PCSI

Room Keauhou II - Session PCSI-TuM

Scanned Probe/2D Materials and Applications/Interfaces and Heterostructures/Optical Properties of 2D Materials

Moderators: Wolfgang Windl, The Ohio State University, Michael Flatté, University of Iowa, Kirstin Alberi, National Renewable Energy Laboratory, Xavier Marie, Institut National des Sciences Appliquées, LPCNO

8:30am **PCSI-TuM-1 "Seeing'' the Covalent Bond: Simulating Atomic Force Microscopy Images***, **James Chelikowsky**,* University of Texas, Austin **INVITED**

Advances in atomic force microscopy (AFM) have made it possible to achieve unprecedented images of covalent bonds, in some cases even to resolve the bond order in polycyclic aromatics. However, fundamental questions remain about interpreting the images and modeling the AFM tip. For example, the bright spots in non-contact AFM images can have a close correspondence to the atomic structure of a given specimen, but there can be contrast changes with tip height that cannot be interpreted directly by atomic positions. While the nature of the tip can be crucial in understanding the details of the image, the atomic structure of the tip is often unknown. This situation is compounded by the difficulty in simulating AFM images. In order to perform computational studies of AFM, one must determine the interatomic forces as a function of the tip height on a fine grid above the specimen.

I will present an efficient first-principles method [1] for simulating noncontact atomic force microscopy (nc-AFM) images using a “frozen density” embedding theory. Frozen density embedding theory enables one to efficiently compute the tip–sample interaction by considering a sample as a frozen external field. This method reduces the extensive computational load of first-principles AFM simulations by avoiding consideration of the entire tip–sample system and focusing on the tip alone. I will demonstrate that our simulation with frozen density embedding theory accurately reproduces full density functional theory simulations of freestanding hydrocarbon molecules while the computational time is significantly reduced. Our method also captures the electronic effect of a Cu(111) substrate on the AFM image of pentacene and reproduces the experimental AFM image of Cu_2N on a Cu(100) surface. This approach is applicable for theoretical imaging applications on large molecules, two-dimensional materials, and materials surfaces.

9:00am **PCSI-TuM-7 Nanoscale Carrier Distribution Imaging of Layered Semiconductor Materials using Scanning Nonlinear Dielectric Microscopy***, **Kohei Yamasue**, Y Cho,* Tohoku University, Japan

Layered materials are nowadays rising class of materials owing to their various superior and anomalous properties. In particular, layered semiconductors have recently attracted much interest. For example, since molybdenum disulfide (MoS_2), one of layered semiconductors, can maintain relatively high carrier mobility even for atomic monolayer of this material, its electronic device applications have been studied extensively. Optoelectronic applications of MoS_2 are also explored, because a monolayer MoS_2 has a direct transition bandgap. For boosting research and development of layered semiconductor materials and devices, we need tools for characterization and analysis of carrier and charge distribution in a nanoscale. A promising candidate is scanning nonlinear dielectric microscopy (SNDM), which is a scanning probe microscopy method based on the detection of tip-sample capacitance. By measuring tiny variation in tip-sample capacitance to an applied voltage , SNDM can obtain information on dominant carrier (electrons or holes) and its spatial distribution in a nanoscale. In this talk, we demonstrate SNDM is even applicable to few- to mono-layer of layered semiconductors. Our images show n- and p-type MoS_2 flakes exfoliated on SiO_2/Si substrates were clearly distinguished as regions with negative and positive signals, respectively. In particular, we could obtain significant intensity even for a monolayer MoS_2. Our results suggest that SNDM will be useful for nanoscale characterization of carrier distribution in layered semiconductor materials.

9:05am **PCSI-TuM-8 Effect s of Edge Structures on the Oxygen Reduction Reaction Activity of Nitrogen-doped Graphene Nanoribbons***, **Shun-ichi Gomi**, H Matsuyama, A Akaishi, J Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

Recently, much attention has been devoted to the oxygen reduction reaction (ORR) on nitrogen (N) -doped graphene [1]. It has been reported that N atoms prefer to be doped at the edge of graphene [2]. The structure of graphene edge can be classified into two types, zigzag and armchair edges. However, the effect of edge structures on ORR activity has not been fully understood.

