different thickness were studied.

4:40pm **SP+BI+NS+SS+TF-ThA8 Sulfur-induced Structural Motifs on Cu(111) and Au(111) Surfaces, Holly Walen[‡]**, Iowa State University, D.-J. Liu, Ames Laboratory, J. Oh, H. Lim, RIKEN, Japan, J.W. Evans, Iowa State University, C.M. Aikens, Kansas State University, Y. Kim, RIKEN, Japan, P.A. Thiel, Iowa State University

The interaction of sulfur with copper and gold surfaces plays a fundamental role in important phenomena that include coarsening of surface nanostructures, and self-assembly of alkanethiols. Here, we identify and analyze unique sulfur-induced structural motifs observed on the (111) surfaces of these two metals. We choose very specific conditions: very low temperature (5 K), and very low sulfur coverage (≤ 0.05 monolayers, ML). In this region of temperature-coverage space, which has not been examined previously for these adsorbate-metal systems, the effects of individual interactions between metals and sulfur are most apparent and can be assessed extensively with the aid of theory and modeling. Furthermore, at this temperature diffusion is minimal and relatively-mobile species can be isolated. The primary technique is scanning tunneling microscopy (STM).

On Cu(111), at 0.004 ML S, we find unexpected heart-shaped Cu_2S_3 complexes on the terraces, made up of intersecting linear S-Cu-S units. With supporting density functional theory (DFT) and reaction-diffusion equation analysis, we propose that these hearts are a viable candidate for S-enhanced mass transport of Cu on Cu(111) at higher temperature. As S coverage increases (up to 0.05 ML), a diverse group of Cu-S structures develops which includes concatenated hearts, and eventually the known ($\sqrt{43} \times \sqrt{43}$) $R \pm 7.5^\circ$ reconstruction[1-2]. Analysis of the step edges of Cu(111) indicates that S decorates the step edges preferentially (relative to the terraces) and that the complexes observed on terraces originate at the step edges.

In contrast, no metal-sulfur complexes are observed on Au(111) under similar conditions (0.03 ML). Instead, we observe striking $\sqrt{3}R30^\circ$ rows made up of S adatoms. Using DFT and *ab-initio* Monte Carlo analysis, we construct and test a lattice gas model. This analysis shows that these short rows of S adatoms form because of a complex set of through-metal interactions: a linear three-body attraction, as well as long-range pairwise interactions (up to $5a$) between S atoms.

These experimental observations for Cu(111) and Au(111) surfaces—made under essentially-identical conditions—together with extensive DFT analyses, allow comparisons and insights into factors that favor the existence of metal-sulfur complexes, vs. chemisorbed atomic sulfur, on metal terraces.

[1] E. Wahlström, I. Ekvall, H. Olin, S. A. Lindgren, and L. Wallden, Phys. Rev. B **60** 10699 (1999).

[2] E. Wahlström, I. Ekvall, T. Kihlgren, H. Olin, S. A. Lindgren, and L. Wallden, Phys. Rev. B **64** 155406 (2001).

* Morton S. Traum Award Finalist

5:00pm **SP+BI+NS+SS+TF-ThA9 Surface Strain-Modulated Binding of Adsorbates on TiO₂(110)**, *D.V. Potapenko, Richard Osgood, Jr.*, Columbia University

Mechanical elastic strain is commonly present in nanostructured materials and it has been found to change chemical and electronic properties in a broad range of solids. Systematic study of reactivity-strain relationship on surfaces is difficult because of the fact that only very low values of strain (~0.1%) are achievable through mechanical deformation of macroscopic samples. We have developed a method of preparation of nano-scale strain fields on TiO₂ rutile(110) surface by low energy (1keV) Ar ion bombardments combined with specific thermal treatment. Titanium oxide is a brittle material regarded as a prototypical photocatalyst with numerous applications in the areas of solar energy utilization. Subsurface Ar clusters, which are formed through our preparation procedure, cause 5 – 25 nm wide surface deformations with the tensile strain values as high as 4 %. Surface distributions of various molecular and atomic adsorbates on TiO₂(110) have been studied with atomically resolved STM imaging. Our results indicate significant strain-related variations in the surface binding properties. In this presentation we will concentrate on surface hydroxyl groups (OH) as a mobile adsorbate. We derive the O-H binding energy from the statistical analysis of the adsorbate distribution. Then we demonstrate a roughly linear relationship between the values of surface strain and the O-H binding energy.

5:20pm **SP+BI+NS+SS+TF-ThA10 STM/STS Investigation of Organic Charge Transfer Complex TTF-TCNQ on Noble Metal Surfaces at 4.3K**, *Seokmin Jeon, P. Doak, P. Ganesh, B. Sumpter*, Oak Ridge National Laboratory, *J.I. Cerda*, Instituto de Ciencia de Materiales de Madrid, Spain, *P. Maksymovych*, Oak Ridge National Laboratory

TTF-TCNQ (TTF = tetrathiafulvalene; TCNQ = 7,7,8,8-tetracyanoquinodimethane) is a prototypical organic charge-transfer complex providing with a metallic conductivity (up to 900 ohm-1cm-1 at 300K). It also represents a broad class of organic electronic compounds that exhibit strong electron correlations and a rich gamut of phase transitions involving charge ordering, Mott and Peierls metal-insulator transitions and superconductivity, etc. Despite decades of research in this area, quantitative understanding of this compound is still elusive and their low-dimensional form is barely explored. We investigated ultrathin films of TTF-TCNQ on silver surfaces using scanning tunneling microscopy/spectroscopy (STM/STS) at 4.3 K. TTF-TCNQ forms self-assembled molecular lattices on noble metal surfaces with a few different TTF-to-TCNQ ratios depending on evaporation condition. Among them the islands with 1 to 1 stoichiometric ratio are found ubiquitously in less dependent on the evaporation condition. Structures of the monolayer islands are elucidated from sub-molecular resolution STM topography images. Single-point conductivity spectroscopy and conductivity mapping elucidate new electronic states which do not stem from their molecular orbital states are spatially located in the void areas of the TTF-TCNQ molecular lattices. We propose the *sp*-derived metal surface states are confined in the molecular lattices. Due to small periodicity of the lattice, the band minimum of the *sp*-derived metal surface states is shifted by as much as 1eV. This shift is much more significant than the ones normally observed in organic self-assemblies. As a result, we can also infer the height of the potential barrier within a 1D potential well model, which in turn is directly related to strong molecular dipole associated with large charge transfer and bent molecular geometry due to metal-molecule interactions.

