2D Materials

Room On Demand - Session 2D-Contributed On Demand

2D Materials Contributed On Demand Session

2D-Contributed On Demand-1 Direct Imaging and Interaction Spectroscopy of Atomic-Scale Ripples on MoS_2 via Atomic Force Microscopy, *O. Dagdeviren,* McGill University, Canada*; O. Acikgoz,* University of California Merced*; P. Grütter,* McGill University, Canada*; **Mehmet Z. Baykara,*** University of California Merced

Theory predicts that two-dimensional (2D) materials may only exist in the presence of out-of-plane deformations on atomic length scales, frequently referred to as *ripples*. While such ripples can be detected via electron microscopy, their direct observation via surface-based techniques and characterization in terms of interaction forces and energies remain limited, preventing an unambiguous study of their effect on physicochemical characteristics. Here, we employ high-resolution atomic force microscopy (AFM) to demonstrate the presence of atomic-scale ripples on supported samples of few-layer molybdenum disulfide (MoS_2). Three-dimensional force / energy spectroscopy is utilized to study the effect of ripples on the interaction landscape. Our experiments contribute to the continuing development of a rigorous understanding of the physicochemical characteristics of 2D materials.

2D-Contributed On Demand-4 CVD Growth and Characterization of Ferromagnetic Manganese (IV) Selenide-Epitaxial Graphene Heterostructures*, **Ihteyaz Aqaeed Avash,** M. Pedowitz, G. Cassuto, K. Daniels,* University of Maryland, College Park

In recent years, several transition metal dichalcogenides (TMDs) have been found to exhibit intrinsic ferromagnetic properties near the monolayer limit [1,2]. However, manganese diselenide ($MnSe_2$) is of special interest among them since its monolayer 1T polytype has been found to display long-range magnetic ordering and high magnetic moments near room temperature conditions, making it uniquely qualified for various spintronic applications [3,4]. In this study, two-dimensional heterostructure of $MnSe_2$ is grown via Chemical Vapor Deposition (CVD) on few layers epitaxial graphene (EG) synthesized on 6H silicon carbide (SiC) substrate. Two different CVD growth approaches have been investigated in this study: Thermal Vapor Deposition (TVD) and Thermal Vapor Selenification (TVS). In the TVD approach, selenium (Se) powder precursor was used alongside either manganese (IV) oxide (MnO_2) or manganese acetate ($Mn(CH_3CO_2)_2$) powder for direct CVD growth of $MnSe_2$ on epitaxial graphene. In the TVS approach, δ-phase MnO_2 is first electrodeposited on EG using a manganese acetate solution, which is then selenified via CVD using only Se powder precursor.

The samples grown were characterized via Raman, SEM, and AFM tools, all of which demonstrated the presence of $MnSe_2$ growth for both TVD and TVS mechanisms. For both precursor combinations of the TVD approach, the characteristic A_g Raman peak of $MnSe_2$ was visible at 269 cm^{-1}, although its low intensity (almost 40-50% of the control FTA peak of the substrate at 203cm^{-1}) indicates small grain sizes and yield density, a conclusion supported by the SEM and AFM images (around 0.1-0.3µm diameter grains). The yield was found to be slightly higher (about 300% larger grain size) for MnAc compared to MnO_2. For the TVS approach, however, both E_g and A_g peaks were found to be visible (at 145cm^{-1} and 267cm^{-1} respectively) with extremely high peak intensity (around 500% of the control peak), implying significantly higher $MnSe_2$ yield, as also evident in the AFM and SEM data characterized by a high deposition density along the graphene step edges. This comparative study of the two approaches clearly shows TVS to be the far superior mechanism compared to TVD for $MnSe_2$ growth on epitaxial graphene. The TVS approach, once optimized, should result in single-crystal monolayer growth of $MnSe_2$ heterolayer on the epitaxial graphene substrate, potentially leading to the wafer-scale synthesis of $MnSe_2$ based spintronic devices.

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2D-Contributed On Demand-7 Room Temperature Chemical Sensors Based on Molybdenum Disulfide Nanoflower/Epitaxial Graphene Heterostructure*, **Soaram Kim,*** University of Maryland College Park*; J. Park,* Korea Research Institute of Standards and Science, Korea (Republic of)*; M. Pedwitz, D. Lewis,* University of Maryland College Park*; S. Lee,* The Ohio State University*; B. Uppalapati, D. Khan, F. Bayram, G. Koley,* Clemson University*; S. Kang,* Korea Research Institute of Standards and Science, Korea (Republic of)*; K. Daniels,* University of Maryland College Park

In recent years, a van der Waals heterostructure device, stacking 2D architectures atomically with synergistic combinations of nanomaterials have attracted tremendous attention with many potential applications such as chemical sensors in environmental and safety monitoring, and medical diagnostics and biomedical health care systems [1,2]. Atomically thin 2D graphene and transition metal dichalcogenides (TMDs) have an extremely high surface-to-volume ratio which is the most critical parameter for chemical sensing applications. Here we have fabricated a heterostructure of molybdenum disulfide (MoS_2) nanoflower and epitaxial graphene on 6H silicon carbide (SiC) substrate for chemical sensing. We have combined the advantages of high sensitivity and fast response time of graphene with the high surface-to-volume ratio of MoS_2 nanoflower to develop a room temperature chemical sensor for health/environmental monitoring systems.

Bilayer epitaxial graphene (EG) was synthesized by Si sublimation on 6H SiC, and MoS_2nanoflowers were grown on graphene/SiC directly using metal-organic chemical vapor deposition (MOCVD). The growth methods of graphene and MoS_2 nanoflowers are discussed in detail elsewhere [3,4]. The structural and optical properties of the samples were investigated by scanning electron microscopy (SEM), atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, photoluminescence (PL), and cyclic voltammetry (CV). To fabricate the chemical sensor, e-beam lithography and reactive ion etching (RIE, CF_4) were used to prepare a simple pattern. Finally, the metal electrode (Ti/Au = 30/120 nm) was deposited using an e-beam evaporator. The prepared chemical sensor was tested with various gases such as 5 ppm of nitrogen dioxide (NO_2) and ammonia (NH_3), and ~1000 ppm of volatile organic compounds (VOCs) and showed a superior chemical response and recovery at room temperature. It is evident that the prepared device is suitable for chemical sensing applications such as health and environmental monitoring systems.