We investigated the ORR activity on N-doped graphene nanoribbons with zigzag (N-ZGNRs) and armchair (N-ACGNRs) edges using first-principles calculations within the density-functional theory. Figure 1 shows the calculation models. The model of “X-Y” indicates a doping site of N (X) and a reaction site (Y). We used the computational hydrogen electrode model [3] to evaluate the maximum electrode potential. ORR mainly proceeds via the direct four-electron ($4e^-$) and the two-electron ($2e^-$) pathways. We also examined the selectivity with respect to these two pathways.

Figure 2 shows the maximum electrode potential of ORR for each doping site. The maximum potential for N-ACGNR becomes positive for each doping and reaction site. On the other hand, the maximum potential for N-ZGNR has a parity dependence with regard to the nitrogen doping site in the vicinity of the zigzag edges. For the even-numbered doping sites from the edge, the maximum potentials are larger than 0 V, while for the odd-numbered ones, the maximum potentials become negative. The reaction selectivity for the $4e^-$ pathway appears only in the vicinity of armchair and zigzag edges.

For the models showing the reaction selectivity, the sp^2 configuration of GNR is maintained, even if reaction intermediates are adsorbed on GNR. One the other hand, reaction intermediates adsorb on GNR with sp^3-like configuration for the other models. The mechanism for appearance of the selectivity will be discussed in the presentation.

[1] K. R. Lee *et al.*, Electrochem. Commun. **12**, 1052 (2010).

[2] S. F. Huang *et al*., Phys. Rev. B **80**, 235410 (2009).

[3] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. Phys. Chem. B **108**, 17886 (2004).

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9:10am **PCSI-TuM-9 2D or not 2D? How Nanoscale Surface Roughness Impacts the Frictional Properties of Graphene and MoS_2***, **James Batteas**, M Elinski, Z Liu, M Negtiro,* Texas A&M University

Control of friction and wear is a ubiquitous challenge in numerous machined interfaces ranging from biomedical implants, to engines, to nano- and micro-scaled devices, with the energy losses associated with friction and wear having significant impacts on the economies of the world. Notably, the combined energy losses and the associated system downtime for maintenance of machines due to friction and wear, contribute to an estimated loss of ~$200 billion/year in the United States alone. As such, developing new approaches for the control of friction at interfaces is a critical need. One of the key challenges in developing boundary lubrication schemes for such systems, is how to reduce friction and wear at the rough surfaces typical of machined interfaces, where nanoscaled asperities of ~ 10 – 20 nm rms roughness, dominate the interfacial contacts. The robust mechanical properties of two-dimensional (2D) nanomaterials has made them of significant interest for modifying surface frictional properties. It has been found that many 2D materials can readily adapt to surface structure on the atomic scale however, when deposited on substrates with nanoscopic roughness, a conformal coating cannot be fully formed due to competition between adhesion to the nanoscopic asperities of the substrate and the corresponding bending strain of the material. This often leaves a mixture of supported (bonded) and unsupported regions which respond differently to applied load. To investigate this in detail, we have developed a model platform to study friction in true nanoscaled asperity-asperity contacts using silica nanoparticles to form substrates with asperities of controlled radius of curvature (*ca.* 3 – 35 nm), matching those found in many machined interfaces. Here we describe a combination of AFM structural, nanomechanical and confocal Raman spectroscopic studies of graphene and MoS_2 on silica surfaces with controlled nanoscopic roughness, to examine the how surface roughness impacts their frictional properties. Additionally, as noted above, since substrate adhesion is a critical factor in the control of friction at these interfaces, we have also explored how the deposition of self-assembled monolayers (SAMs) of alkylsilanes with varying terminal functional groups (e.g. $–NH_2$, $-CH_3$, $-C_6H_6$) on the substrates also influence the corresponding structure, and the adhesion and friction in these 2D nanomaterials, when deposited on top of the SAM layers. The ability to tune and control roughness in these materials on the nanoscale also has other implications in the applications of these materials in electronics and catalysis.