Acknowledgement: A portion of this research (SJ, PD, PG, BS, PM) was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Thursday Evening Poster Sessions

Scanning Probe Microscopy Focus Topic

Room: Hall 3 - Session SP-ThP

Scanning Probe Microscopy Poster Session

SP-ThP1 Extreme Magnetic Properties of Co Atoms on MgO Films.
Christopher Lutz, S. Baumann, A. Heinrich, W. Paul, T. Choi, IBM Research - Almaden

The magnetic moment of a free atom arises from the spin and orbital angular momentum. In a solid state environment, anisotropy in the orbital moment due to the ligand field, together with spin-orbit coupling, gives directionality and stability to the magnetization. Here we use a low-temperature scanning tunneling microscope (STM) to show that Co atoms bound to O sites on a MgO layer achieve a record-high zero-field splitting of 58 meV, which closely approaches the theoretical limit given by the spin-orbit coupling in a 3d transition metal atom. The zero-field splitting gives the energy of the first quantum step required to surmount the anisotropy barrier and reverse the magnetization. The combination of large moment and large anisotropy energy results in magnetic-state lifetimes exceeding 0.2 ms. The high symmetry of the Co atom's binding site gives a ligand field that is effectively cylindrical, which yields a large axial anisotropy while preserving nearly all of the free-atom's orbital angular momentum. All-electrical pump-probe measurements reveal the large magnetic moment (5.5 μB) directly in STM. These results provide a symmetry-based strategy for the design of stable nanomagnets.

SP-ThP2 High Resolution qPlus NC-AFM with a New Cryogen-Free Variable Temperature UHV SPM.
C. Troepfner, M. Atabak, S. Molitor, J. Koebler, Bjoern Piglosiewicz, J. Chrost, Oxford Instruments

We present first qPlus[1] NC-AFM results of a new cryogen-free cooled ultra-high vacuum compatible scanning probe microscope capable of high stability STM and qPlus NC-AFM operation at temperatures ranging from low temperature up to above room temperature.

The microscope features a cold-sample and cold-tip design. Overcoming the limits of hold time of cryogenic liquids by the cryogen-free approach this microscope provides access to new classes of experiments. Combining drift values much smaller than 1Å/h and stable tip conditions enable e.g. unsurpassed long-term spectroscopic SPM measurements.

Decoupling the strong mechanical vibrations induced by the pump of the closed cycle cooler represents a major technical challenge. Our design of the cryogen-free microscope effectively decouples the inherent mechanical vibrations to a level of state-of-the art low temperature SPM's utilizing cryogenic liquids.

References

[1]] patented, cf. Franz J. Giessibl, APL, Vol. 73, No. 26 (1998)

SP-ThP3 Surface Reconstruction for Accuracy Improvement in Nanoparticle Size Characterization.
James Su, N.N. Chu, C.T. Lin, P.L. Chen, M.H. Shiao, C.N. Hsiao, F.Z. Chen, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China

In this study compares the analytical results of atomic force microscopy (AFM) and scanning electron microscopy (SEM) for characterizing size distributions of various nanoparticles in the size range of (10 – 300) nm. Polymer nanospheres, mixture of colloidal gold and GaN quantum dots were characterized by both techniques. Both techniques were recalibrated with transfer standards traceable to the international metrology institute PTB where the combined uncertainty of measurement results were less than 1%. Average SEM values for mono-size dispersed particles of polymer and gold were slightly lower than the nominal values where AFM values were slightly higher on the contrary. Additional AFM deconvolution process has efficiently reduced the slight broadening of measurement results due to tip effects. Supported by comparisons to published data obtained on quantum dots of increasing diameters, the results show that the apparent size of small details appears to be larger than their actual dimension and the apparent distance between small objects may appear less than their actual dimension. The same method allows us to develop strategies to minimize the errors when the dimension of details is of less the order than the effective resolution of the operated SEM. Most of the size distributions were easily identified with AFM, and the modified average particle size for mono-size dispersed particles is in a good agreement with the nominal values. AFM characterization of nanoparticles using effective deconvolution process and statistical analysis software provides both accurate and rapid analysis for nanoparticle characterization.

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,¹ 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 biosensing² or sloughing off chemical warfare agents.³

¹ ACS Nano, **2014**, 8 (12), pp 12410–12417

² BioTechniques, Vol. 57, No. 1, July 2014, pp. 21–30

³ 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 MoTe₂ with Adsorbed Atoms and Molecules, Yao Zhou, E.J. Reed, Stanford University**

Of the Mo- and W- dichalcogenide monolayers, MoTe₂ is particularly interesting because it exhibits a small energy difference (approximately 31 meV per MoTe₂) 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 MoTe₂ 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 MoTe₂. 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_xW_{1-x}Te₂ 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 sp² 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 1st 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 1st 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].

