Atom Probe Tomography Focus Topic
Room: 230A - Session AP+AS+MC+MI+NS-MoM

Atom Probe Tomography of Nanomaterials

Moderator: Daniel Perea, Pacific Northwest National Laboratory

8:20am **AP+AS+MC+MI+NS-MoM1 Correlative Multi-scale Analysis of Nd-Fe-B Permanent Magnet**, ***Taisuke Sasaki***, *T. Ohkubo, K. Hono*, National Institute for Materials Science (NIMS), Japan **INVITED**

(Nd,Dy)–Fe–B based sintered magnets are currently used for traction motors and generators of (hybrid) electric vehicles because of their excellent combination of maximum energy product and coercivity. However, there is a strong demand to achieve high coercivity without using Dy due to its scarce natural resources and high cost. In Nd-Fe-B sintered magnets, thin Nd-rich grain boundary (GB) phase is a key microstructural feature affecting the coercivity. Although Nd-rich phases, e.g. Nd-rich oxides and metallic Nd, located at grain boundary triple junctions affect the formation of the Nd-enriched grain boundary phase during post-sinter annealing, their phase constitution, distribution and orientation relationships are still under debate.

This presentation will introduce examples of advanced characterization works to establish the global microstructural feature that controls the coercivity of Nd-Fe-B sintered magnets, e.g. the clarification of phase constitution and distribution of Nd-rich phases at the grain boundaries by correlative SEM and TEM characterization, and the identification of the structure and chemistry of thin Nd-rich grain boundary phases by high resolution HAADF-STEM and 3D atom probe. We found the coercivity decrease by carbon impurity can be explained by the decrease in the RE (RE: Rare earth) content in the thin Nd-rich grain boundary phase.

9:00am **AP+AS+MC+MI+NS-MoM3 Atom-Probe Tomography of Materials with Dimensions in the Nanometer Range**, ***Dieter Isheim***, Northwestern University **INVITED**

Nanometer-sized materials and particles seem to naturally lend themselves for investigation by atom-probe tomography (APT) which provides analytical imaging with subnanometer-scale spatial resolution in three dimensions. The material's characteristic dimensions may already be close to the one required to produce the electric field necessary for analysis by field-evaporation in an atom-probe tomograph and thus analysis seems straight forward. In practice, however, controlled manipulation and positioning of these nanoparticles or nanowires for APT analysis proves challenging since the support structure of an APT tip must be strong enough to resist the mechanical stresses exerted by the high electric fields involved. Additionally, the nanoparticles should ideally not be altered or damaged in the preparation process. These requirements can be met by modern processing techniques that combine suitable deposition methods for packaging nanoparticles in structures that are either ready for analysis, or suitable for subsequent APT tip preparation by a standard technique. Focused-ion-beam (FIB) microscopes equipped with a micro- or nanomanipulator and gas injection systems for electron- or ion-beam induced deposition provide a versatile platform for packaging, cutting, joining, and manipulating nanostructured materials, and thus to capture and target nanoparticles or specific microstructural features for APT analysis. This presentation explores these techniques to characterize a variety of nanometer sized and nanostructured materials, including nanodiamond particles and catalytically grown silicon nanowires.

9:40am **AP+AS+MC+MI+NS-MoM5 Exploring Atom Probe Tomography for Energy Storage and Conversion Materials**, ***Pritesh Parikh***, University of California, San Diego, *A. Devaraj*, Pacific Northwest National Laboratory, *S. Meng*, University of California, San Diego

The Sun forms the largest and most abundant source of energy on earth, yet it is not exploited to its full potential. Solar energy is a burgeoning field with a real chance to replace fossil fuels. The intermittent presence of sunlight can be mitigated by combining energy conversion devices such as solar panels with energy storage devices, namely Li ion batteries. A true solution is possible with the integration of both solar panels and batteries. With the general impetus towards adopting renewable sources for large scale energy storage and supply, fundamental studies on solar panels and batteries will provide new clues to design the next generation of energy devices. A Perovskite solar cell is one such technology that has the potential of high efficiency and low processing costs but a clear understanding of the role of different materials and their individual interactions is still lacking. The ability to identify and understand interfaces and multiple layers in a complex device such as solar cells and batteries is the need of the hour. Here we report on laser assisted atom probe tomography of energy storage and conversion devices to identify the spatial distribution of the elements comprising the various layers and materials. Recent progress and significant challenges for preparation and study of perovskite solar cells and battery materials using laser assisted atom probe tomography will be discussed. This opens up new avenues to understand complex mutli-layer systems at the atomic scale and provide a nanoscopic view into the intricate workings of energy materials.

10:00am **AP+AS+MC+MI+NS-MoM6 Atom Probe Tomography of Pt-based Nanoparticles**, ***Katja Eder***, *P.J. Felfer, J.M. Cairney*, The University of Sydney, Australia

Pt nanoparticles are commonly used as catalysts in fuel cells. There are a lot of factors which influence the activity of a catalyst, including the surface structure and geometry [1], d-band vacancy of the metal catalyst [2], the type of metal oxide support [3] and the oxidation state of the surface [4]. It is not yet fully understood in which way these factors influence the activity of the catalyst, since it is experimentally very difficult to get atomic scale information about the distribution of the atoms within such particle with conventional methods like transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunnelling microscopy (STM) and others. Models available which try to explain the structure-activity relationships therefore vary widely and there is much debate in the scientific literature about the underlying mechanisms of catalysis. For this reason it is crucial to conduct more research with methods that are able to obtain chemical information with a resolution on the atomic scale. In the past few years atom probe tomography (APT) has successfully been used in several studies to analyse nanoparticles [4-6]. APT provides a 3D reconstruction of the original specimen, which gives information about the chemical composition and the microstructure at a very high resolution. This method will enable us to have a closer look at the surface and interfaces as well as the composition of individual nanoparticles and solute atoms. In this talk we will present APT results of Pt nanoparticles, describing our efforts to prepare specimens with a reasonable yield and improved throughput compared to earlier studies, as well as some of the approaches used to overcome the difficulties that this challenge presents.