9:15am **PCSI-TuM-10 Synthesis and Characterization of Atomic and Electronic Properties of Graphene-based Heterostructure*, Young Jae Song,*** Sungkyunkwan University, Republic of Korea

Electronic structure of graphene is affected by number of graphene layers and stacking order.[1,2] Control of layer number as well as scalability has been the main issues for device applications based on graphene. A new and unique CVD method is proposed to synthesize epitaxial multilayer graphene on copper by an iterative process of graphene growth and h-BN etching in chemical vapor deposition (CVD). A h-BN thin film is utilized to provide a gap of well-defined thickness for introducing the precursors and to play the role of the epitaxial growth of multilayer graphene. A thin h-BN film, initially-CVD grown on copper,[3] is locally etched out by hydrogen atoms decomposed from CH4 during the sequential graphene growth, which generates additional growth channels of graphene adlayers again under the first graphene layer. The crystallinity with AB stacking was confirmed by Raman analysis and selected-area electron diffraction measurements as well as statistical studies of optical microscope images. Graphene growth with a h-BN template suggests a potential way for controlling the specific layer number of large-area graphene in CVD for the device applications of graphene.

[1] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov & A. K. Geim, Rev. Mod. Phys. 81 (2009) 109–162

[2] A. K. Geim & K. S. Novoselov, Nat. Mater. 6 (2007) 183–191

[3] M. Wang *et al*., Adv. Mater. 25 (2013) 2746–2752

9:20am **PCSI-TuM-11 Quantitative Relation between the Structural Stability and the Aromaticity of Graphene Nanoflakes***, M Ushirozako, H Matsuyama, A Akaishi,* ***Jun Nakamura,*** The University of Electro-Communications (UEC-Tokyo), Japan

Recently, nano-scale graphene nanoflakes (GNFs) have attracted great attention as one of the promising materials for electronics and spintronics. Kim et al. have successfully fabricated GNFs with various sizes up to 35 nm and have reported that the photoluminescence property of GNFs depends on the size and the edge shape [1]. From the view point of the structural stability of GNFs, we have not yet acquired the systematic comprehension with regard to effects of shapes and sizes of GNFs on the stability. In the present study, we have examined how the stability of GNFs is dominated by the edge shape and the size of GNFs, using first-principles calculations within the density functional theory.

In order to evaluate the stability of GNFs, we calculated the edge formation energy. First, we consider GNFs with the six-fold symmetry (D_{6h}) and classify them into zigzag GNFs (ZZGNFs) and armchair GNFs (ACGNFs). ACGNFs have two subtypes, AC(1) and AC(2), depending on whether carbon atoms are just at the corner of the outermost envelope hexagon of GNFs. In addition, we also evaluate the structural stabilities of triangular and rhombus GNFs.

Figure 1(a) shows the edge formation energy of the GNFs. The formation energy of ZZGNFs is higher than that of ACGNFs irrespective of the size of GNFs. This instability of ZZGNFs is attributed to the presence of the so-called edge state. Indeed, it has also been shown that the formation energy of the zigzag graphene nanoribbon is higher than that of the armchair one. It is noted that AC(2) is slightly more stable than AC(1), whereas the purity of AC(2) is lower than that of AC(1). Such peculiar stabilization can be reasonably explained in terms of the aromaticity of GNFs. Figure 1(b) shows the rela-tionship between the edge formation energies and the average NICS values. In addition to ACGNFs, we calculated those for trigonal-GNFs and rhombus-GNFs. As clearly seen, the edge formation energy is proportional to the average NICS value. The slope is almost the same for each type of GNFs and the intercept depends on the type. The average NICS values have one-to-one correspondence with the formation energy regardless of the GNF size. This means that the stability of the GNF edge is dominated by the degree of the aromaticity over the whole rings of GNFs. Therefore, it is concluded that the NICS values are not just the measure of aromaticity but also are relevant to the structuralstability of GNFs [2].