1–W. Lu, P. Soukiassian, J. Boeckl “Graphene: fundamentals and functionalities” *MRS Bull.* **37**, 1119 (2012)

2–P. Soukiassian “Will graphene be the material of the 21th century?” *MRS Bull.* **37**, 1321 (2012)

3–V. Derycke, P. Soukiassian, F. Amy, Y.J. Chabal, M. D’angelo, H. Enriquez, M. Silly, “Nanochemistry at the atomic scale revealed in hydrogen-induced semiconductor surface metallization”, *Nature Mat.* **2**, 253 (2003)

4–P. Soukiassian, E. Wimmer, E. Celasco, Cl. Giallombardo, S. Bonanni, L. Vattuone, L. Savio, A. Tejada, M. Silly, M. D’angelo, F. Sirotti, M. Rocca “Hydrogen-induced nanotunnel opening within semiconductor subsurface” *Nature Com.* **4**, 2800 (2013)

5–P. Merino, M. Švec, J.I. Martinez, P. Jelinek, P. Lacovig, M. Dalmiglio, S. Lizzit, P. Soukiassian, J. Cernicharo, J.A. Martin-Gago “Graphene etching on SiC grains as a path to interstellar PAHs’ formation” *Nature Com.* **5**, 3054 (2014)

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/O₃ 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

[1] Zhiting Li; et al.; Nature Materials, 12, 925-931, (2013)

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 H₂O medium without external reducing agent. It was found that the deposited amount of palladium varied with pH, meanwhile, the bivalent Pd²⁺ 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 MoS₂ 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 (H₂O₂) and Cl⁻ and generate hypochlorous acid (HOCl). This is a short-lived and powerful diffusible oxidant strong oxidizer and could react with O²⁻ to produce OH⁻. 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, MoS₂ nanosheets and nanoparticles. However, detection of free radicals at cellular level is still a challenge.

In this attempt, layered molybdenum disulfide (MoS₂) were synthesized via hydrothermal method. SBA-15 polymer template were utilized during hydrothermal process to grow MoS₂ 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 MoS₂ crystal. Wet chemical exfoliation of MoS₂ were carried out in aqueous solution of Pluronic[®] F-127 having hydrophobic and hydrophilic chains. Pluronic[®] F-127 was used to bring down the buoyant density of MoS₂. 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 MoS₂ 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. MoS₂ 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 MoS₂ 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 MoS₂, 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 MoS₂ 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 MoS₂, enhancing its catalytic properties, (2) the binding energies of CO and dissociated H₂ increase by 0.3 eV in comparison to that on unsupported MoS₂, indicating stronger interactions, and (3) the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS₂. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syn gas on single-layer MoS₂ 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.

[1] D. Le, T. B. Rawal, and T. S. Rahman, *J. Phys. Chem. C* **118**, 5346 (2014).

*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.

[1]Cavallo, Francesca, et al. "Exceptional Charge Transport Properties of Graphene on Germanium." *ACS nano* 8.10 (2014): 10237-10245.

[2] R. M. Jacobberger, et al. "Oriented Bottom-Up Growth of Armchair Graphene Nanoribbons on Germanium." *Nature Comm.*, under review.

[3] R. Rojas, et. al "Passivation of Ge by Graphene.", in process.

Scanning Probe Microscopy Focus Topic

Room: 212A - Session SP+AS+MI+NS+SS-FrM

Probe-Sample Interactions

Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

8:20am **SP+AS+MI+NS+SS-FrM1 Direct Visualization of Magnetoelectric Domains in Hexagonal Manganites**, *Weida Wu*, Rutgers University **INVITED**

Multiferroics are materials with coexisting magnetic and ferroelectric orders, where the cross-coupling between two ferroic orders can result in strong magnetoelectric effects [1-4]. Therefore, it is of both fundamental and technological interest to visualize cross-coupled magnetoelectric domains and domain walls in multiferroics. Recently, intriguing topological defects with six interlocked structural antiphase and ferroelectric domains merging into a vortex core were revealed in multiferroic hexagonal REMnO₃ (R=rare earths) [5, 6]. Many emergent phenomena, such as enhanced conduction and unusual piezoelectric response, were observed in charged ferroelectric domain walls protected by these topological defects [7-9]. More interestingly, alternating uncompensated magnetic moments were discovered at coupled structural antiphase and ferroelectric domain walls in hexagonal manganites using cryogenic magnetic force microscopy (MFM) [10], which demonstrates the cross-coupling between ferroelectric and magnetic orders. Here we present the application of a magnetoelectric force

microscopy (MeFM) technique that combines MFM with *in situ* modulating high electric fields. This new microscopy technique allows us to image the magnetoelectric response of the domain patterns in hexagonal manganites directly [11, 12]. We find that this response changes sign at each structural domain wall, a result that is corroborated by symmetry analysis and phenomenological modelling, and provides compelling evidence for a lattice-mediated magnetoelectric coupling. The direct visualization of magnetoelectric domains at mesoscopic scales opens up explorations of emergent phenomena in multifunctional materials with multiple coupled orders.

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- [11] Y. Geng, and W. Wu, *Rev. Sci. Instrum.* 85, 053901 (2014).
- [12] Y. Geng et al., *Nat. Mater.* 13, 163 (2014).

9:00am **SP+AS+MI+NS+SS-FrM3 Kelvin Probe Force Microscopy Studies of Magnetic Atoms on Ultrathin Insulating MgO Film**, *Taeyoung Choi, W. Paul, S. Baumann, C.P. Lutz, A. Heinrich*, IBM Almaden Research Center

The interplay of single atoms and their local environment on surfaces influences the atoms' spin excitations and dynamics, which can be utilized in progress toward atomic-scale memory and quantum information processing. We find that spin-excitation energy of Fe atoms on an insulating MgO film shifts depending on the tip-to-atom separation. This may be attributed to the electric field across the tunneling junction, as well as to local charge and structural changes around the atom. The Kelvin Probe Force Microscopy (KPFM) has been very useful tool to measure changes of local contact potential differences between a tip and a sample at the atomic level [1]. In this talk, we employ tuning fork KPFM/STM and show preliminary results on the charge character and spin excitations of Fe atoms.