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[2] M.-K. Min, J. Cho, K. Cho, H. Kim, Electrochimica Acta, 45 (2000) 4211-4217.

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10:40am **AP+AS+MC+MI+NS-MoM8 APT & TEM Observations on Local Crystallization of NbO_2 used in Switching Devices**, *J.-H. Lee*, Pohang University of Science and Technology (POSTECH), Samsung Electronics, Republic of Korea, *J.-B. Seol*, ***C.-G Park***, Pohang University of Science and Technology (POSTECH), National Institute for Nanomaterials Technology (NINT), Republic of Korea **INVITED**

Threshold switching is the basis of electrical or thermal-driven phase change mechanism of oxide layer. That is, some oxide can change their conductivity from the level of insulators to that of metals with above certain current density. Although the mechanism responsible for threshold switching is not fully understood at present, it can be used as a switching device for the solution of sneak leakage problem. In order to apply the bipolar switching materials as the active layer of Resistive-switching Random Access Memory (RRAM), selection device which can minimize the sneak leakage current is needed. Among various candidates, we chose Nb-oxide for the selection device due to its superior compatibility with semiconductor structure. We have elucidated the mechanism of threshold switching of the amorphous NbO_2 layer by using in-situ transmission electron microscopy (TEM) technique combined with atom probe tomography (APT).

In this study, we proved that through an ex-situ experiment using TEM the threshold switching of amorphous NbO_2 accompanies local crystallization. The change in I-V characteristics after electroforming was examined by evaluating the concentration profile. APT combined with in-situ TEM probing technique was performed to understand the threshold switching in

amorphous NbO_2. The local crystallization in amorphous NbO_2 was validated by the observed difference in time-of-flight (ToF) between amorphous and crystalline NbO_2. We concluded that the slower ToF of amorphous NbO_2 (a-NbO_2) compared to that of crystalline NbO2 (c-NbO_2) is due to the resistivity difference and trap-assisted recombination.

11:20am **AP+AS+MC+MI+NS-MoM10 Correlating Atom Probe Tomography with High-Resolution Scanning Transmission Electron Microscopy and Micro-Photoluminescence Spectroscopy: The Case of III-Nitride Heterostructures**, ***Lorenzo Rigutti***, University of Rouen **INVITED**

Correlating two or more microscopy techniques on the same nanoscale object may yield a relevant amount of information, which could not be achieved by other means. In this contribution, we present several results of correlated studies of micro-photoluminescence (μ-PL), high-resolution scanning transmission electron microscopy (HR-STEM) and laser-assisted atom probe tomography (APT) on single nano-objects containing AlGaInN quantum well and quantum dot systems. We will show how this approach can be applied to the study of heterostructure interface definition, presence of defects, carrier localization and optical emission in III-N quantum confined systems [1]. Furthermore, we will show how the use of complementary techniques may be extremely helpful for a correct interpretation of atom probe results [2]. The possible implementation of micro-photoluminescence as an in-situ technique within the atom probe itself will finally be discussed [3].

[1] L. Rigutti et al., Nano letters (2014), 14, 107–114.

[2] L. Mancini et al. J. Phys. Chem. C (2014) 118, 24136-24151.

[3] L. Rigutti et al., Ultramicroscopy (2013), 132, 75-80.

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

2D Materials: Devices and Applications
Moderator: Joshua Goldberger, The Ohio State University, Arend van der Zande, University of Illinois at Urbana Champaign

2:20pm **2D+EM+MC+MS+NS-MoA1 Designer Materials from the Assembly of 2D Layered Heterostructures**, ***Cory Dean***, Columbia University **INVITED**
The capability to assemble two-dimensional (2D) materials into layered heterogeneous structures presents an exciting new opportunity in materials design. For example, encapsulating graphene with hexagonal BN yields enhanced transport properties with reduced environmental sensitivity, and allows for complex band structure engineering. This has enabled graphene to be exploited as a model experimental platform to study a wide range of fundamental physics arising both from conventional single-particle considerations, as well as more exotic emergent behaviour in the strongly interacting regime. Graphene however represents just one of a larger subset of layered materials, which are now receiving growing attention due to their diverse array of intrinsic properties. The opportunity to "mix and match" these disparate crystals to realize fundamentally new hybrid material properties provides an almost unbounded new direction as we look for quantum materials beyond graphene. In this talk I will outline some of the fundamental questions, and technical challenges facing these efforts and highlight some of our recent innovations in this direction. Implications for the development of new device geometries and scientific pursuits will be discussed.

3:00pm **2D+EM+MC+MS+NS-MoA3 Structural Semiconducting-to-Metallic Phase Transition in Monolayer Transition Metal Dichalcogenides Induced by Electrostatic Gating**, ***Yao Li***, *K.-A. Duerloo, E.J. Reed*, Stanford University
Dynamic electrical control of conductivity in two-dimensional (2D) materials is one of the most promising schemes for realizing energy-efficient electronic devices. Monolayer transition metal dichalcogenides (TMDs) are 2D materials that can exist in multiple crystal structures, each of different electrical conductivity. Using density functional approaches, we discover that a structural semiconducting-to-metallic phase transition in some monolayer TMDs can be driven by electrical stimuli, including change of charge density and bias voltage. We find that a bias voltage approximately 0.5~1 V can trigger the phase transition in $MoTe_2$, while a larger voltage is required for the transition in other monolayer TMDs. The threshold bias voltage is strongly influenced by the substrate on which the monolayer is placed. Carefully choosing the substrate could greatly reduce the threshold bias voltage for the phase transition, and therefore consume much less energy, suggesting potential applications in electronics with very high energy efficiency. The dynamic control of this semiconducting-to-metallic phase transition can be achieved utilizing standard electronic devices like the electrostatic gating employed in a field-effect transistor. We have also calculated the phase boundary of a reported metallic-to-metallic phase transition in $TaSe_2$ to compare with earlier STM experimental results and reasonable agreement is observed. Our findings open up the possibility of manufacturing ultrathin flexible two-dimensional phase change electronic devices with potential for higher energy efficiency than conventional electronic devices.