[1] S.Kim *et al.*, *ACS Nano*, **6**, 9, 8203 (2012)

[2] A.Akaishi, M.Ushirozako, H.Matsuyama, and J.Nakamura, *Jpn.J.Appl.Phys.***57** (2018), in press.

9:25am **PCSI-TuM-12 Formation of Water Bilayer on Graphene Surfaces***,* ***Akira Akaishi****, J Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

Water wettability of graphitic surfaces is of great interest to the fundamental understanding of graphene surfaces and for practical applications of graphene-based materials since the wettability is closely related to whether the surface is hydrophobic or hydrophilic. One of the characteristic measures of the wettability is a contact angle that is the angle of the edges of a water droplet placed on target surfaces. While graphitic surfaces are believed to be hydrophobic, in recent studies, it has been reported that the water contact angle of the graphene surfaces becomes relatively small by removing surface contamination [1]. This observation is also confirmed by evaluating the water contact angle with molecular dynamics (MD) simulations [2]. The wettability of pristine graphene surfaces is controversial.

We have examined the structure of water molecules on graphene surfaces with MD simulations. As the number of water molecules increases, the droplet covers the surface and the layered-structure of molecules on the surface is formed. This indicates that, at the level of an empirical model, a graphene surface is capable of wetting.

The formation of water layers on the surface can be seen by the density profile of water molecules. Figure 1 shows the probability density distribution of oxygen atoms, hydrogen atoms, and hydrogen bonds of water along the normal direction to the graphene surface. For the oxygen atoms, the density distribution has two peaks, indicating the bilayer of water molecules is definitely formed. Moreover, the distinct peaks of the hydrogen atoms and the hydrogen bonds distributions indicate that the oxygen-hydrogen (O-H) bonds are not randomly formed but are certainly oriented. Our analyses on the angle distribution of O-H bonds show that hydrogen bonds are formed within and between the water layers. Above the second layer, there are no dangling hydrogen bonds that are pointing perpendicular to the layer plane, which means that a graphene surface covered with the water double-layer has a hydrophobic character.

[1] Z. Li, et al., Nat. Mater. 12, 925 (2013).

[2] Y. Wu and N. R. Aluru, J. Phys. Chem. B 117, 8802 (2013).

[3] A. Akaishi, T. Yonemaru, and J. Nakamura, ACS Omega 2, 2184 (2017).

9:30am **PCSI-TuM-13 Scanning Electrochemical Microscopy of Graphene-based Hybrids: Insights into Physicochemical Interfacial Processes and Electroactive Site Distribution***,* ***Sanju Gupta,*** Western Kentucky University

Surface (and interfacial) chemistry is found in various environments of scientific significance including biomembranes, ocean and atmospheric chemistry and applied electrochemistry. Molecular redox behavior on the surface and at the interface is drastically different than their bulk counterpart. Scanning electrochemical microscopy (SECM) is a powerful tool to investigate interfaces determining ion transfer kinetic rate, diffusion coefficient, imaging topography and electrochemical redox reactions. The significant advantage offered by SECM is its capability of probing chemical information of interfacial electron and ion transfer processes at solid/liquid interface irrespective of substrates. A constant potential is applied to the tip and electrochemical working electrode (*i.e.* the substrate in electrolyte) to drive reaction in bulk electrolyte solution of redox species (or mediator) to probe the surface of certain thickness of graphene-based hybrids. The microscaled cyclic voltammograms, probe approach (current *versus* tip–substrate distance) curves, 2D and 3D micrographs in feedback mode, were chosen for graphene/CNT, graphene/transition metal oxide as supercapacitors to probe ion adsorption and to map highly electroactive (‘hot spots’) sites. The SECM setup has a resolution of ~40 nm and can locate and relocate areas of interest precisely after a coarse image. We present our findings from viewpoint of reinforcing the roles played by heterogeneous electrode surfaces comprised of graphene nanosheets (conducting)/nanomaterials (semiconducting) via higher/lower probe current distributions. SECM approach curves as well as two dimensional scans elucidated the existence of regions of different conductivity and the data is analyzed in terms of edge plane defects distribution within the probes regions, determining diffusion coefficient and heterogeneous rate constant.