This work is supported by grants from IBM.

- [1] Leo Gross et al., *Phys. Rev. B* 90, 155455 (2014).

9:20am **SP+AS+MI+NS+SS-FrM4 Nanoscale Schottky Barrier Height Mapping Utilizing Ballistic Electron Emission Microscopy**, *C. Durcan, W. Nolting*, College of Nanoscale Science and Engineering, *Vincent LaBella*, SUNY Polytechnic Institute

The Schottky barrier is the electrostatic barrier between a metal and a semiconductor that results in rectification and is found in many types of devices such as source drain contacts to sub 20-nm-node transistors. Naturally, the Schottky barrier height can fluctuate across the interface due to variations in bonding, compositional fluctuations in the materials, and the presence of defects. However measuring and mapping these electrostatic fluctuations is impossible with bulk IV or CV techniques. This presentation will demonstrate how the Schottky barrier height can be mapped to nanoscale dimensions using an STM based technique called ballistic electron emission microscopy (BEEM). The STM tip is positioned on a regularly spaced grid and BEEM spectra are acquired from which the barrier height can be extracted. A map and histogram is then generated by measuring and fitting thousands of these spectra. These maps provide detailed insight into the electrostatic fluctuations occurring at the buried interface with nanoscale resolution that cannot be accomplished with other bulk measurements.

9:40am **SP+AS+MI+NS+SS-FrM5 Electron Transport Studies of Metal Films Utilizing Ballistic Electron Emission Microscopy**, *Christopher Durcan*, SUNY College of Nanoscale Science and Engineering, *V. LaBella*, SUNY Polytechnic Institute

Understanding scattering of electrons in nanometer thick metal films is of fundamental and technological importance. One method to study electron scattering is with ballistic electron emission microscopy (BEEM), which is a three terminal STM based technique that measures both scattering through a metal film and the Schottky barrier height for metal-semiconductor junctions with both nanometer spatial resolution and meV energy resolution. This presentation will describe our work at understanding the

relationship between the metal resistivity and the electron scattering lengths measured with BEEM by exploring metals with a range of resistivities from Ag (1.7 $\mu\Omega\text{-cm}$) to Cr (12.6 $\mu\Omega\text{-cm}$). In addition, nanoscale mapping of the Schottky barrier height of these metals to silicon will also be presented to understand the spatial uniformity of the transport.

10:00am **SP+AS+MI+NS+SS-FrM6 Utilizing Ballistic Electron Emission Microscopy to Study Sidewall Scattering of Electrons**, *Westly Nolting, C. Durcan, R. Balsano*, College of Nanoscale Science and Engineering, University of Albany, *V. LaBella*, College of Nanoscale Science and Engineering, SUNY Polytechnic Institute

Sidewall scattering of electrons within aggressively scaled metallic interconnects increases the resistance since the mean free path (~40 nm) is larger than the dimensions of the material. One method to study hot-electron scattering in nm-thick metallic films is Ballistic Electron Emission Microscopy (BEEM), which is an STM based technique. In this work, we perform BEEM scattering measurements on lithographically patterned fin structures with a Schottky diode interface to determine its ability to measure sidewall scattering. This is accomplished by acquiring BEEM spectra on a regularly spaced grid and fitting the results to determine both the Schottky barrier height and the slope of the spectra. The slope of the spectra is related to the scattering in the film and interface. The position of fin structures are then determined by mapping both the Schottky height and slope over a square micron to observe scattering at the interface caused by the patterned structures. The poster will discuss the fabrication of the patterned 50-nm-pitched sidewall structures that are used for mapping the sidewall scattering. In addition, it will present the preliminary BEEM measurements on these structures.

10:20am **SP+AS+MI+NS+SS-FrM7 Progress in Nanoscale Magnetic Resonance Imaging**, *Daniel Rugar*, IBM Research Division **INVITED**

Nuclear magnetic resonance (NMR) is the basis of powerful spectroscopic and imaging techniques, but extension to nanoscale samples has been a longstanding challenge due to the insensitivity of conventional detection methods. We are exploring the use of individual, near-surface nitrogen-vacancy (NV) centers in diamond as atomic-size magnetometers to detect proton NMR in organic material located external to the diamond. Using a combination of electron spin echoes and proton spin manipulation, the NV center senses the nanotesla field fluctuations from the protons, enabling both time-domain and spectroscopic NMR measurements on the nanometer scale. By scanning a small polymer test object past a near-surface NV center, we have recently demonstrated proton magnetic resonance imaging (MRI) with spatial resolution on the order of 10 nm.

One key issue in NV-NMR experiments is the loss of spin coherence when the NV center is located near the diamond surface. Although this loss of coherence is frequently attributed to the effect of magnetic noise emanating from unpaired spins on the diamond surface, we will show evidence that electric field noise from fluctuating surface charge may be the dominant factor.

Work performed in collaboration with M. Kim, H. J. Mamin, M. H. Sherwood, C. T. Rettner, K. Ohno, and D. D. Awschalom

11:00am **SP+AS+MI+NS+SS-FrM9 Reactive Intermediates Created and Analyzed by Scanning Probe Microscopy**, *Bruno Schuler*, IBM Research - Zurich, Switzerland, *N. Pavliček*, IBM Research - Zurich, *S. Collazos*, CIQUS, Universidade de Santiago de Compostela, *N. Moll*, *S. Fatayer*, IBM Research - Zurich, *D. Pérez*, *E. Guitán*, CIQUS, Universidade de Santiago de Compostela, *G. Meyer*, IBM Research - Zurich, *D. Peña*, CIQUS, Universidade de Santiago de Compostela, *L. Gross*, IBM Research - Zurich

Reactive intermediates are involved in most chemical transformations. However, their characterization is a great challenge because of their short lifetime and high reactivity.