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2D-Contributed On Demand-10 Structural Characterization of Cobalt Sulfide Sheets Supported on Au(111)*, **Mahesh Krishna Prabhu**, I. Groot,* Leiden University, Netherlands

Transition metal dichalcogenides (TMDCs) are a type of 2D materials widely investigated by both experimentalists and theoreticians, because of their unique properties.In the case of cobalt sulfide, density functional theory (DFT) calculations on freestanding S-Co-S sheets suggest there are no stable 2D cobalt sulfide polymorphs, whereas experimental observations clearly show TMDC-like structures on Au(111). In this study we resolve this disagreement by using a combination of experimental techniques and DFT calculations, considering the substrate explicitly. We find a 2D CoS(0001)-like sheet on Au(111) that delivers excellent agreement between theory and experiment.Uniquely this sheet exhibits a metallic character, contrary to most TMDCs, and exists due to the stabilizing interactions with the Au(111) substrate.

2D-Contributed On Demand-13 Edge Channels of Broken Symmetry Quantum Hall States in Graphene probed by Atomic Force Microscopy, ***Sungmin Kim,** J. Schwenk,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; D. Walkup,* National Institute for Science and Technology (NIST)*; Y. Zeng,* Columbia University*; F. Ghahari,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; S. Le,* National Institute of Standards and Technology (NIST)*; M. Slot,* National Institute for Science and Technology (NIST)*; J. Berwanger,* University of Regensburg, Germany*; S. Blankenship,* National Institute for Science and Technology (NIST)*; F. Giessibl,* University of Regensburg, Germany*; N. Zhitenev,* National Institute for Science and Technology (NIST)*; C. Dean,* Columbia University*; J. Stroscio,* National Institute for Science and Technology (NIST)

The quantum Hall (QH) effect, a topologically non-trivial quantum phase has brought into focus the concept of topological order in physics. The topologically protected quantum Hall edge states are the essential features of the QH effect, however microscopic local probe studies of edge state have been limited. The QH edge states in graphene are special since they emerge from four-fold nearly-degenerate Landau levels. In this talk, we present a microscopic study a of the QH edge states originating from the broken symmetry zero Landau level (zLL) in graphene. The edge states emerging from integer filling factors of $v = 0, \pm 1$ are spatially mapped across the quantum Hall edge boundary using atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) technique. The measurements of chemical potential within the four-fold degenerate zLL suggest a change in the microscopic spin/valley ordering as a function of magnetic field caused by the interplay of the moiré superlattice potential of the graphene/hBN system and other symmetry breaking effects.

2D-Contributed On Demand-16 Band Gap Tuning in Lateral Heterostructures of Mose$_{2(1-x)}$S$_{2x}$-Wse$_{2(1-x)}$S$_{2x}$ TErnary Alloys*, Florence Ann Nugera, P. Sahoo,* University of South Florida*; Y. Xin,* National High Magnetic Field Laboratory, Florida State University*; H. Gutierrez,* University of South Florida

Transition metal dichalcogenides (TMDs) ternary alloys have composition dependent electronic properties, such as bandgap, work function, and electrical response (n-type or p-type conductivity). When individual ternary alloys are combined to form heterostructures, their functionality can be greatly expanded compared to heterostructures based on binary alloys. Thus, opening a path for new optoelectrical applications with flexible designs and enhanced properties. In this work, we successfully synthesize lateral heterostructures with monolayer, bilayer and trilayer thicknesses based on ternary alloys of the type MoSe$_{2(1-x)}$S$_{2x}$-WSe$_{2(1-x)}$S$_{2x}$, where x is the chalcogen atom composition. The continuous tuning of the band gap for both materials, is demonstrated. The composition homogeneity of each domain was studied by photoluminescence (PL) and Raman spectroscopy, while Kelvin probe force microscopy (KPFM) was used to study the tunable band alignment at the heterojunctions.

2D-Contributed On Demand-19 Nonuniform Debye Temperatures in Quasi-One-Dimensional TiS$_3$ and ZrS$_3$*, Archit Dhingra, P. Dowben,* University of Nebraska-Lincoln, USA

TiS$_3$ and ZrS$_3$ are quasi-one-dimensional n-type van der Waals semiconductors that offer an opportunity to fabricate transistors with widths < 10 nm, as they lack undesirable edge effects unlike other well-studied two-dimensional materials (namely: graphene and transition metal dichalcogenides). TiS$_3$ and ZrS$_3$ have modest band gaps of ~1 eV and ~1.8–2.1 eV, respectively, and both the materials are highly anisotropic. The combination of adequate band gaps and appreciable electron mobilities indicates some potential for these metal trichalcogenides materials in applications in beyond CMOS sensor electronics. Temperature dependent x-ray photoemission spectroscopy (XPS) measurements were employed to obtain a quantitative picture of electron-phonon scattering in these materials. The Debye–Waller factor plots for S 2p core-level of TiS$_3$, based on the temperature dependent XPS measurements, hint that effective Debye temperatures of the two different kinds of sulfur coordination are 464 ± 35 K and 547 ± 26 K. Whereas the Debye–Waller factor plots for the S 2p core-level of ZrS$_3$ suggest effective Debye temperatures of 558 ± 30 K and 667 ± 35 K for, again, the two different sulfur coordination. The apparent difference between the effective Debye temperatures of different sulfurs, within the material, is an expected consequence of dissimilar coordination number. Additionally, the high effective Debye temperatures of the different sulfur species in ZrS$_3$ than in TiS$_3$ imply that the trichalcogenide of zirconium is stiffer than its titanium counterpart, which translates to reduced electron-phonon scattering in the former. This conclusion is further supported by the temperature dependent filed-effect mobility measurements, which consistently indicate that the carrier mobility of ZrS$_3$ is less sensitive to temperature changes in comparison with that of TiS$_3$. Even though the electron-phonon scattering is implicated as the cause for the much lower measured mobilities compared to the predicted high carrier mobilities (~10,000 cm^{2}V^{-1}s^{-1} for TiS$_3$ and ~1,800–2,500 cm^{2}V^{-1}s^{-1} for ZrS$_3$), the relatively high Debye temperatures indicate that there are only a limited number of soft phonon modes for these materials, which can be possibly suppressed, leading to improved mobilities.