11:00am **PCSI-TuM-31 Realization of 2D Group-III Materials Through Thermal Evaporation-Based Intercalation***,* ***Natalie Briggs****, B Bersch, A De La Fuente,* Pennsylvania State University*; C Lopez Pernia,* Technical University of Madrid, Spain*; K Wang, J Robinson,* Pennsylvania State University

Recent years have seen continued developments in the synthesis of 2D materials, and along with improved deposition techniques have come new strategies and approaches to realizing 2D compounds. One such strategy utilizes intercalation of metal atoms as a pathway to forming graphene-encapsulated 2D materials. This approach has allowed for the realization of a 2D form of gallium nitride (GaN) by annealing intercalated metal atoms in ammonia, as a result, expanding the pallet of materials that may be realized in 2D forms[1]. However, initial studies of 2D GaN synthesized from intercalation have relied on involved metal organic chemical vapor deposition techniques, and the resulting materials have suffered small domain sizes. We report a method of intercalating group-III (GIII) metal atoms gallium and indium through simple vaporization of metallic precursors in the presence of graphene layers. Through this method, micron-scale intercalation is possible. Following the intercalation of GIII metals, graphene-encapsulated gallium and indium layers are selenized and nitridated through exposure to selenium and ammonia at high temperatures. Ongoing work aims to elucidate the requirements of forming encapsulated 2D materials, as well as the resulting structures, and electronic and optical properties.

[1] Balushi, Z. Y. Al *et al*. Two-dimensional gallium nitride realized via graphene encapsulation. *Nat. Mater.* **15**, 1166-1171 (2016).

11:15am **PCSI-TuM-34 Strain and Compositional Fluctuations in $Al_{0.81}In_{0.19}N$/GaN Heterostructures***, **Verena Portz**,* Academia Sinica, National Taiwan University, Forschungszentrum Jülich GmbH, Republic of China*; M Schnedler,* Forschungzentrum Jülich, Germany*; M Duchamp,* Nanyang Technological University, Singapore*; F Hsiao,* National Taiwan University, Republic of China*; H Eisele,* Technische Universität Berlin, Germany*; J Carlin, R Butté, N Grandjean,* École Polytechnique Fédérale de Lausanne, Switzerland*; R Dunin-Borkowski, P Ebert,* Forschungzentrum Jülich, Germany

The strain and compositional fluctuations of nearly lattice-matched $Al_{0.81}In_{0.19}N$/GaN heterostructures are investigated by cross-sectional scanning tunneling microscopy and selected area electron diffraction measurements in scanning electron transmission microscopy. The presence of strain induces height modulations governed by different roughness components at the cleavage surfaces. The surface height modulations are compatible with a relaxation of alternatingly compressive and tensile strained domains, indicating compositional fluctuations. Changes of the *a*-lattice constant are traced to interface misfit edge dislocations.

11:20am **PCSI-TuM-35 Theoretical Investigations for Strain Relaxation and Resultant Growth Mode in InAs/GaAs Heteroepitaxial System***, **Tomonori Ito**, T Akiyama, K Nakamura,* Mie University, Japan

It is well known that InAs grown on GaAs(001) produces three-dimensional (3D) island shaped quantum dots. Despite a constant lattice mismatch, InAs thin films fabricated on the GaAs(111)A and GaAs(110) exhibit two-dimensional (2D) growth contradicting the 3D growth of InAs on GaAs(001) [1]. In this study, the growth mode of InAs/GaAs depending on orientations is systematically investigated using macroscopic free energy, microscopic emprical interatomic potential, and nanoscopic ab initio calculations to clarify the contribution of strain relaxation at their interfaces and surfaces to the resultant growth modes.