Here we report on the creation of single radicals and diradicals on a thin insulating surface by means of atomic manipulation. Importantly, the thin insulating film facilitates the stabilization of these reactive intermediates at cryogenic temperatures. The molecules were characterized by atomic-resolution atomic force microscopy (AFM) imaging with a CO functionalized tip [1] and scanning tunneling microscopy (STM) orbital imaging [2]. We show that the molecules' reactivity is preserved even at low temperatures by performing different on-surface reactions by atomic manipulation. As an example, the generation of aryne is discussed, a very reactive intermediate caught for the first time [3].

References:

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[3] N. Pavliček et al. On-surface generation and imaging of arynes by atomic force microscopy. (submitted)

11:20am **SP+AS+MI+NS+SS-FrM10 The Negative Stiffness and Positive Damping of Squeezed Air in Dynamic Atomic Force Microscopy**, x. Yu, M. Tao, Nancy Burnham, Worcester Polytechnic Institute

By oscillating a micro-sized cantilever beam at a certain frequency and observing its interaction with the sample surface, dynamic mode atomic force microscopy (AFM) has gained attention for characterizing mechanical properties of a variety of materials at the micro and nano scales. The thin air film, confined between the oscillating cantilever beam and the stationary sample surface, causes the so-called "squeeze-film effect" when the gap between the two boundaries is less than a hundred microns. Although studies have shown that the squeeze film can act as a spring and a damper in accelerometers and microelectromechanical systems [1], the influence of the squeeze-film effect on the dynamics of an AFM cantilever has not been previously explored, to the authors' knowledge. In this project, the stiffness and damping properties of the squeeze film between an oscillating AFM cantilever and a glass slide were calculated from the cantilevers' amplitude and phase responses as recorded by the AFM digital system. The smaller the cantilever-sample gap, the larger the absolute values of the stiffness and the damping of the squeeze film. Results from different cantilevers (consequently having different spring constants and resonant frequencies) indicated that the air film exhibited **negative stiffness and positive damping**, with normalized changes from free values of up to 40%. Theoretical analysis was conducted using an equivalent-circuit model [2] along with the phasor diagram, and the derived stiffness and damping values were in excellent agreement with the experimental ones. Interestingly, a rotation angle between 20° and 30° in the fit of the data to the model reveals a phase *lead* of the squeeze-film damping before the usual air damping when the cantilever is far from a surface: the maximum squeeze-film damping occurs before the maximum velocity of the cantilever because air becomes less dense as it rushes out of the tip-sample gap. The surprising sign of the stiffness is thus explained by the phase lead. Future work includes incorporating the squeeze-film effect into more accurate measurements of a material's stiffness and damping properties using dynamic AFM.

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Jensen, L.: NS+AS+SP-MoA7, 4