3:20pm **2D+EM+MC+MS+NS-MoA4 Use of Voltage-Contrast and Dynamical XPS for Characterization of Graphene-Based Devices in Operation**, ***Sefik Suzer***, Bilkent University, Turkey
A noncontact chemical and electrical technique of XPS is performed to investigate a number of deviecs under operation. The main objective of the technique is to trace chemical and location specified surface potential variations as shifts of the XPS peak positions under operating conditions. To implement the measurements we apply D.C. (Voltage-Contrast) and/or A.C. (Dynamical) voltage biases externally to the sample, while recording XPS data. Accordingly, we extract chemically resolved static and/or time-resolved information related with certain electrical properties of materials and devices made from them. Details of the technique and applications to a number of graphene-based devices, configured in a transistor geometry with and without gating, will be presented.

4:00pm **2D+EM+MC+MS+NS-MoA6 Avalanche Photodiodes based on MoS_2/Si Heterojunctions**, ***Oriol López Sánchez***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *G. Fiori*, *G. Iannaccone*, Università di Pisa, Italy, *D. Dumenco*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *E. Charbon*, Delft University of Technology, Netherlands
Avalanche photodiodes (APDs) are the semiconducting analogue of photomultiplier tubes offering very high internal current gain and fast response. APDs are interesting for a wide range of applications in communications, laser ranging, biological imaging, and medical imaging where they offer speed and sensitivity superior to those of classical p-n junction-based photodetectors. The APD principle of operation is based on photocurrent multiplication through impact ionization in reverse-biased p-n junctions. Here, we demonstrate APDs based on vertically stacked monolayer MoS_2 and p-Si, forming an abrupt p-n heterojunction. With this device, we demonstrate carrier multiplication exceeding 1000 at 10 V reverse bias . Our devices show little degradation of SNR at high gains. These heterostructures allow the realization of simple and inexpensive high-performance and low-noise photon counters based on transition metal dichalcogenides.

4:20pm **2D+EM+MC+MS+NS-MoA7 From Black Phosphrus to Phosphorene**, ***Peide Ye***, Purdue University **INVITED**
Phosphorus is one of the most abundant elements preserved in earth, constructing with a fraction of ~0.1% of the earth crust. In general, phosphorus has several allotropes. The two most commonly seen allotropes, white and red phosphorus, are widely used in explosives and safety matches. In addition, black phosphorus, though rarely mentioned, is a layered semiconductor and has great potentials in optical and electronic applications. Remarkably, this layered material can be reduced to one single atomic layer in the vertical direction owing to the van der Waals structure, known as phosphorene, where the physical properties can be tremendously different from its bulk counterpart. In this talk, we trace back to the 100 years research history on black phosphorus from the synthesis to material properties, and extend the topic from black phosphorus to phosphorene. The physical and transport properties are highlighted, aiming at further applications in electronic and optoelectronics devices.

5:00pm **2D+EM+MC+MS+NS-MoA9 Ambient Oxidation and Alumina Passivation of Exfoliated Black Phosphorus Transistors**, ***Joshua Wood***, *S. Wells, D. Jariwala, K.-S. Chen, X. Liu, V. Sangwan, E. Cho, L. Lauhon, T.J. Marks, M.C. Hersam*, Northwestern University
Exfoliated black phosphorus (BP) is an elemental, two-dimensional (2D) nanomaterial with high carrier mobility (~100 $cm^2V^{-1}s^{-1}$), a layer-dependent band gap (~0.3 to 2.0 eV), and in-plane anisotropy. Further, 2D BP is air sensitive, culminating in undesirable surface reactions that degrade device performance. We find that unencapsulated, exfoliated BP flakes form oxidized derivatives following ambient exposure, as ascertained by X-ray photoelectron spectroscopy, atomic force microscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, and electrostatic force microscopy measurements. BP ambient oxidation is driven by oxygen-saturated H_2O, as we observe two-fold faster degradation for BP on hydrophobic substrates versus hydrophilic ones. After 48 hours of ambient oxidation, unencapsulated BP field-effect transistors (FETs) decline in mobility and current on/off ratio by factors of over 1000. In contrast, alumina (i.e., AlO_x) passivated BP flakes and FETs are robust and unoxidized for over seven months in ambient conditions. Alumina-passivated BP FETs possess mobilities of ~100 $cm^2V^{-1}s^{-1}$, on/off ratios of 1000, and ambipolar transport, even following extensive ambient exposure [1]. This understanding of BP ambient oxidation—and how to prevent it—is also impacting ongoing work in solution-phase BP separation [2], BP chemical modification, and high-performance BP optoelectronic applications.

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

5:20pm **2D+EM+MC+MS+NS-MoA10 Electro-Acoustic Characterization of Transition Metal Dichalcogenide Films on $LiNbO_3$**, ***Edwin Preciado***, UC Riverside, *F.J.R. Schülein, A. Wixforth*, Universität Augsburg, Germany, *A. Nguyen, D. Barroso, M. Isarraraz, G. von Son, I. Lu, L. Bartels*, UC Riverside, *H. Krenner*, Universität Augsburg, Germany
We demonstrate mm-scale CVD growth of single layer molybdenum disulfide directly onto piezoelectric lithium niobate and present the fabrication of a hybrid FET – SAW (field effect transistor – surface acoustic

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

Materials Characterization in the Semiconductor Industry Focus Topic
Room: 114 - Session MC-TuM

Characterization of 3D structures

Moderator: Paul van der Heide, GLOBALFOUNDRIES, Inc.