Figure 1 shows the calculated free energy differences among various growth modes as a function of layer thickness *h* for InAs/GaAs with different orientations. The growth mode in (110) (Fig. 1(a)) changes from the 2D-coherent (2D-coh) to the 2D growth with misfit dislocation (2D-MD) at *h*~1 monolayer (ML), while the 2D-3D growth mode transition appears inserting $In_{0.25}Ga_{0.75}As$ layer between InAs and GaAs that reduces surface energy *g* from 51 to 49 meV/Å^2. On the other hand, (111)A (Fig. 1(b)) keeps the 2D growth mode from the 2D-coh to the 2D-MD via stacking-fault tetrahedron (SFT) formation (2D-SFT) at *h*~3 ML. The SFT formation near surface reduces strain energy more effectively than island and MD formations at the initial growth stage. For (001) (Fig. 1(c)), the strain relaxation occurs at *h*~0.5-0.6 ML where the macroscopic theory is no longer applicable. At this early stage, the strain is relaxed on the InAs reconstructed surface with missing surface dimer to substitute for In-As dimer going so far as to break the electron counting rule. These suggest that the growth mode in InAs/GaAs is closely related to the strain relaxation at the interface for (110), at both the surface and the interface for (111)A, and on the surface for (001).

11:25am **PCSI-TuM-36 Electric Field-Driven Defect Diffusion at Oxide Semiconductor-Metal Interfaces***, H Gao, G Foster,* The Ohio State University*; G Mackessy,* Columbus School for Girls*; A Hyland, M Allen,* University of Canterbury, New Zealand*; **Leonard Brillson**,* The Ohio State University

We used depth - resolved cathodoluminescence spectroscopy (DRCLS) to measure how native point defects move under applied electric fields at metal-ZnO and metal-$SrTiO_3$ interfaces. Native point defects can be electrically active, acting as donors or acceptors that increase or compensate free carrier densities, altering Schottky barrier depletion regions as well as forming interface states that "pin" Fermi levels. For many compound semiconductors, these defects exhibit pronounced segregation toward free surfaces and metal contacts, amplifying their interface electronic effects. Here we report that native point defects in ZnO and $SrTiO_3$, representative wide band gap semiconductors with and without built-in polarization fields, respectively, can move hundreds of nanometers under applied electric fields that are comparable to electric fields in conventional Schottky barriers. In turn, such voltage gradients can account for the pronounced defect segregation typically reported at oxide semiconductor interfaces.

To gauge how electric fields can affect defect distributions in ZnO, we measured DRCLS vs. increasing incident electron beam energy E_B and increasing depth below a 20 nm Pt electrode on a 0.5 mm thick commercial (MTI) ZnO single crystal. Without bias, DRCLS through the Pt showed significant increases in zinc vacancies (V_{Zn}) and Cu on Zn sites (Cu_{Zn}), analogous to previous studies.^{3} An applied bias of +917V corresponding to 18.3 kV/cm across the entire crystal width increased this segregation by > 2x nearest the Pt/ZnO interface. This enhancement extends tens of nanometers into the bulk – comparable to the semiconductor depletion width, suggesting that the applied field falls primarily across the Schottky depletion region. With bias removed, these defects redistribute. Applied bias up to 2.5 kV/cm produces analogous oxygen vacancy (V_O) diffusion in commercial (Crystek) $SrTiO_3$ wafers. Here, positive bias drives the positive donors away from the anode, but with bias removed, these defects don't redistribute.

Electric fields applied laterally across ZnO surfaces also drive defect diffusion. Hyperspectral imaging (HSI) maps of V_{Zn} and Cu_{Zn} spatial distributions between a 32 nm thick, 300 nm diameter IrO_x Schottky diode and ground on a low-Li Tokyo Denpa Ltd. single crystal wafer displayed acceptor movement toward the diode with increasing positive bias corresponding to 10^4V/cm. These effects have general significance since voltage gradients of this magnitude are comparable or less than those in conventional band bending regions.

The authors gratefully acknowledge support from NSF Grant No. DMR-1305193 (T. Paskova).