- Jeon, S.: SP+BI+NS+SS+TF-ThA10, **20**
 Jiang, N.: NS+AS+SP-MoA7, **4**
 Jin, M.: NS+AS+SP-MoA3, **4**
 Jung, M.: SP+2D+AS+NS+SS-WeA8, **16**
— K —
 Kalanyan, B.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
 Kang, J.H.: NS+SP-TuM1, **6**
 Karim, A.:
 2D+EM+MC+MI+NS+SP+SS+TF-TuA7, **9**
 Kim, H.: 2D+EM+MC+MI+NS+SP+SS+TF-TuA11, **9**
 Kim, T.H.: SP+2D+AS+NS+SS-WeA12, **17**
 Kim, T.-H.: SP+2D+AS+NS+SS-WeA4, **16**
 Kim, Y.: SP+BI+NS+SS+TF-ThA8, **19**
 Kimes, W.A.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
 Kimmel, G.A.: SP+AS+NS+SS-ThM4, **18**
 Kimura, K.: SP+AS+NS+SS-WeM12, **12**
 Kis, A.: 2D+EM+IS+MC+NS+SP+SS-WeA2, **14**
 Knowles, T.P.J.: NS+AS+SP-MoA1, **4**
 Ko, C.: NS+AS+SP-MoA8, **4**
 Kobayashi, K.: SP+AS+NS+SS-WeM12, **12**
 Koeble, J.: SP-ThP2, **21**
 Kolmakov, A.:
 2D+EM+NS+PS+SP+SS+TF-MoM8, **2**
 Kondo, T.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **22**
 Kosaka, Y.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **22**
 Krueger, P.: SP+AS+NS+SS-WeM3, **11**
 Kuk, Y.: SP+2D+AS+NS+SS-WeA1, **16**
 Kummel, A.C.:
 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**
 Kungas, R.: SP+AS+NS+SS-ThM6, **18**
 Kwak, I.J.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**
— L —
 LaBella, V.: SP+AS+MI+NS+SS-FrM4, **24**;
 SP+AS+MI+NS+SS-FrM5, **24**;
 SP+AS+MI+NS+SS-FrM6, **24**
 Labuda, A.: SP+AS+NS+SS-WeM13, **13**
 Lagally, M.G.: 2D+EM+IS+NS+PS+SP+SS-FrM10, **23**
 Lai, K.: SP+AS+NS+SS-WeM10, **12**
 Lashuel, H.: NS+AS+SP-MoA1, **4**
 Lauderbach, L.M.: NS+SP-TuM10, **7**
 Le, D.: 2D+EM+IS+NS+PS+SP+SS-FrM9, **23**
 Lee, K.: SP+2D+AS+NS+SS-WeA8, **16**
 Lee, S.H.: NS+SP-TuM1, **6**
 Lee, S.-H.: SP+2D+AS+NS+SS-WeA4, **16**
 Lee, W.K.:
 2D+EM+MC+MI+NS+SP+SS+TF-TuA3, **9**
 Leinen, P.L.: SP+AS+NS+SS-WeM3, **11**
 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**;
 SP+AS+NS+SS-WeM6, **12**
 Lim, H.: SP+BI+NS+SS+TF-ThA8, **19**
 Lin, C.T.: SP-ThP3, **21**
 Lin, Y.-C.: 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
 Liu, D.-J.: SP+BI+NS+SS+TF-ThA8, **19**
 Liu, H.: 2D+EM+IS+NS+PS+SP+SS-FrM5, **22**
 Liu, L.: SP+2D+AS+NS+SS-WeA7, **16**
 Liu, X.: 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**; 2D+MN+NS+SP+SS+TF-WeM12, **11**
 Lu, F.: NS+AS+SP-MoA3, **4**
 Luna, L.E.: NS+SP-TuM3, **6**
 Lutz, C.P.: SP+2D+AS+NS+SS-WeA9, **17**;
 SP+AS+MI+NS+SS-FrM3, **24**; SP-ThP1, **21**
 Lyubinetzky, I.: SP+AS+NS+SS-ThM4, **18**
— M —
 Ma, C.: SP+2D+AS+NS+SS-WeA7, **16**
 Maboudian, R.: NS+SP-TuM3, **6**
 Maksymovych, P.: SP+BI+NS+SS+TF-ThA10, **20**
 Mandrus, D.: SP+BI+NS+SS+TF-ThA6, **19**
 Manoharan, H.C.: SP+AS+NS+SS-WeM1, **11**
 Marinov, K.M.:
 2D+EM+IS+MC+NS+SP+SS-WeA2, **14**
 Mariolle, D.: SP+AS+NS+SS-WeM4, **12**
 Martinez, J.:
 2D+EM+MC+MI+NS+SP+SS+TF-TuA4, **9**
 Maslar, J.E.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
 Matsuyama, H.:
 2D+EM+IS+MC+NS+SP+SS-WeA12, **15**
 McDonnell, S.:
 2D+EM+IS+MC+NS+SP+SS-WeA8, **14**
 McGuire, M.: SP+2D+AS+NS+SS-WeA3, **16**
 McKeown, J.T.: NS+SP-TuM2, **6**
 Mende, P.: 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
 Meyer, G.: SP+AS+MI+NS+SS-FrM9, **24**
 Molitor, S.: SP-ThP2, **21**
 Moll, N.: SP+AS+MI+NS+SS-FrM9, **24**
 Movva, H.C.P.:
 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**