2D-Contributed On Demand-22 3D Spin Polarized – Angle Resolved Photoemission Spectroscopy (SP-ARPES) setup at IMDEA Nanociencia*, **Beatriz Muñiz Cano**, M. Valbuena Martinez,* IMDEA Nanociencia, Spain

Angle-Resolved Photoemission Spectroscopy (ARPES) is a fundamental tool to visualize the momentum-dependent electronic bands of materials, revealing relevant characteristics, parameters and new interactions [1, 2] in them. Spin-ARPES (SR-ARPES) adds up spin resolution and, by measuring spin polarization, allows the complete determination of a quantum state [3]. The SRARPES technique has been proven to be extremely powerful in recent years as it allows studying spin-polarized electronic states in two-dimensional (2D) systems with strong spin-orbit coupling

(SOC), whose related phenomena, such as the Rashba effect or the appearance of topological insulators (TI), give rise to new interactions and particularly relevant electronic states, which can be exploited in spintronics and spin-orbitronics [4]. In this sense, interfacing Rashba or topological surface electronic states with ferromagnetic thin films (FM/SOC) [5, 6] can modify their spin texture and be at the origin of emerging phenomena as spin-charge conversion, switching out-of-plane magnetization by spin transfer-torque, DM Interaction and chiral spin structures as skyrimions, or the

quantum anomalous Hall Effect [7]. Thus, controlling interfacial interactions and their effect on spin-polarized electronic states is crucial. In this contribution we will present the new SR-ARPES facility at IMDEA Nanoscience which includes a 3D mini-Mott Spin Detector, which allows the determination of the 3D spin components (two in-plane and one out-of-plane). So far, we have measured the Rashba surface state spin texture in Au(111) (Fig. 1), including Fermi surface (FS) mapping and spin resolved measurements in valence band (VB) and surface state (SS). Finally, some perspectives for the study of 2D topological quantum materials or emerging phenomena in FM/SOC interfaces will be presented as well as some experiments related to the abovementioned phenomena arising from SOC and that, in the light of previous results obtained in the group, are expected to be continued with this new system and further developed in different synchrotron facilities.

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2D-Contributed On Demand-25 Tuning Ferromagnetic Properties of Monolayer CrI$_3$ via Molecular Adsorption*, **Jiho Yang**, B. Shong,* Hongik University, Korea (Republic of)

Two-dimensional (2D) materials with various electrical and optical properties are attracting large research interests. Moreover, ferromagnetic(FM) 2D materials possess interesting possible applications such as sensors and data storage. For example, CrI$_3$ has been shown to exhibit FM properties as either bulk or monolayer structures. However, its relatively low Curie temperature of ca. 45K hinders device application of CrI$_3$. In this work, we employ density functional theory (DFT) calculations with spin orbit coupling (SOC) to examine the adsorption of NH$_3$, PH$_3$, NO and NO$_2$ on 2D monolayer CrI$_3$. The variations in the adsorption energy and charge transfer, and the resulting changes in the band structure and the magnetic anisotropy are analyzed. In addition, the shifts in the Curie temperature according to the molecular adsorption are estimated via Monte Carlo simulations assuming Ising model.

2D-Contributed On Demand-28 Electron Emission from Quasi-freestanding Bilayer Epitaxial Graphene Microstructures*, **Daniel Lewis**, K. Daniels,* University of Maryland, College Park

Graphene microstructures have been shown to exhibit controllable directional electron emission when carrying a current under an accelerating electric field. Through Phonon-Assisted Electron Emission (PAEE), graphene microstructures demonstrate electron emission at electric field intensities and lattice temperatures below what would be expected for carbon to demonstrate field emission or thermionic emission, respectively. Furthermore, such emissions tend to be out of the plane of the graphene microstructure, allowing control of the directionality of the emission current even before being directed with an applied electric field.

Thus far, such arrangements have tended to involve structural dimensions in the range of micrometers, commonly with CVD-transferred graphene and carbon nanotubes. However, even with hundreds of kV/cm applied fields, emission currents rarely exceed a few nA. Herein are examples of the characteristics and tunable variables demonstrated by multiple epitaxial graphene structures, with dimensions up to cm, capable of producing >1 µA emission currents in applied fields of 2 kV/cm.

Quasi-freestanding epitaxial graphene on a silicon carbide substrate offers several advantages compared to transferred graphene or unzipped nanotubes, including lower defect density, greater structural integrity, ease of handling, and compatibility with simple photolithography fabrication techniques. The devices presented here were fabricated with a low-cost, wafer scalable, single-photomask process that obviates the need for material transfer to a second substrate and is easily tailored to create any variation in design parameters.

Initial tests demonstrate clear patterns of behavior in device performance linked to multiple testable variables, including device and substrate temperature, input power, applied field, dimensions, morphology and orientation, and cycle time. Results presented here show these influences affecting device output by up to an order of magnitude in some cases, while investigations of device durability and operational lifetime are ongoing. These graphene microstructure electron sources may provide a means for device implementation in a 2D heterostructure environment or as a vehicle for further miniaturization of constructs requiring controllable electron emissions, such as electron microscopy or X-ray generation.

2D-Contributed On Demand-31 From Energy Dissipation on Dirac Materials to Intermediate Stages of Hexagonal Boron Nitride Growth*,* ***Anton Tamtögl****, A. Ruckhofer,* Graz University of Technology, Austria*; N. Avidor,* University of Cambridge, UK*; M. Sacchi,* University of Surrey, UK*; M. Bremholm, P. Hofmann,* Aarhus University, Denmark*; G. Benedek,* University of Milano-Bicocca, Italy*; W. Allison,* University of Cambridge, UK

We have been studying various processes of energy dissipation in order to understand the nanoscale surface dynamics of Dirac materials experimentally and theoretically. Among this material class, topological insulators such as Bi_2Te_3 exhibit an insulating gap in the bulk while the surface is electrically conducting [1]. However, in real samples and at finite temperatures, their ideal zero-Kelvin behaviour is perturbed and scattering processes via electron-phonon (e-ph) coupling can give rise to energy losses. In this context atom-surface scattering has been demonstrated to be a sensitive probe to determine the surface phonon dispersion and the e-ph interaction parameter [1-3]. We will discuss the influence of the dimensionality on the e-ph coupling [4], when considering low-dimensional or quasi one-dimensional systems [5].

Furthermore, the lineshape broadening upon inelastic scattering from surfaces can be used to determine the characteristics of energy dissipation upon the motion of atoms and molecules [6,7]. Using this technique, we have studied the diffusion of water on the surfaces of Dirac materials (graphene and the topological insulator Bi_2Te_3)[7].Thus, we can specify the mechanisms underlying the motion of water and, by comparison with first-principle calculations, we identify aspects of its adsorption geometry, as well as the energy landscape for the motion. We see clear evidence for repulsive interactions between water molecules, which is contrary to the expectation that attractive interactions dominate the behaviour and aggregation of water. We are also able to make a qualitative assessment of the rates of energy transfer between water molecules and the topological insulator on which they move.[7].