11:30am **PCSI-TuM-37 General Abscence of Electron Accumulation at Stoichiometric Indium-containing Semiconductor Surfaces***, **Holger Eisele**,* Technische Universität Berlin, Germany

During recent years electron accumulation was assigned to many different indium containing semiconductor materials: it almost looked like a universal property [1]. Typically, in technologically usable samples it seems to be a persistently existing effect. But still, the question rises, whether this is an intrinsic or extrinsic semiconductor material property, meaning whether the effect is coming from the material itself or from changes in composition, complete decomposition, or due to oxidation at surfaces. Therefore, we prepared different indium containing semiconductor samples, i.e. InN, AlInN, and In_2O_3, just by cleavage without any annealing step. This process typically leads to stoichiometric surfaces, at least for a certain time of experimental investigation. After the investigation we also aged the sample in order to see changes. The investigations of the electronic states were performed by cross-sectional scanning tunneling spectroscopy, probing occupied and unoccupied states at the same time. For all materials—as long as their surfaces stay stoichiometric—we find no intrinsic electron accumulation at all non-polar surface, i.e. the ones without intrisic polarization field. For InN [2,3] we can exclude intrisic electron accumulation at both non-polar surfaces, the *a*- and the *m*-plane, for InAlN [4] at the *m*-plane, and for In_2O_3 at the (111) surface. The electronic structure of these surfaces are all different from each other: InN show no electronic surface state within the fundamental bulk bandgap, for InAlN at least one (depending on the In/Al ratio probaly more) state shifts into the fundamental bulk band gap, and In_2O_3 has different intrisic surface states within it. So the absence of electron accumulation is further independent of the intrinsic electronic properties of the material. Nevertheless, by aging In_2O_3 under ambiant conditions we receive a completely different image: the surface shows metallic behavior, as also surface electron accumulation does.

[1] P.D.C. King, *et al.*, Appl. Phys. Lett. **91**,092101 (2007).

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[3] H. Eisele, *et al.*, Phys. Rev. B **94**, 245201 (2016).

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11:35am **PCSI-TuM-38 InAsSbBi/GaAsSbBi Type-II Heterostructures for Mid- and Long-wavelength Infrared Applications***, **Shane Johnson**, S Schaefer, R Kosireddy, A Shalindar, P Webster,* Arizona State University

Alloying bismuth with InAsSb provides an active material near the GaSb lattice constant that covers the technologically important 3 – 5 µm and 8 – 12 µm atmospheric transmission windows. A significant advantage of the InAsSbBi quaternary is that strain and bandgap can be independently selected (Fig. 1). Furthermore, independent tuning of the band offsets can be achieved when adding the larger bandgap GaAsSbBi quaternary to the mix, either as quinary random alloys or type-II quantum well/superlattice heterostructures.

The molecular beam epitaxy growth and structural and optical properties of InAsSbBi/ GaAsSbBi heterostructures on GaSb are examined using reflection high-energy electron diffraction, Rutherford backscattering spectrometry, X-ray diffraction, spectroscopic ellipsometry, and photoluminescence spectroscopy. Near stoichiometric group-V fluxes and lower growth temperatures are utilized to facilitate the incorporation of the Bi atoms. The Rutherford backscattering spectrum from InAsSbBi has a unique energy range characteristic of Bi, allowing independent determination of Bi mole fraction (Fig. 1). The As and Sb mole fractions are then uniquely determined from the layer strain provided by X-ray diffraction. The InAsSbBi bandgap and band offsets determined from photoluminescence and spectroscopic ellipsometry are parametrized in terms of mole fraction. The results indicate that the InAsSbBi material system forms a type-I band alignment with InAsSb and a type-II band alignment with GaSb and GaAsSbBi.

11:45am **PCSI-TuM-40 Excitons in $MoS_2/MoSe_2/MoS_2$ Trilayer Metal Dichalcogenides***, **Paulina Plochocka**,* LNCMI, CNRS, France **INVITED**

Monolayer transition metal dichalcogenides (TMDC) are rapidly emerging as potential building blocks for novel electronic and optoelectronic devices. In this talk I will discuss the optical properties of excitons in tri – layer transitions metal dichalcogenides (TMDC).