8:00am **MC-TuM1 Expanding Roles of Materials Characterization and Metrology in Advancing Moore's Law**, *Z. Ma,* ***Ying Zhou***, Intel Corporation **INVITED**

Moore's law scaling in the past decade was propelled by important technology breakthrough and innovation. Wide acceptance of popular low power devices such as smartphone and tablet continues to drive dimension scaling to achieve desired performance, power consumption and cost. However, traditional geometrical scaling for devices and interconnects encountered some fundamental material issues and scaling limits. To address these challenges, new classes of materials and device structures are being investigated for possible applications. The evaluation and introduction of disruptive process technologies and novel devices are driving strong interests in new material characterization techniques and methods. Process monitoring and control put stringent requirements on metrology capabilities at both technology development and manufacturing stages. This presentation will talk about the growing needs for materials characterization and metrology and their pivotal roles in enabling technology breakthrough and manufacturing sustaining. A comprehensive metrology approach is recommended to push ultimate analytical capabilities and accuracy while delivering required measurement consistency and data turns through automation and design for metrology.

8:40am **MC-TuM3 X-ray based Characterization of Strained SiGe on FinFETs**, ***Kriti Kohli***, *M.A. Smith, A. Madan, Z. Zhu, J.R. Holt,* GLOBALFOUNDRIES, *M. Klare*, Revera

The introduction of complex three-dimensional structures in device design presents challenges that require ever more sophisticated metrology with high accuracy and precision. One such example is the measurement of composition and thickness of epitaxially grown thin films on fins. Due to the preferential growth in the <111> plane of SiGe on fins, the film creates complex multi-faceted shapes on top of the fins. These 3D structures are challenging even for reference metrology to characterize due to the effects of shading and variability in geometrical area. The goal is to develop an inline metrology that measures composition and thickness of epitaxially grown SiGe directly on fins since blanket pads are no longer correlated to device performance. In this paper, we present a comprehensive characterization of a set of samples with varying geometry, thickness, strain and composition of SiGe films on fins using HRXRD, XPS, XRF and compare to reference metrology. With each technique, we have developed a methodology for measuring directly on 3D fins and compare the techniques to determine the most robust, precise and accurate metrology solution.

9:00am **MC-TuM4 Atomic Scale Analysis by Atom Probe on 3D Semiconductor Structures**, ***Ajay Kumar Kambham***, *S. Shintri, D. Flatoff, P. van der Heide*, Globalfoundries

Device structures are rapidly scaling down to the nanometer regime with the ongoing development in semiconductor device technology. Along with this, it is ever critical need to engineer dopant profiles and to define the formation of junctions in Metal-oxide field effect transistors (MOSFETs). This is increasingly challenging considering the severity of short channel effects (SCEs). Indeed, one type of SCE in MOSFET devices known to cause performance degradation is Drain Induced Barrier Lowering (DIBL). To reduce DIBL, dopant junction profiles are made more abrupt. This can be done through the introduction of Sigma/cavity structures and the modulation of stress through optimal engineered epitaxial buffer layers. To assess the quality over nanometer scale regions requires the use of analysis techniques such as Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM). This presentation will discuss the role of APT and how elemental distributions vary depending on type of faces employed, i.e. Si (100) vs Si (111) along with the challenges involved in sample preparation.

9:20am **MC-TuM5 Preparing and Characterizing Nanoscale Topological Insulators**, ***Kenneth Burch***, Boston College **INVITED**

Topological Insulators present new opportunities to control and manipulate spin in future nano-devices. A key difficulty has been realizing the rather high mobilities they promise and detecting unambiguous signatures of surface transport at high temperatures. I will discuss our groups efforts to prepare these materials on the nano-scale using mechanical exfoliation on various substrates with the aim of understanding the role of the substrate in their transport properties. In addition I will discuss the various optical probes (Raman and Infrared) we have applied to understand the phonons and their role in limiting the surface transport properties of these materials.

11:00am **MC-TuM10 "More than Moore": Could Silicene Be the Future of Electronics?**, *J. Avila, Ch. Chen, S. Lorcy,* ***Maria Asensio***, Synchrotron SOLEIL, France

For more than forty years, the miniaturization of circuits by scaling down the transistor has been the principal driver for the semiconductor technology. As the number of components per chip increases, the total chip size has to be reduced within workable limits. Consequently, the technology roadmap for semiconductors or "Moore's Law"(1), which states that the number of components integrated in a circuit would increase exponentially over time, has been successfully achieved by a continuous downscaling of the critical dimensions in the integrated circuit. Hence, since 1970, the number of components per chip has doubled every two years. However, we are nowadays nearing the basic limits of the scaling, thus for further improvement we may need "More than Moore"(2). This new attractive trend adds value to devices by incorporating more functionalities to them, which do not necessarily scale according to Moore's Law. Graphene is one of the best-placed novel materials to be included in a "More than Moore" approach. A close relative of graphene, a 2D honeycomb lattice of Si atoms called Silicene has been recently reported as nanoribbons and single layers on silver (111) oriented monocrystals, (3,4). As silicon, unlike carbon, prefers sp3 hybridization instead of sp2 hybridization, silicone possess several stable buckled structures, which are compatible with the opening of a small gap (5). This ability makes silicene very attractive to be integrated to the already well-developed silicon-based electronics.