Finally, we will discuss some recent experimental findings about the growth of hexagonal boron nitride (hBN) on Ru(0001). The growth of hBN on metal substrates, based on chemical vapour deposition, is well documented in literature [8]. In contrast to the reported structure of hBN after following the“ideal” growth conditions, we observe several intermediate structures, prior/parallel to the hBN growth, which, depending on the experimental conditions, can be transferred into each other or hBN.

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2D-Contributed On Demand-34 Observation of Intra-Unit-Cell Nematic Order in Epitaxial Bilayer FeSe Films on $SrTiO_3$(001)*,* ***Lian Li****, H. Zhang,* West Virginia University, USA*; M. Weinert,* University of Wisconsin, Milwaukee

Epitaxial FeSe thin films provide an ideal platform to probe the interplay of superconductivity and nematicity, due to the absence of long-range magnetic order. Here, we systematically investigate the nematic order in high quality bilayer FeSe/$SrTiO_3$ films grown by molecular beam epitaxy.Using low temperature scanning tunneling microscopy/spectroscopy, we observe features associated with Se atoms to be elongated along the Fe-Fe lattice direction within a specific energy window, demonstrating symmetry breaking from fourfold to twofold. Detailed analysis of Fourier transformation of the STM images reveals that the intensity of Fe Bragg peak breaks rotational symmetry within each Fe unit cell, indicative of an intra-unit-cell nematicity.Our results provide critical information on nematicity in Fe-based superconductors, an essential element in understanding superconducting transition in these materials.

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2D-Contributed On Demand-37 Phase Dependent-Nanoscale Friction on Two Dimensional Layers*,* ***Dooho Lee****, H. Lee, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Molybdenum disulfide (MoS_2) is one of the transition metal dichalcogenides (TMDs), having a layered structure like graphene. The monolayer of MoS_2 is an atomically thin semiconductor with a bandgap of 1.8 eV, which makes it good potential applications in nanoelectronics, optoelectronics, and sensors. Unlike graphene, which takes a significant portion in the studies about two-dimensional (2D) material, MoS_2 has many crystalline structures. Nanotribological study about the phase dependence will provide an important fundamental understanding of MoS_2, as well as TMDs.

In this contribution, we turned mechanically exfoliated 2H-MoS_2 into 1T-MoS_2 by lithiation process. We measured atomic-scale tribological and electrical properties of MoS_2 including friction, with atomic force microscopy (AFM). We report that with the phase transition of 2H to 1T, the friction of MoS_2 monolayer has greatly increased. We show that friction proportion of 2H-MoS_2 and 1T-MoS_2 is 0.19 : 1.1, with normalization to the value of mica. We attribute the friction increase of 1T-MoS_2 with increased overlap of phonon density of states (DOS) with mica substrate.

We also measured friction of $MoTe_2$, of which the pure 1T phase is commercially available since it shows stable 1T phase, as well as 2H phase. Friction proportion of exfoliated 1T-$MoTe_2$ and 2H-$MoTe_2$ is 0.12 : 1.07, normalized with the friction of mica. This study gives insight to the universal trend of the phase-dependent tribological effects on two-dimensional atomic layers.

2D-Contributed On Demand-40 A Full Gap Above the Fermi Level: The Charge Density Wave of Monolayer VS_2*, C. van Efferen,* II. Physikalisches Institut, University of Cologne, Germany*; J. Berges,* Institut für Theoretische Physik, University Bremen, Germany*; J. Hall,* II. Physikalisches Institut, University of Cologne , Germany*; E. van Loon,* Institut für Theoretische Physik, University Bremen, Germany*; S. Kraus,* II. Physikalisches Institut, University of Cologne, Germany*; A. Schobert,* Institut für Theoretische Physik, University Bremen, Germany*; T. Wekking, F. Huttmann, E. Plaar,* II. Physikalisches Institut, University of Cologne, Germany*; N. Rothenbach,* Fakultät für Physik und Center für Nanointegration, University Duisburg-Essen, Germany*; K. Ollefs,* Fakultät für Physik und Center für Nanointegration, University Duisburg Essen, Germany*; L. Machado-Arruda,* Institut für Experimentalphysik, FU Berlin, Germany*; N. Brookes,* European Synchrotron Research Facility, France*; G. Schönhoff,* Institut für Theoretische Physik, University Bremen, Germany*; K. Kummer,* European Synchrotron Research Facility, France*; H. Wende,* Fakultät für Physik und Center für Nanointegration, University Duisburg-Essen, Germany*; T. Wehling,* Institut für Theoretische Physik, University Bremen, Germany*;* ***Thomas Michely,*** II. Physikalisches Institut, University of Cologne, Germany

In the weak-coupling Peierls' view, charge density wave (CDW) transitions are metal-insulator transitions, creating a gap at the Fermi level. However, with strong electron-phonon coupling, theoretically the effects of the periodic lattice distortion could be spread throughout the electronic structure and give rise to CDW gaps away from the Fermi level. Here, using scanning tunneling microscopy and spectroscopy, we present experimental evidence of a full CDW gap residing in the unoccupied states of monolayer VS2. Our ab initio calculations show anharmonic coupling of transverse and longitudinal phonons to be essential for the formation of the CDW and the full gap above the Fermi level. The CDW induces a Lifshitz transition, i.e., a topological metal-metal instead of a Peierls metal-insulator transition. Additionally, x-ray magnetic circular dichroism reveals the absence of net magnetization in this phase, pointing to a coupled CDW-antiferromagnetic ground state.

2D-Contributed On Demand-43 Ferroelectrics Meet Ionics in the Land of van der Waals*, **Petro Maksymovych**, S. Neumayer,* Oak Ridge National Laboratory*; A. Ohara, S. Pantelides,* Vanderbilt University*; N. Balke,* Oak Ridge National Laboratory

Ionic conductivity is often considered a limiting factor for polarization switching or even incompatible with ordered ferroelectric states. Indeed, ionic conduction breaks down the dielectric state and gives rise to disorder, both of which should be detrimental for ferroelectricity. Recently we carried out comprehensive analysis of $CuInP_2S_6$ [1] – a lesser known ferroelectric material that represents a broad family of chalcogenophosphate van der Waals crystals. The polarization in this material is mainly governed by the displacement of Cu ions, which is also the most mobile ionic species. In this talk we will show that the van der Waals structure of this material combined with the high intrinsic mobility of Cu enables the intersection of ionic and ferroelectric properties, and gives rise to a rich spectrum of intriguing properties rare or even non-existent in known ferroelectric and ionic conductor materials.