 Mowll, T.R.: 2D+EM+NS+PS+SP+SS+TF-MoM2, **1**
 Mueller, T.: NS+AS+SP-MoA9, **5**
 Muller, T.: NS+AS+SP-MoA1, **4**
— N —
 Nakamura, J.: 2D+EM+IS+MC+NS+SP+SS-WeA12, **15**;
 2D+EM+IS+NS+PS+SP+SS-FrM7, **22**;
 2D+MN+NS+SP+SS+TF-WeM11, **10**
 Nath, A.: 2D+EM+NS+PS+SP+SS+TF-MoM3, **1**
 Natterer, F.D.: 2D+MN+NS+SP+SS+TF-WeM10, **10**
 Neek-Amal, M.: 2D+MN+NS+SP+SS+TF-WeM3, **10**
 Nolting, W.: SP+AS+MI+NS+SS-FrM4, **24**;
 SP+AS+MI+NS+SS-FrM6, **24**
 Nonnenmann, S.S.: SP+AS+NS+SS-ThM6, **18**
 Nyakiti, L.O.: 2D+EM+NS+PS+SP+SS+TF-MoM3, **1**
— O —
 Ogletree, D.: NS+AS+SP-MoA8, **4**
 Oh, J.: SP+BI+NS+SS+TF-ThA8, **19**
 Oh, T.: SP+AS+NS+SS-ThM6, **18**
 Oleynik, I.I.: 2D+EM+IS+MC+NS+SP+SS-WeA1, **14**; 2D+MN+NS+SP+SS+TF-WeM1, **10**
 Ong, E.W.: 2D+EM+NS+PS+SP+SS+TF-MoM2, **1**
 Ooki, W.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **22**
 Orzali, T.: 2D+EM+NS+PS+SP+SS+TF-MoM4, **1**
 Osgood, Jr., R.M.: SP+BI+NS+SS+TF-ThA9, **20**
 Ovchinnikov, D.:
 2D+EM+IS+MC+NS+SP+SS-WeA2, **14**
— P —
 Pang, Z.: SP+AS+NS+SS-ThM5, **18**
 Park, C.: SP+AS+NS+SS-WeM6, **12**
 Park, J.: SP+2D+AS+NS+SS-WeA7, **16**;
 SP+2D+AS+NS+SS-WeA8, **16**;
 SP+AS+NS+SS-WeM6, **12**
 Park, J.H.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**
 Park, K.: SP+AS+NS+SS-ThM3, **18**
 Paul, W.: SP+2D+AS+NS+SS-WeA9, **17**;
 SP+AS+MI+NS+SS-FrM3, **24**; SP-ThP1, **21**
 Pavliček, N.: SP+AS+MI+NS+SS-FrM9, **24**
 Paw U, C.K.B.: NS+SP-TuM11, **7**
 Peeters, F.: 2D+MN+NS+SP+SS+TF-WeM3, **10**
 Peña, D.: SP+AS+MI+NS+SS-FrM9, **24**
 Perez, C.: SP+AS+NS+SS-ThM6, **18**
 Pérez, D.: SP+AS+MI+NS+SS-FrM9, **24**
 Perriot, R.: 2D+EM+IS+MC+NS+SP+SS-WeA1, **14**; 2D+MN+NS+SP+SS+TF-WeM1, **10**
 Petrik, N.G.: SP+AS+NS+SS-ThM4, **18**
 Piglosiewicz, B.: SP-ThP2, **21**
 Podlesak, D.: NS+SP-TuM10, **7**
 Potapenko, D.V.: SP+BI+NS+SS+TF-ThA9, **20**
 Pouch, S.: SP+AS+NS+SS-WeM4, **12**
 Pozzi, E.: NS+AS+SP-MoA7, **4**
 Proksch, R.: SP+AS+NS+SS-WeM13, **13**
— Q —
 Qin, S.: SP+2D+AS+NS+SS-WeA12, **17**
— R —
 Rack, P.D.: NS+SP-TuM2, **6**
 Rahman, T.S.: 2D+EM+IS+NS+PS+SP+SS-FrM9, **23**
 Ramalingam, G.: SP+BI+NS+SS+TF-ThA3, **19**
 Rawal, T.B.: 2D+EM+IS+NS+PS+SP+SS-FrM9, **23**
 Reed, E.J.: 2D+EM+IS+NS+PS+SP+SS-FrM2, **22**
 Reinecke, T.L.:
 2D+EM+IS+NS+PS+SP+SS-FrM1, **22**
 Reinke, P.: SP+BI+NS+SS+TF-ThA3, **19**
 Renault, O.J.:
 2D+EM+MC+MI+NS+SP+SS+TF-TuA11, **9**
 Rigg, P.: NS+SP-TuM10, **7**
 Ringstrand, B.: NS+SP-TuM10, **7**
 Robertson, J.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **14**
 Robinson, J.A.:
 2D+EM+NS+PS+SP+SS+TF-MoM9, **2**
 Robinson, J.T.:
 2D+EM+IS+NS+PS+SP+SS-FrM1, **22**;
 2D+EM+MC+MI+NS+SP+SS+TF-TuA3, **9**
 Robinson, Z.R.:
 2D+EM+NS+PS+SP+SS+TF-MoM1, **1**;
 2D+EM+NS+PS+SP+SS+TF-MoM2, **1**
 Rohlfing, M.R.: SP+AS+NS+SS-WeM3, **11**
 Rojas Delgado, R.:
 2D+EM+IS+NS+PS+SP+SS-FrM10, **23**
 Romming, N.: SP+2D+AS+NS+SS-WeA9, **17**
 Rousseau, R.: SP+AS+NS+SS-ThM4, **18**
 Rowley, J.T.: 2D+MN+NS+SP+SS+TF-WeM4, **10**
 Ruan, W.Y.: 2D+MN+NS+SP+SS+TF-WeM10, **10**
 Rugar, D.: SP+AS+MI+NS+SS-FrM7, **24**
 Ruggeri, F.S.: NS+AS+SP-MoA1, **4**
— S —
 Sahin, O.: NS+SP-TuM5, **7**
 Salmeron, M.B.: NS+AS+SP-MoA8, **4**
 Sanchez Perez, J.R.:
 2D+EM+IS+NS+PS+SP+SS-FrM10, **23**
 Sankaran, R.M.: NS+SP-TuM4, **6**