The task to create a new "fabric" as silicene has been, however, very difficult because silicene does not exist in Nature and it is not as easy to form as graphene due surely to its particular electronic structure and larger atomic size. Over the last decade, research groups from around the world have claimed to have prepared silicene, a one atom-thick layer of silicon. However, just recently our team has created silicone single sheets of silicon on silver single crystal surfaces and has further characterized this novel material; using atomic resolution STM spectroscopy and high-resolution angle resolved photoemission, proving unambiguously the existence of one of the most stable phases of this unique material. (3)

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11:20am **MC-TuM11 Challenges in Measuring Strain in Nanoscale 3D FinFET Structures**, ***Anita Madan***, GLOBALFOUNDRIES, *S. Mochozuki*, IBM Albany Nanotech Center, *C. Murray,* IBM, T. J. Watson Research Center, *D. Cooper,* CEA, LETI, MINATEC Campus, France, *Y. Wang, W. Weng, T. Pinto*, GLOBALFOUNDRIES

Strain engineering has been adopted as a key element for scaling high performance complementary metal-oxide-semiconductor (CMOS) devices. Complex 3D structures (FinFETs) have been introduced for the 14 nm technology node and beyond. Typically, strain is introduced by replacing the Si channel with SiGe for pFET devices. Characterization of strain in the fins is challenging due to the complexity of their three-dimensional geometries and their nanoscale dimensions.

In this paper, we present the methodology developed to characterize strain and crystallinity in both strained SiGe FinFET structures and FinFET structures with epitaxial embedded SiGe (eSiGe). We compare 2 complementary techniques used for characterization of strain on 3D fins. High Resolution X-ray Diffraction techniques with a spot size and a spatial resolution of 50 to 200 microns are non-destructive and the signal (averaged over many fins) is sensitive to defectivity, strain and Ge content. On the other hand, Transmission Electron Microscopy (spot size 0.3 – 5nm) is a destructive technique, dependent on the lamella thickness, and gives localized information on a few fins.

All measurements were made on blanket and fin array pads on specially designed macros. For XRD measurements, strain was evaluated using peak position information from the XRD Reciprocal Space Maps collected both parallel and perpendicular to the fin arrays. Measurements show that the stress in the SiGe fins is uniaxial – the SiGe fins are fully strained along the direction of the fins. The SiGe is partially relaxed perpendicular to the fins – the amount of relaxation dependent on the %Ge and the height of the SiGe fins. Advanced TEM analytical techniques (Nano beam diffraction, Dark Field holography and Energy-dispersive X-ray spectroscopy) were used to map the strain and %Ge over the height and the width of the SiGe fins. There was good correlation between the average strain and %Ge as determined from the TEM and XRD techniques. Results of the measurements will be compared with theoretical modeling, which is used to quantify the triaxial stress tensor components based on the experimentally determined lattice parameter values.

The advent of new HRXRD tools with 1D detectors and high intensity sources enable these measurements to be made over a couple of hours. Since XRD techniques are non-destructive, we will also discuss how this methodology can be easily adapted as in-line metrology to monitor the change in strain with processing.

This work was performed by the Research and Development Alliance Teams at various IBM Research and Development Facilities.

11:40am **MC-TuM12 Strain Measurement using Electron Beam Techniques**, ***Jean-Luc Rouviere***, CEA-University Grenoble Alps, France, *N. Bernier*, CEA, LETI, MINATEC Campus, France, *D. Cooper*, CEA-LETI, France **INVITED**

Strain can modify deeply material properties such as optical emission, transport properties or structural strength. With the development of nanotechnologies, the need of tools that can measure strain with high accuracy (about 0.01%) and high spatial resolution (about 1 nm) has appeared. The demand of Microelectronics industry has been particularly strong since Intel has implemented strained channels to boost the transport performance of their devices, and during the last decade, many new TEM base techniques have been developed to reach these goals. Of course, not only the microelectronics industry, but also any fields involving nanomaterials will benefit from these developments.

In this presentation, after a short review of the different TEM techniques, we will focus on the solution we have developed and chosen: **Nanobeam Precession Electron Diffraction (N-PED)**. Like in all TEM diffraction techniques, a small electron beam is made and diffraction patterns are acquired at different positions of the electron beam. In addition, in N-PED, the incident electron beam is rotated by a small angle around the observation direction and a descan is applied after the sample in order to bring back the diffracted beams to their unprecessed positions. In fact there is a compromise between spot size, beam convergence and precession angle. We adopted a setting where the beam convergence is about 2.2 mrad, the probe diameter is of about 1 nm, and the precession angle is below 0.5°. The advantages of this setting for strain measurement are mainyfold : (i) the diffraction spots have disk shapes and do not saturate, (ii) the intensity within the diffraction disks is more uniform (iii) more diffraction disks are visible (iii) a greater accuracty is obtained by locating the edges of the disks, (iv) the measurements are very stable versus changes in sample thickness or orientation and (v) strain maps of 4 components of the 3D strain tensor can be obtained with one zone axis orientation. **We will show how this simple and robust N-PED technique has been used successfully for the analysis of microelectronics devices and nanostructures**. In our FEI TITAN ultimate microscope where we used a Gatan Ultrascan CCD camera, the main drawbacks of N-PED are (i) its relatively slow speed and (ii) the amount of stored data to acquire large maps. For instance, to acquire 100x50 diffraction patterns containing 1Kx1K pixels, it took 90 minutes and 12 Gbytes on the hard disk. However with the new available fast cameras and larger disks, these issues are greatly reduced.

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 SiO_2 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 Kω/□), only 10x that of the pristine graphene, and their Dirac points before and after e-beam irradiation appear at comparable gate voltages.

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

3:20pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA4 Large-Area Low-Pressure Synthesis of Single-Layer MoS_2 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 are monolayer MoS_2 films. Organic chalcogen precursors are released into the growth chamber and react with a Mo filament creating films up to $2cm^2$ in size that are uniform and free of oxides. The films have pronounced photoluminescence intensity and are in Raman spectroscopy indistinguishable from exfoliated material. Metal contact formation to these films was investigated under UHV conditions utilizing X-Ray Photoelectron Spectroscopy . These measurements permit us to follow the formation of a Schottky Barrier with increasing metal film thickness on the Angstrom scale. We utilize core level spectroscopy to indicate the evolution of the MoS_2 valence band under metal deposition.