The very large (by standards of ferroelectricity) displacement can be viewed as incipience of ionic conductivity. Density functional theory calculations and piezoresponse force microscopy have revealed that owing to such displacements, four distinct uniaxial polarization states arise in $CuInP_2S_6$ [2], including a previously unknown state that doubles spontaneous polarization. The resulting highly anharmonic potential for Cu motion in the ferroelectric state furthermore enables giant negative electrostriction, and a free energy potential highly susceptible to strain. Electric fields can also activate ionic currents [3], even in the ferroelectric state. Through a careful analysis of piezoelectric imaging data, we have concluded that activating ionic conduction by above-threshold fields unexpectedly switches polarization orientation inside the film. This ionically mediated mechanism is fundamentally different from dipole rotation that is typically expected for ferroelectrics. This symbiotic interplay of ferroelectric and ionic phenomena enables new approaches to control polarization. Moreover, it inspires a change in perspective on nucleation, domain wall dynamics and other ferroelectric characteristics in material systems where ionic and ferroelectric phenomena manifest.

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2D-Contributed On Demand-46 Multicomponent Monolayer Manipulation Through Successive Ultraviolet Irradiation*, **Cynthia Gerber**,* University of Connecticut

Mixed self-assembled monolayers can be manipulated to potentially control surface functionality through the facilitation of multi-molecule organization. The incorporation of anthracene dicarboxylic acid (AnDCA) in the monolayer causes greater disorder in the octanethiol domains. In this study, we analyzed the effects of ultraviolet radiation on a mixed monolayer of octanethiol and anthracene dicarboxylic acid. The UV radiation was sequentially applied in 10 minute increments and imaged by scanning tunneling microscopy after each round. The initial doses of UV light caused the octanethiol domains to diminish and further doses caused the octanethiol to reconstruct in striped phases with separate ordered domains of hydrogen-bonded AnDCA. This research contributes to the understanding of how exposure to ultraviolet light affects multicomponent monolayer construction of ordered domains and phase changes.

2D-Contributed On Demand-49 Thermally Induced Complex Reactions Pathways between Ws_2 and Au-Ti Substrates*, A. Costine ,* University of Virginia, USA*; J. Fonseca Vega, J. Robinson, C. Cress,* Naval Research Laboratory, USA*; **Petra Reinke**,* University of Virginia, USA

The fabrication of transistors which make use of the unique and versatile properties of transition metal dichalcogenides requires development of enabling technology for integration. This includes contacts, packaging, and stacking of electronically functional components. Ti-Au layers are common in transistor design and function as adhesion layer (Ti) and contact (Au). In our work the WS_2 flakes are transferred onto the Au-surface using micromechanical cleavage with a common adhesive, and subsequently integrated in a device structure. We probed the thermal stability of the Ti-Au-WS_2 stack by combining in-situ annealing with XPS analysis with small temperature intervals of 10-30°C in the temperature range from 200° to 625°C. The WS_2 layer itself is surprisingly stable with the onset of S-loss around 350°C, which is followed by formation of W-carbide and oxide (reaction with residue), and reduction to W(0) above 550°C. At the same time the Au-contact undergoes a dramatic change, and alloying with Ti occurs through rapid diffusive processes starting at 250°C, and concomitant reaction of surface Ti to form Ti-carbide and oxides through reaction with the residue from the TMD transfer. Ti-S compounds emerge only above 500°C. Alloying is suppressed if the Ti can rapidly react with surface carbon, oxygen and Ti diffusion is therefore transient limiting the formation of an alloy. However, if the concentration of the residue is low or a high coverage with WS_2 is achieved, the Ti-carbide and oxide formation is limited and Au-Ti alloys dominate. This reaction sequence leads to modification of the contact and can contribute to erratic, or irreproducible device performance. We will discuss the reaction pathways in detail, and use samples with and without WS_2, which acts as a control, and for different annealing conditions which interrupt Ti diffusion, to support our interpretation. The temperature induced modulation of the Au-TMD interface will degrade device performance, and requires to adapt the current strategies for device integration.

2D-Contributed On Demand-52 The (Mostly) Unwelcome Guest in 2D Chalcogenides: Native oxidation rates and the effects of oxygen during processing MoS_2, TiS_2, and $Zr(S,Se)_2$*, **Rafael Jaramillo**,* Massachusetts Institute of Technology

Being a very hard anion, oxygen bonds very differently to transition metals than do the chalcogens. Trace oxygen in a transition metal dichalcogenide (TMD) has a substantial impact on material processing and properties, much more so than for instance trace selenium in a sulfide. Since oxygen is all around us, even in our high-vacuum chambers, it is essential to understand and control the effects of oxygen on processing 2D materials. We report the results of three studies of the effect of oxygen on processing TMDs. We find that lowering trace oxygen concentration in the reactor makes it possible to lower the processing temperature for large-area TiS_2 films, made by reacting Ti thin films with H_2S gas. We quantify how lowering oxygen concentration enables faster metal sulfurization at lower temperatures (down to 500°C), leading to thin films that are smooth and homogeneous. In contrast, we find the opposite trend for MoS_2: *adding* trace oxygen enables lower processing temperatures (down to 375°C) for large-area MoS_2 films, made by sulfurizing Mo thin films. We understand these contrasting effects in the light of particulars of Ti-O and Mo-O bonds, including molecular dynamics (MD) simulations that suggest that oxygen is a catalyst for Mo-S bond formation. We also report a quantitative study of the rate of oxidation of freshly-cleaved surfaces of MoS_2 and $Zr(S,Se)_2$. MoS_2 surfaces remain pristine for over a year in laboratory ambient conditions, without a trace of oxide formation. In contrast, $Zr(S,Se)_2$ alloys oxidize rapidly, with the native oxide growing at a rate up to 0.5 Å/min. MD simulations reveal the kinetic mechanisms that limit native oxide growth for MoS_2 and promote it for $Zr(S,Se)_2$, despite oxide formation in ambient conditions being thermodynamically-favorable in all cases.