First, I will demonstrate a novel approach to neutralize the intrinsic defects of CVD-grown TMDCs, using transfer tools routinely employed in the fabrication of van-der-Waals heterostructures. We investigate the optical properties of trilayer stacks composed of external CVD-grown MoS_2 flakes as capping layers and an internal CVD-grown $MoSe_2$ flake which has a smaller band gap. Remarkably, this fabrication approach strongly suppresses the localized exciton emission in $MoSe_2$ yielding a low temperature PL comparable to that observed in mechanically exfoliated samples [1]. Our results pave the way for the production of large area high quality TMDCs. Furthermore, I will demonstrate that tuning the excitation laser to the A-exciton resonance of the larger band gap MoS_2 leads to a considerable charge transfer towards lower band gap $MoSe_2$. The conservation of the spin during the charge transfer opens new possibilities for spintronics and spin injection. In addition, the investigation of the charge transfer between the $MoS_2/MoSe_2$ layers allows us to demonstrate a novel way to introduce the valley polarization in $MoSe_2$, which is difficult to achieve in non resonant excitation conditions [2].

Finally, I will discuss optical properties of the long lived inter-layer exciton formed between the $MoSe_2$ and MoS_2 monolayers. Under circularly polarized excitation, the inter-layer exciton emission is intriguingly counter polarized. Such an effect has never been observed previously. Our results show that a careful choice of the TMDs forming the van der Waals heterostructure makes it possible to control the circular polarization of inter-layer exciton emission. This unexpected phenomenon gives an additional degree of freedom for tailoring the properties of van-der-Waals heterostructures [3].

[1] A. Surrente, PP et al Nano Letters 17, 4130 (2017)

[2] M. Baranowski, PP et al 2D materials 4, 025016 , (2017)

[3] M. Baranowski, PP et al Nano Letters in press DOI: 10.1021/acs.nanolett.7b03184

12:15pm **PCSI-TuM-46 Photo-assisted Modulation of Thermal Transport and Thermopower in Single-layer Transition Metal Dichalcogenides***, **Parijat Sengupta**, J Shi,* University of Illinois at Chicago

Transition metal dichalcogenides (TMDCs) have the representative formula MX_2, where *M* is a transition metal element from group IV–VI and *X* belongs to the set of elements S, Se, and Te, collectively identified as chalcogens They are layered materials of covalently bonded atoms held together by weak van der Waals forces. Thin TMDC films are considered promising thermal materials with the possibility of a large figure of merit, . Here, ***S*** is the Seebeck coefficient, the electrical (thermal) conductivity is denoted by ***σ*** (***κ***), and ***T***is the temperature. Beginning with a *k.p* representation of the Hamiltonian that describes the carriers in the vicinity of the two valleys, ***K*** and ***K`,*** as massive Dirac fermions, we theoretically demonstrate the modulation of ***S*** aided by a driven periodic perturbation. We use a high-intensity circularly-polarized illumination to drive the TMDC into a Floquet *off-resonant* phase that enlarges the fundamental band gap, say, at ***K***, while ***K`*** suffers an equal reduction. This dual transformation is simply an outcome of the time-reversal principle connecting the two valleys and manifests as unequal conductivities for respective carriers. This inequality is also mirrored in their thermopower (***S***) behaviour. The conductivity (intra-band) calculations are performed using the Kubo formalism. To determine the thermopower for carriers (that lie close to *K* and *K`*), in the low-temperature limit, we use Mott's formula furnishing a valley-resolved thermopower. Specifically, the carriers from the valley that has an optically-lowered band gap reveal a higher thermopower vis-à-vis the ensemble located in its time-reversed counterpart. Further, a simple application of the Wiedemann-Franz law (WFL) relates *σ* to *κ* from which we obtain low-temperature *ZT*, using the pre-computed thermopower.

The thermal conductivity is integral to Peltier-type solid state cooling methods and thermopower generation; while the former requires a higher *κ* for unimpeded heat flow from deep-seated hot-spots in a miniaturized chip, the latter relies on localized heat production for efficient energy-conversion. To this end, in accord with WFL, to achieve a desirable *κ*, it is prudent to investigate conditions that permit an adjustable *σ*. We show that in conjunction with optical modulation, disorder, which can establish a variable hopping regime and quench *σ,* allows the sought control over *κ* within the purview of our stated applications.

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