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

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

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

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

5:40pm **2D+EM+MC+MI+NS+SP+SS+TF-TuA11 Combining Photoemission and Photoluminescence Microscopy to Study Substrate Transfer Process Effects in Chemical Vapor Deposited MoS_2 Monolayers**, ***Olivier Renault***, *M. Frégnaux*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *J. Bleuse*, Univ. Grenoble-Alpes & CEA-INAC, France, *H. Kim*, Univ. Grenoble Alpes/ CEA, LETI, MINATEC Campus, France, *D. Voiry, M. Chhowalla*, Rutgers University

Within the perspective of integrating two-dimensional transition metal dichalcogenides (2D TMDs) such as molybdenum disulfide (MoS_2), into devices, it becomes of utmost importance to assess the influence of each step of the device fabrication process on the optical and transport properties of the MoS_2 single layer (1L) domains. Particularly at the deposition stage the properties may be influenced by substrate effects [1], and later, transfer processes may further alter the desired properties of TMDs. This requires effective microscopic characterization techniques.

We present a characterization method combining photoemission microscopy (XPEEM and Kpeem) and photoluminescence microscopy to compare the structural, optical and electronic properties of both as-deposited and transferred MoS_2 1L domains onto different substrates. XPEEM is used with laboratory sources in both direct space imaging for work function and core-level mapping [2] and particularly in the momentum microscopy mode (k-PEEM) to perform parallel angular imaging and retrieve the band structure in a one shot experiment [3]. Micro-photoluminescence spectroscopy at low (5K) and room temperature is used to detect the specific radiative recombination that occurs in MoS_2 1L (direct band gap semiconductor behavior) and to evidence the eventual presence of midgap states caused by process-induced defects. The results of both characterization techniques will be presented for MoS_2 1L domains transferred onto silica and gold substrates highlighting the roles of substrate nature (metal or insulant), surface roughness, and the presence of structural defects whether induced by the preparation process or intrinsic such as grain boundaries.

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

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

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

Materials Characterization in the Semiconductor Industry Focus Topic
Room: Hall 3 - Session MC-TuP

Materials Characterization in the Semiconductor Industry Poster Session (All areas)

MC-TuP1 Effect of Aromatic Compounds on Semiconducting Boron Carbide Heterojunctions, ***Elena Echeverria***, University of Nebraska - Lincoln, *R. James, F. Pasquale, B. Dong*, University of North Texas, *A. Enders*, University of Nebraska - Lincoln, *A. Kelber*, University of North Texas, *P.A. Dowben*, University of Nebraska - Lincoln

A new class of semiconducting boron carbide devices was fabricated based on a carborane icosahedra ($B_{10}C_2H_{12}$) precursor via plasma enhanced chemical vapor deposition in the presence of aromatic linking units. Our studies have showed that these novel superconducting boron carbide films have excellent rectifying characteristics when deposited on n-type Si, making this heterojunctions extremely promising for neutron detection and other device applications. Films were fabricated by co-deposition of aromatic compounds (pyridine, benzene, diaminobenzene, etc.) with ortho-carborane using plasma enhanced chemical vapor deposition (PECVD). In the case of samples containing pyridine, the characteristic I–V curves for the heterojunction diodes exhibit strong rectification and largely unperturbed normalized reverse bias leakage currents with increasing pyridine content. Similar results are showed when benzene or diaminobenzene are used as linking groups, with a threshold voltage lower for diaminobenzene compared to benzene. These results suggest that modifications to boron carbide may result in better heterojunction diodes, and point the way to a whole family of future studies that may ultimately lead to boron carbides better suited to low power and low flux neutron detection.

MC-TuP2 3 Dimensional Quantitative Composition and Structure Profiling of As Implanted Si USJ and FINFET with TOF-MEIS, ***WonJa Min***, *K.S. Park, K.-S. Yu*, KMAC, Republic of Korea, *S.J. Joo, Y.-S. Kim*, KRISS, Republic of Korea, *D.W. Moon*, DGIST, Republic of Korea

Using a recently developed time-of-flight (TOF) medium energy ion scattering spectrometer (MEIS), we have investigated 3D elemental composition, morphology, and atomic defect structures for As implanted Si ultrashallow junctions (USJs) and As implanted FINFET nanostructures.

As depth profiles in As/Si ultra shallow junctions (USJs) were measured by TOF-MEIS for 2 keV As implantation ion energy before and after annealing. Electrically inactive arsenic (As) complexes in silicon are investigated. In heavily As-doped Si, the As atoms segregated in the interface Si region just below the SiO_2 layer are found to be in interstitial forms (As_i), while the As in the bulk Si region are found to be in the substitutional form (As_{Si}). Despite the substitutional form of As, most of the As are found to be electrically inactive in the bulk region, and we identify that the As forms the <111> oriented As_{Si}-Si-vacancy (As_{Si}-V_{Si}) complex. The As_i's in the interface Si region are found to exist together with Si-interstitials (Si_i). It is suggested that the As_i deactivation centers in the interface Si region possibly accompany Si_i defects.

3D compostional distributions of As implanted FINFET structure were also analyzed with TOF-MEIS. Progresses in TOF-MEIS analysis of other nano-structured materials and devices in various nano & bio technology will be also discussed.

MC-TuP3 Characterization of the Doped Amorphous Carbon Hardmask Film Prepared by Hybrid Plasma CVD Systems, ***Jaeyoung Yang***, *K.P. Park, G.H. Hur*, TES Co. Ltd., Republic of Korea

We investigated the single and laminated stacked doped amorphous carbon film with additive gas as boron and nitrogen, and so on. The film properties was characterized by XPS, SIMS, and FT-IR spectroscope. Boron doped carbon film with B concentration-had > 30 % had the highest selectivity to oxide of over 10:1. In this study we had a choice of hybrid plasma chemical vapor deposition (CVD), and it was very stable plasma condition for a long time process and the specified laminated stacked carbon hardmask films were consisted with nitrogen and boron. We considered our optimised doped carbon films can be applied to use as the hardmask for designing about photolithograph and etching process. We can be easily controlled to dopant ratio by the plasma deposition system with the pulsed source feed-through module. Our new hardmask material prepared by hybrid plasma CVD process will be candidate on future material for advanced logic and memories, including DRAM and 3D VNAND chip integration process. We introduced the several behavior of deposited film' properties with varying the deposition parameters into the hybrid plasma CVD systems.