2D-Contributed On Demand-55 Correlative Analysis Strategies for Transition Metal Dichalcogenides*, **Umberto Celano**,* IMEC, Belgium

Considering their widespread use in future electronics and photonic applications, 2D materials are attracting the attention of the metrology community.[1] Considered an exciting class of 2D materials, transition metal dichalcogenides (TMDs) can be used to build devices whose optoelectronic properties are strongly influenced by the intrinsic and extrinsic defects, growth and transfer methods involved in their fabrication. Furthermore, considering complex integration schemes and stacked TMDs heterostructures, the detailed comprehension of the interaction of defects between layers and the capability to sense them have an even higher importance.[2]Therefore, it is crucial to develop metrology solutions to interpret defects-related phenomena on the nanometer scale for TMDs, and this remains a challenge for the community. Notwithstanding the complexity, the well know flexibility of atomic force microscopy (AFM) offer multiple alternatives for sensing TMDs properties in individual layers and heterostructures. For example, using electrical and electrostatic tip-sample interactions, as in conductive atomic force microscopy (C-AFM) and Kelvin probe force microscopy (KPFM), various atomic-scale defects can be identified and characterized.[3] Similarly, near-field methods such as tip-enhanced Raman spectroscopy (TERS) and compositional techniques such as secondary ions mass spectroscopy (SIMS), can team up to obtain the direct correlation between growing substrates and TMDs films quality. Here, using these and other techniques, we present a metrological analysis scheme that allow the (averaged) electrical characteristics of TMDs-devices to be correlated to the local material properties for a deeper connection to device physics.

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2D-Contributed On Demand-58 Measuring Van der Waals Interactions of Monolayer Materials*, Stanislav Tsoi,* US Naval Research Laboratory*; S. Sivaram,* Sila Nanotechnologies Inc.*; M. Rosenberger,* University of Notre Dame*; K. McCreary,* US Naval Research Laboratory*; H. Chuang,* Nova Research*; B. Jonker,* US Naval Research Laboratory

Van der Waals interactions play a major role in the science of monolayer materials, yet their measurement has received a limited attention. We exploit AFM to measure an attractive van der Waals (vdW) force acting on a sharp AFM tip from a composite sample consisting of a monolayer material supported on a thick substrate. The force is measured as a function of a separation between the tip and the monolayer/substrate stack in the range from 2-20 nm for graphene/silicon oxide, fluorinated graphene/silicon oxide, MoS_2/graphite and $MoSe_2$/graphite. The obtained results indicate that distinct contributions to the force from the monolayer and substrate can be distinguished by their different dependence on the separation, an inverse cubed for the former and inverse square for the latter. Thus, van der Waals interaction for different monolayer materials is determined and compared to the traditional bulk materials. Further, we demonstrate that the monolayer materials screen van der Waals interactions of the underlying substrate, with full screening in graphene/silicon oxide and partial screening in fluorinated graphene/silicon oxide, MoS_2/graphite and $MoSe_2$/graphite.

2D-Contributed On Demand-61 Measuring Surface Phonon Dispersion*, Timo Watjen,* Scienta Omicron, Sweden

Many interesting material properties cannot be described without a many body electronic structure approach. Electrons may interact not just with other electrons but also couple to bosons, for instance by electron-phonon coupling (EPC). ARPES measurements have revealed 'kinks' in the electron dispersion curves and EPC has been discussed as one possible origin [1-4]. This interaction highlights the need of phonon dispersion data which today largely relies on simulations. An experimental technique to access surface phonon dispersion is high resolution electron energy loss spectroscopy (HREELS). Traditionally, HREELS involved mechanically rotating the setup probing one angle and energy channel at the time. Operating such a setup is time consuming and has limited angular resolution. Here, we present a HREELS solution with monochromatic collimated electron source and a hemispherical analyzer [5]. The 2D detector of the analyzer, which simultaneously spans hundreds of channels in both the energy and angular directions, enables a massive speed-up in data collection. While ARPES enables electron dispersion measurements, HREELS can complement these with surface phonon dispersion curves in the same instrument.

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2D-Contributed On Demand-64 Two Dimensional TMDs Based Thermo-Electric Devices for Energy Harvesting from Waste Heat*, Sangram Pradhan,* *M. Mbaye, M. Behera, M. Bahoura,* Norfolk State University

High conformal with large area transition metal dichalcogenides (TMDs) crystalline thin films were grown at optimum substrate temperature using physical vapor deposition. Fundamental films properties were investigated using Structural, morphological and electrical techniques. XRD data revealed that TMDs (MoS_2 and WS_2) films are highly crystalline in nature and oriented in 00l plane. Thermal conductivity behavior of MoS_2 film also shows low value at room temperature which is excellent to achieve higher thermoelectric figure of merit close to 2. Raman spectroscopy data shows two distinct MoS_2 vibrational modes corresponding to signature E^1_{2g} and A^1_g peak of TMDs. Electrical, thermoelectric transport studies further demonstrated that MoS_2 films show p-type thermoelectric characteristics, while WS_2 is an n-type material. Finally, highly-efficient thermal energy harvesting pn-junction based thermoelectric generator were fabricate out of these TMDs for waste heat recovery and converted to electrical energy.

2D-Contributed On Demand-67 Behind the Scenes of Electron Induced Deposition of Amorphous-BN_x on Graphene - A Surface Science Study*, Virginia Boix,* Lund University, Sweden*; C. Struzzi,* MaxIV laboratory, Sweden*; T. Gallo, N. Johansson, G. D'Acunto, Z. Yong,* Lund University, Sweden*; A. Zakharov,* MaxIV laboratory, Sweden*; Z. Li,* Aarhus University, Denmark*; J. Schnadt, A. Mikkelsen, J. Knudsen,* Lund University, Sweden

A necessary tool for reducing the environmental impact of electronic devices is developing higher-performance and more energy-efficient components. Stacked heterostructure devices of two-dimensional (2D) materials are emerging as promising building blocks for such applications [1]. In such devices, conductive, semiconductive, and dielectric 2D materials are combined to reach the desired electrical function. The most used dielectric in 2D applications is hexagonal boron nitride (h-BN). However, direct synthesis of h-BN on top of 2D materials is complex due to their inert nature and the low growth temperature requirements for stacked electronics.

An exciting solution for these manufacturing constraints is to substitute the crystalline 2D h-BN with a thin film of amorphous-BN (a-BN) [2]. It has been recently reported that ultrathin films of a-BN have a bandgap similar to their crystalline counterpart and retain much of the valued chemical inertness and high thermal stability of h-BN [3]. Moreover, a-BN can be easily manufactured with high spatial resolution and low-temperature processing using Focused Electron Beam Induced Deposition (FEIBD) [4]. However, even though FEIBD is a widely used method [5], a thorough understanding of the electron assisted deposition, where multiple simultaneous processes compete with each other, is lacking.