- Sanne, A.M.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 14
- Satpathy, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Schroeder, D.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 23
- Schuck, P.: NS+AS+SP-MoA8, 4
- Schuler, B.: SP+AS+MI+NS+SS-FrM9, 24
- Seal, S.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 23
- Seideman, T.: NS+AS+SP-MoA7, 4
- Seifert, S.: NS+SP-TuM10, 7
- Selvan, T.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 23
- Sheehan, P.E.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 22;
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 9
- Shiao, M.H.: SP-ThP3, 21
- 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, 11
- Sinclair, N.: NS+SP-TuM10, 7
- Singh, C.V.: NS+SP-TuM12, 7
- Smyth, C.M.: 2D+EM+IS+MC+NS+SP+SS-WeA8, 14
- Sohn, S.-D.: SP+2D+AS+NS+SS-WeA8, 16
- Soukiassian, G.:
2D+EM+IS+NS+PS+SP+SS-FrM3, 22
- 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
- Stenger, B.H.: NS+SP-TuM11, 7
- Stine, R.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 22
- Stolbov, S.: 2D+EM+IS+NS+PS+SP+SS-FrM6, 22
- Stranick, S.J.: 2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Stroschio, J.A.: 2D+MN+NS+SP+SS+TF-WeM10, 10
- Su, J.Y.: SP-ThP3, 21
- Suh, J.: NS+AS+SP-MoA8, 4
- Sumpster, B.: SP+BI+NS+SS+TF-ThA10, 20
- Sun, Y.: NS+SP-TuM12, 7
- **T** —
- Tang, S.: SP+BI+NS+SS+TF-ThA6, 19
- Tao, M.: SP+AS+MI+NS+SS-FrM10, 25
- Tautz, F.S.T.: SP+AS+NS+SS-WeM3, 11
- Temirov, R.T.: SP+AS+NS+SS-WeM3, 11
- Thibado, P.: 2D+MN+NS+SP+SS+TF-WeM3, 10
- Thiel, P.A.: SP+BI+NS+SS+TF-ThA8, 19
- Thron, A.: NS+AS+SP-MoA8, 4
- Tieckelmann, R.:
2D+EM+NS+PS+SP+SS+TF-MoM4, 1
- Tongay, S.: NS+AS+SP-MoA8, 4
- Troepfner, C.: SP-ThP2, 21
- Tsoi, S.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 22
- Tyagi, P.: 2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- **U** —
- Uchida, Y.: 2D+MN+NS+SP+SS+TF-WeM11, 10
- **V** —
- Valentin, M.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA4, 9
- Van Bui, H.: NS+SP-TuM13, 7
- van Buuren, T.: NS+SP-TuM10, 7
- van der Zande, A.M.:
2D+EM+NS+PS+SP+SS+TF-MoM5, 2
- Van Duyn, R.P.: NS+AS+SP-MoA7, 4
- van Ommen, J.R.: NS+SP-TuM13, 7
- van Zijll, M.S.: NS+SP-TuM11, 7
- Vanfleet, R.: 2D+MN+NS+SP+SS+TF-WeM4, 10
- Ventrice, Jr., C.A.:
2D+EM+NS+PS+SP+SS+TF-MoM2, 1
- Viani, M.: SP+AS+NS+SS-WeM13, 13
- Vishwanath, S.:
2D+EM+IS+MC+NS+SP+SS-WeA7, 14;
2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Vlassioug, I.: SP+2D+AS+NS+SS-WeA3, 16
- Vohs, J.: SP+AS+NS+SS-ThM6, 18
- Voiry, D.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA11, 9
- **W** —
- Wagner, C.W.: SP+AS+NS+SS-WeM3, 11
- Wagner, M.: NS+AS+SP-MoA9, 5
- Walen, H.: SP+BI+NS+SS+TF-ThA8, 19
- Wallace, R.M.:
2D+EM+IS+MC+NS+SP+SS-WeA8, 14
- Walters, D.: SP+AS+NS+SS-WeM13, 13
- Walton, S.G.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 22
- Wan, J.: 2D+EM+IS+MC+NS+SP+SS-WeA11, 15
- Wang, F.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA9, 9
- Wang, Z.: 2D+MN+NS+SP+SS+TF-WeM5, 10
- Wang, Z.-T.: SP+AS+NS+SS-ThM4, 18
- Watkins, E.: NS+SP-TuM10, 7
- Weber-Bargioni, A.: NS+AS+SP-MoA8, 4
- Weitering, H.H.: SP+2D+AS+NS+SS-WeA12, 17
- Wheeler, V.D.:
2D+EM+NS+PS+SP+SS+TF-MoM1, 1
- Whitener, K.E.:
2D+EM+IS+NS+PS+SP+SS-FrM1, 22;
2D+EM+MC+MI+NS+SP+SS+TF-TuA3, 9
- Willey, T.M.: NS+SP-TuM10, 7
- Willman, J.T.:
2D+EM+IS+MC+NS+SP+SS-WeA1, 14
- Wind, J.: 2D+MN+NS+SP+SS+TF-WeM13, 11
- Wood, J.D.: 2D+MN+NS+SP+SS+TF-WeM12, 11
- Wu, J.: NS+AS+SP-MoA8, 4
- Wu, R.: SP+2D+AS+NS+SS-WeA12, 17
- Wu, S.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Wu, W.: SP+AS+MI+NS+SS-FrM1, 23
- Wu, Y.: NS+SP-TuM2, 6
- Wyrick, J.: 2D+MN+NS+SP+SS+TF-WeM10, 10
- **X** —
- Xia, Y.: SP+AS+NS+SS-ThM3, 18
- Xing, H.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 14;
2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- Xu, X.D.: 2D+EM+NS+PS+SP+SS+TF-MoM9, 2
- **Y** —
- Yamada, H.: SP+AS+NS+SS-WeM12, 12
- Yang, K.: SP+2D+AS+NS+SS-WeA9, 17
- Yang, Y.: 2D+MN+NS+SP+SS+TF-WeM13, 11; SP+AS+NS+SS-WeM5, 12
- Yao, A.: SP+AS+NS+SS-WeM12, 12
- Yazyev, O.V.:
2D+EM+IS+MC+NS+SP+SS-WeA3, 14
- Yeom, H.W.: SP+2D+AS+NS+SS-WeA4, 16
- Yi, J.: SP+BI+NS+SS+TF-ThA6, 19
- Yoon, M.: SP+AS+NS+SS-WeM6, 12
- Yoon, Y.: SP+AS+NS+SS-ThM4, 18
- Young, A.F.:
2D+EM+MC+MI+NS+SP+SS+TF-TuA1, 9
- Yu, x.: SP+AS+MI+NS+SS-FrM10, 25
- Yulaev, A.: 2D+EM+NS+PS+SP+SS+TF-MoM8, 2
- **Z** —
- Zhang, J.: NS+AS+SP-MoA8, 4
- Zhang, P.P.: SP+BI+NS+SS+TF-ThA1, 19
- Zhang, X.: 2D+MN+NS+SP+SS+TF-WeM13, 11; SP+2D+AS+NS+SS-WeA3, 16
- Zhang, X.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, 22
- Zhang, Y.: NS+AS+SP-MoA8, 4;
SP+2D+AS+NS+SS-WeA12, 17
- Zhang, Z.: SP+AS+NS+SS-ThM3, 18
- Zhao, Y.: 2D+MN+NS+SP+SS+TF-WeM10, 10
- Zhitenev, N.B.: 2D+MN+NS+SP+SS+TF-WeM10, 10
- Zhou, Y.: 2D+EM+IS+NS+PS+SP+SS-FrM2, 22
- Zhu, H.: 2D+EM+IS+MC+NS+SP+SS-WeA8, 14
- Zhu, J.: SP+AS+NS+SS-ThM6, 18
- Zhu, K.: SP+AS+NS+SS-ThM3, 18
- Zhu, Z.: SP+AS+NS+SS-ThM4, 18