MC-TuP4 Surface Structure and Morphology of GaAs Nanowires Grown by Aerotaxy, ***Sofie Yngman***, *S. McKibbin, J. Knutsson, F. Yang, E. Lundgren, M. Magnusson, R. Timm, A. Mikkelsen*, Lund University, Sweden

III-V semiconductor nanowires (NWs) continue to show promising results as components in energy saving devices. GaAs NW arrays recently beat the record for photovoltaic solar cells presenting a conversion efficiency of 15.3% [1]. Given the large surface to volume ratio of NWs, performance in such devices may be strongly determined by surface characteristics for example, morphology, the presence of various oxide species and surface structure. We study GaAs NWs grown by using the novel growth technique aerotaxy [2]. In aerotaxy growth the NWs are catalyzed from Au aerosol nanoparticles floating freely in a continuous N_2 flow mixed with group III and V precursor gases. The growth rate of NWs using aerotaxy is much faster than for epitaxially grown NWs and the absence of expensive crystal substrate allows large scale economic production. A detailed understanding of the surface properties of these aerotaxy NWs is highly relevant in order to optimize device performance.

We compare surface structure and morphology of GaAs aerotaxy NWs to GaAs NWs grown epitaxially on a substrate. We obtain images of the NWs from microns to the atomic scale using both Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). Comparing this to chemical information obtained via X-ray Photoemission Spectroscopy (XPS) we find that the different growth techniques results in NWs with very different morphology. Using in air AFM phase measurements we show that the aerotaxy NWs exhibit a rounder cross section with few or no large facets in comparison to the hexagonal geometry of epitaxially grown NWs. XPS measurements show that by annealing the NWs in the presence of atomic hydrogen, we can remove the native oxides which form on them when exposed to air as previously observed for the expitaxially grown NWs[3][4]. From the XPS studies we can identify the different oxides present in the aerotaxy NWs before cleaning. We examine clean NWs using STM in Ultra High Vacuum. The morphology of the NWs is similar to as what is found in the AFM studies, however by direct atomic resolved imaging we can identify that even the round shaped aerotaxy NWs contain a considerable fraction of small unreconstructed patches of the {110} surface.

[1] http://www.solvoltaics.com/news.shtml (2015-05-01).

[2] M. Heurlin, et al. "Continuous gas-phase synthesis of nanowires with tunable properties", Nature 492, 90-94 (2012).

[3] E. Hilner, et al. "Direct atomic scale imaging of III-V nanowire surfaces", Nano Letters 8, 3978 (2008).

[4] M. Hjort, et al. "Direct imaging of atomic scale structure and electronic properties of GaAs wurtzite and zinc blende nanowire surfaces", Nano Letters 13, 4492 (2013).

MC-TuP5 Characterization of Si/Ru and Si/B_4C/Ru Multilayers using X-ray Reflectivity, X-ray Diffraction and Synchrotron-based EUV Reflectometry, ***Mohammad Faheem***, GLOBALFOUNDRIES Inc., *P. van der Heide*, GLOBALFOUNDRIES, Inc., *O. Wood, Y. Liang, A. Kumar Kambham, K. Wong, V. Park, P. Mangat*, GLOBALFOUNDRIES Inc.

Future photomasks for extreme ultra violet lithography (EUVL) would be improved with broader bandwidth reflective multilayer coatings especially below the 7 nm technology node. Owing to its lower index of refraction, higher numerical aperture and contamination resistance Ruthenium (Ru) is a potential candidate for use on future generation EUVL masks. We characterized 20 layer stacks of Si/La, Si/Ru and Si/B_4C/Ru on Si (100) substrates. X Ray Reflectivity (XRR) and Atom Probe Tomography (APT) were carried out on a Si/La stack for period comparison. Si/Ru and Si/B_4C/Ru were prepared for phase comparison using XRR and X Ray Diffraction (XRD). Four samples of Si/B_4C/Ru multilayers with less than 1 Å period difference were compared using synchrotron-based EUV reflectometry.

XRR measurements were carried out using a Bruker D8 Discover with Cu K-alpha (λ = 1.542 Å) and a scintillator detector. Measurements were made at small detector angles, 2θ = 0-10°. For texture and crystallite size, locked coupled scans were carried out using 0.2 mm beam slit and Lenxeye detector in 1D mode along 2θ = 10-110°. Bruker's Eva software was used to measure the peak positions and the ICDD PDF-4 data base was used to identify the Ru peaks. The APT measurements were performed by LEAP 4000X-Si instrument under UV laser illumination.

The result indicates the close agreement between XRR and APT for a 20 layer La/Si stack. XRR spectra of Si/Ru and Si/B_4C/Ru showed the

multilayer period of ~ 7nm with sharp peaks which indicate the uniformity of deposited multilayers. Ru and B_4C showed polycrystalline behavior compared to amorphous Si. XRD results demonstrate that Ru layers tend to have (002) texture both in Si/Ru and Si/B_4C/Ru samples. Ru crystallite size in Si/Ru was observed to be larger than in Si/B_4C/Ru. The difference in crystallite size can be due Ru film thickness and its deposition on Si and B_4C. In the case of four Si/B_4C/Ru samples, the change in period was found to be correlated to changes in bandwidth and shifts in the position of peak EUV reflectivity. These results are not only of fundamental importance but also beneficial for improving the performance of Ru-based EUVL reflectors.