In this contribution, we report on our surface science study of electron beam-induced deposition of amorphous-BN_x on graphene at room temperature [6]. Using a combination of X-ray Photoelectron Spectroscopy, Low Energy Electron Microscopy, and Scanning Tunneling Microscopy, we identify the essential steps of the deposition process, which highly influence the morphology of the heterostructure, its chemical composition, and its interaction with the substrate. We reveal a much higher decomposition of the precursor molecule than previously thought and a strong interaction with the substrate, which does not affect the structural integrity of the graphene. These results help explain the high boron concentration usually found in FEBID BN films and the thermal stability of the resulting structure.

Our studies provide a valuable surface science insight into using electron beams to synthesize stable and inert layers in 2D heterostructures. Moreover, we aim to spark a discussion about further applications of FEBID, such as confined doping and functionalization of graphene (or other 2D films), patterned adsorption of mass-selected ions, or patterning of adsorbates as anchors for attaching bigger molecules.

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2D-Contributed On Demand-70 Formation, Structure and Properties of 2D Silica and Transition Metal Silicates on Gold*, N. Doudin, K. Saritas, S. Ismail-Beigi,* ***Eric Altman,*** Yale University

Two-dimensional silica has attracted attention as model catalysts, ultimate permeation membranes, while related 2D transition metal silicates have potentially interesting piezoelectric and magnetic properties. Gold's inert, non-magnetic nature makes it an attractive substrate for model catalyst studies and investigation of 2D magnetic layers. Here we report on experimental and theoretical studies on the growth and structure of 2D silica and transition metal silicates on polycrystalline Au and Au(111). Experimental reflection absorption infrared spectroscopy, electron diffraction and scanning tunneling microscopy (STM) indicate that 2D silica bilayers can be formed by both atomic layer deposition and molecular beam epitaxy. By adjusting the imaging bias, it was possible to peer through the insulating 2D silica to image the underlying Au surface which revealed that the Au(111) herringbone reconstruction was scarcely affected by the 2D silica bilayer, consistent with the expected weak van der Waals interaction between the 2D material and gold substrate. The results also suggest the coexistence of the 2D crystalline and amorphous polymorphs. STM measurements following sequential deposition of SiO and Fe followed by high temperature annealing in low pressure oxygen reveal ordered Fe silicate phases. Density functional theory and ab initio theory has been employed to identify stable Fe-Si-O phases on Au(111) and assess their potential for ferromagnetic coupling. A broader theoretical survey of magnetic coupling in first row transition metal layered silicates has identified structural motifs that favor ferromagnetic order.

2D-Contributed On Demand-73 Transition Metal -Silicates at the 2-D Limit*,* ***Nassar Doudin****, K. Saritas, S. Ismail-Beigi, E. Altman,* Yale University

Low-dimensional materials display novel emergent properties at the forefront of solid-state physics and chemistry and thus are of both fundamental scientific and applied technological interest. Here, van der Waals (VDW) materials at the 2-D limit, that is transition metal silicates in "quasi-bilayer" phases, supported on a different metal surface (e.g., epitaxial metal film[1]). The electronic and elastic coupling of the oxide nanophase to the underlying metal support creates a hybrid system with novel physical and chemical properties that are not shared by the individual constituents. I will investigate two topics in this talk: i) a 2-D oxide phase, which we have prepared by a solid state chemical reaction in two dimensions; and ii) a post-growth hydroxylation study of Fe-silicates on Pd(111) and Au(111) surfaces by using H_2O, H_2, and O_2 as probe molecules, both to gauge the electronic and chemical properties of the M-silicates systems and to investigate its functioning as multiferroic materials in the future. In the first part of the talk, I will concentrate on new structure concepts and their relation to the electronic and magnetic behavior of 2-D systems. In the case of the Fe-silicates, I will introduce a new approach to fabricate well-ordered oxide systems in low dimensions. The computational studies further reveal that the M-silicates (M= Fe, Co, Ni, Mn)can be stable, and further that the transition metal oxidation state may be tuned through the M:Si ratio and by altering the hydroxylation of the layer.[2]

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2D-Contributed On Demand-76 Designing Transition Metal Dichalcogenide Alloys for Photonic Integrated Circuit Applications*,* ***Yifei Li****, R. Jaramillo,* Massachusetts Institute of Technology

Transition metal dichalcogenides (TMDs) exist in several polymorphs including 2H (usually semiconducting), and 1T/1T' (usually semi-metallic). Our theoretical calculations and experimental measurements show that TMDs are optically-dense and can feature a difference in refractive index greater than unity between phases in the near-infrared (NIR). Fast, non-thermal martensitic phase-change behavior has been observed in TMDs, and transformation strains are expected to be low due to the layered crystal structure. For these reasons, we suggest that TMDs may be useful as active materials to control the phase of light in integrated photonic circuits, surpassing the performance of traditional phase-change materials.

Sulfide TMDs are attractive for application to photonics because they present lower optical loss and higher material stability than selenides or tellurides. However, sulfide TMDs also have higher transformation energy barriers. We address this problem by designing sulfide TMD alloys that are thermodynamically-adjacent to phase boundaries. We use density-functional theory (DFT) and the quasi-harmonic approximation to calculate free energy-composition diagrams at finite temperature for polymorphs in the MoS_2-TiS_2-ZrS_2 system. Our calculations predict that the free energy difference between phases can be reduced to near-zero through alloy design. We then synthesize sulfide TMD thin films through a two-step process of metal sputtering, followed by sulfurization in H_2S in a chemical vapor deposition (CVD) furnace. This two-step method, combined with combinatorial sputtering, enables rapid exploration of composition space and phase boundaries. By controlling the CVD furnace conditions, and in particular the trace oxygen concentration, we are able to lower the processing temperature for large-area alloy thin films below 500 °C; this is important for yielding good film morphology and for photonic integrated circuit integration. Finally, we demonstrate a test concept to study phase-change behavior with electrical stimulation and optical readout for a composition spread across a wafer, and we characterize the phase-change behavior of sulfide TMD alloys by Raman spectroscopy, spectroscopic ellipsometry, and infrared spectroscopy.