Key words: EUVL, XRR, XRD, APT, Synchrotron

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

Dopants and Defects in 2D Materials
Moderator: Daniel Gunlycke, Naval Research Laboratory, Zenghui Wang, Case Western Reserve University

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

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

2:40pm **2D+EM+IS+MC+NS+SP+SS-WeA2 Investigation of Grain Boundaries in CVD Grown MoS_2**, ***Kolyo Marinov***, *D. Ovchinnikov*, *D. Dumcenco*, *A. Kis*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

We present the characterization of grain boundaries in polycrystalline CVD-grown MoS_2 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 MoS_2.

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.

[1] O. V. Yazyev and Y. P. Chen, Nature Nanotechnology **9**, 755 (2014).

[2] O. V. Yazyev and S. G. Louie, Phys. Rev. B **81**, 195420 (2010).

[3] Y. Tison *et al.,* Nano Lett. **14**, 6382 (2014).

[4] O. V. Yazyev and S. G. Louie, Nature Materials **9**, 806 (2010).

[5] J. H. Chen *et al.,* Phys. Rev. B **89**, 121407(R) (2014).

[6] F. Gargiulo and O. V. Yazyev, Nano Lett. **14**, 250 (2014).

[7] A. Pulkin and O. V. Yazyev, s*ubmitted.*

[8] O. Lehtinen *et al.,* ACS Nano **9**, 3274 (2015).

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

Since layered transition-metal dichalcogenides(TMD) have demonstrated novel electronic and optoelectronic property, intense research has focused synthesis and integration into future electronic devices. Unlike graphene, TMD materials have band gaps, and these band structures can be tuned by thickness. However, in many cases, unintentional defects can be observed on TMD giving rise to the degradation of performance in the devices. Even for mechanical exfoliated TMD, there is a high density of defects, such as vacancies. For successful integration of TMD into devices, proper passivation of defects on TMD requires high stability in ambient conditions. In this study, a TiOPc monolayer was employed for passivation of defects to improve electrical and optical properties in TMD devices. Multilayer MoS_2 flakes were cleaved in ambient condition and transferred into the UHV chamber; afterwards. TiOPc monolayers were deposited on the MoS_2 surfaces by organic molecular beam epitaxy. After deposition, TiOPc forms a monolayer with only few defects, and the TiOPc monolayer structure has square lattice in a 1.5x1.5 nm grid. This crystal structure indicates that each TiOPc in the monolayer is directed outward to vacuum. The deposited TiOPc layer has very high thermal stability on MoS_2; the TiOPc layer on MoS_2 requires annealing above of 673K for desorption. This high thermal stability indicates there are strong interaction between TiOPc and MoS_2 surface. STS shows the band gap of the monolayer is 1.8 eV, while bulk MoS_2 has a 1.3eV band gap. Moreover, the Fermi level of TiOPc/bulk MoS_2 is shifted to the valence band, consistent with a P type shift. However, bulk MoS_2 surface, where less than monolayer of TiOPc was deposited, has Fermi level shifted towards the conduction band, consistent with N type doping. In the single layer MoS_2 deposited TiOPc monolayer, threshold bias is shifted from -30 V to near O V, indicating P-doping of MoS_2. 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 MoS_2 FET, the on/off ratio is enhanced more than 2 orders magnitude. The similar charge transfer behavior also can be observed in TiOPc/WSe_2; on the bilayer WSe_2/HOPG, the TiOPc monolayer deposited on the first layer of WSe_2 shows the a conduction band shifted Fermi level, while a TiOPc monolayer deposited on the second layer of WSe_2 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 FETs 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 (MoS_2, $HfSe_2$, $SnSe_2$, etc.) were investigated. Multiple samples were processed in parallel to ensure that all sample sets saw

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

Significant variations in compatibility between contact metal and TMD were discovered. These variations were dependent upon the metal-TMD pair and the base pressure of the chamber prior to metal deposition. Au exhibits far superior wettability on $MoSe_2$, where uniform thin films were achieved, compared to $ReSe_2$, on which Au grows as clusters. Au wettability varies between that of thin films and clusters for the other TMDs studied. An Au thin film deposited on $SnSe_2$ results in the formation of reaction products such as Sn metal, as evidenced by the evolution of different chemical states in the Sn 3*d* spectrum after deposition. Reactions between MoS_2 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.

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

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

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

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

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

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

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

Transparent electrode materials are critical for optoelectronic devices such as touch screen and solar cells. Graphene has been widely studied as transparent electrodes for its unique physical properties. To further boost the performance of graphene based transparent electrodes, we novelized Li-ion intercalation in graphene, and achieved highest performance of carbon based transparent electrodes.[1] Transmission as high as 91.7% with a sheet resistance of 3.0 ohm/sq is achieved for 19-layer LiC_6, which corresponds to a figure of merit ($Sigma_{dc}/Sigma_{opt}$) at 1,400, significantly higher than any other continuous transparent electrodes. The unconventional modification of ultrathin graphite optoelectronic properties is explained by the suppression of interband optical transitions and a small intraband Drude conductivity near the interband edge. To achieve low cost, large scale graphene-based transparent electrodes, we further developed Na-ion intercalated printed reduced graphene oxide (RGO) film[2]. Unlike pristine graphene that inhibits Na-ion intercalation, the larger layer-layer distance of RGO allows Na-ion intercalation, leading to simultaneously much higher DC conductivity and higher optical transmittance. The typical increase of transmittance from 36% to 79% and decrease of sheet resistance from 83 kohms/sq to 311 ohms/sq in the printed network was observed after Na-ion intercalation. Compared with Li-intercalated graphene, Na-ion intercalated RGO shows much better environmental stability, which is likely due to the self-terminating oxidation of Na ions on the RGO edges. This study demonstrated the great potential of metal-ion intercalation to improve the performance of graphene-based materials for transparent conductor applications.

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

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

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway (2e-) that is reduced to hydrogen peroxide (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 Nørskov et al. [5]. We have taken account of effects of electrode potential, Ph of a solution, a local electric field in double layer, and water environment.

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

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