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2D-Contributed On Demand-79 Direct Imaging of Optoelectronic Properties at Atomically-Thin Semiconductor-Metal Buried Interface*,* ***Kiyoung Jo****, P. Kumar, S. Anantharaman, D. Jariwala,* University of Pennsylvania

Metal contact to two-dimensional semiconductor-Metal is one of the most consequential for high performance and highly scaled electronic and optoelectric devices. For example, fermi-level pinning in semiconductor-metal interface causes non-idealities in any device operation resulting in parasitic energy dissipation when electrical carriers diffuse from metal to semiconductor. Yet, the chemistry of the contact is poorly understood because semiconductor-metal contact is buried interfaces which make it difficult to probe directly. However, for 2-dimensional transition metal dichalcogenides, signals from semiconductor-metal interface are not screened out due to its atomically thin nature. In this talk, we will present spatial imaging of optoelectronic characteristics at the interface. Using a unique metal-assisted flipping technique, it is possible to access the optical and electronic properties of the buried interface. Taking advantage of scanning tip microscopy coupled with spectroscopy, we conducted kelvin probe force microscopy (KPFM), conductive-AFM, tip-enhanced Raman and photoluminescence spectrum, leading to concurrent map of electrical potential, conductivity, charge density, strain and emission spectra at the interface with deep-subwavelength (~20 nm) spatial resolution. We observe that direct evaporation of Au on monolayer MoS_2 creates ohmic contact reaching resistivity of 138 kΩ µm due to large strain of ~5% in the monolayer MoS_2 surface and charge transfer. MoS_2/*h*-BN/Au structure fabricated by the same technique reveals that intimate contact between monolayer MoS_2 and Au is critical for the strain and charge transfer effect. Different contacts out of different types of metal (Au, Ag, In/Au alloy) are explored, revealing that In/Au alloy-MoS_2 records lowest contact resistivity of 63 kΩ µm. The differences in contact quality is attributed to different levels of intimacy between MoS_2 and metal as well as defect creation during metal growth and cooling. Our result emphasizes that the importance of metal deposition schemes and paves a way towards engineering low resistance contacts.

2D-Contributed On Demand-82 Two-Dimensional High-Entropy Transition Metal Dichalcogenide Alloys*,* ***Aditya Deshpande****,* University of California Los Angeles*; C. Ratsch,* Institute for Pure and Applied Mathematics, UCLA*; C. Ciobanu,* Colorado School of Mines, USA*; S. Kodambaka,* University of California Los Angeles

Layered van der Waals (vdW) transition metal dichalcogenides (TMDCs) with the chemical formula MX_2 (M = transition metal from Groups 4-7 and X = S, Se, Te) are a family of widely studied materials that have expanded the range of electronic and electrochemical properties associated with two-dimensional (2D) materials, and their potential technological applications. In this work, we use density functional theory calculations for monolayer TMDCs with multiple cation species to point out the exciting possibility to further expand the range of 2D materials (and their properties) by showing that TMDCs with as many as five cation species, dubbed high-entropy TMDC (HETMDC) can be stable in either the 2H or 1T phases at temperatures between 100 K and 500 K. We have used random alloys of five cations (out of a total of nine cations) and showed that over 200 high-entropy TMDC alloy monolayers are likely to be realized experimentally in 2H or 1T phases, and also have shown that the stacking of such monolayers remains governed by vdW interactions. We have evaluated the sulfur vacancy formation energies in multication alloys and estimated the vacancy populations for a wide range of temperatures. We have found that HETMDC alloys display significantly larger vacancy populations compared to simple TMDCs at the same temperatures, due to a very wide range of vacancy formation: these results imply that the catalytic activity of HETMDC is vastly superior to TMDCs, hence illustrate the possibility of high-activity catalysts based on HETMDCs.

2D-Contributed On Demand-85 Doping of $MoTe_2$ via Surface Charge Transfer in Air, ***Cristian Ciobanu,*** Colorado School of Mines; *G. Stan,* NIST; *S. Likith,* Colorado School of Mines; *A. Rani, S. Zhang, C. Hacker, S. Krylyuk, A. Davydov,* NIST

Doping is a key process that facilitates the use of semiconductors for electronic and optoelectronic devices, by which the concentration and type of majority carriers (electrons or holes) can be modified controllably to achieve desired conduction properties. We report that changes in the surface potential of MoTe2 are determined by air adsorbates and the number of layers of exfoliated material. Changes measured in surface potential and work function could be attributed to the permanent dipole of the adsorbed molecule as well as to the charge transfer between the surface and the adsorbates (induced dipoles). Through density functional theory calculations we are able to remove this ambiguity, showing that (non-polar) oxygen molecules physisorb and drain electrons from the surface, thereby making it p-type and increasing its work function. This is in agreement with our Kelvin probe microscopy measurements; other adsorbates, such as water or hydroxyl, do not lead to agreement with the experimentally measured variations of the work function. Surface charge transfer doping (SCTD) driven by adsorbates can be easily adjusted through thermal annealing of the entire sample, leading to an effective modulation of the surface potential of MoTe2. Furthermore, we also illustrate local control of the surface charge doping by contact electrification using the probe of an electrostatic force microscope as a floating gate. After annealing or contact electrification, the air-exposed MoTe2 surfaces exhibit a slow reversal processes of re-adsorption of oxygen, restoring of the p-type doping. These investigations can complement typical field effect transistor measurements used to extract electronic transport properties of devices based on 2D materials. As a reversible and controllable nanoscale physisroption process, SCTD can thus open new avenues for the emerging field of 2D-TMDC electronics.

2D-Contributed On Demand-88 Stacking-Dependent Optical Properties in Bilayer WSe_2, ***Kathleen McCreary,*** *M. Phillips,* Naval Research Laboratory; *H. Chuang,* NOVA Research; *D. Wickramaratne,* Naval Research Laboratory; *M. Rosenberger,* University of Notre Dame; *C. Hellberg, B. Jonker,* Naval Research Laboratory

It has recently been demonstrated that the angle between layers of two-dimensional materials can strongly impact the resulting properties, inspiring the rapidly developing research area of twistronics. Here, we investigate stacking-dependent optical properties in bilayer WSe_2. Both 2H and 3R stacking orientations are synthesized by chemical vapor deposition. Samples are investigated using photoluminescence, Raman spectroscopy, and reflectivity measurements under ambient and cryogenic conditions. In both 2H and 3R systems, the A_{1g} Raman mode is sensitive to excitation conditions, with orders of magnitude enhancement observed for certain excitation wavelengths. However, the laser wavelength leading to maximum enhancement is distinctly different for the two stacking orientations, with 2H-WSe_2 exhibiting maximum enhancement under 514 nm excitation and 3R-WSe_2 at 520 nm excitation at cryogenic temperatures. DFT calculations and reflectivity measurements indicate differences in band structure between the two systems, evident by shifts in emission energy of excitonic features, and elucidate the source of variation in Raman spectra. Maximum Raman enhancement is achieved when the excitation wavelength is resonant with the stacking-dependent C-excitonic feature. This work provides a comprehensive investigation of optical properties in 2H- and 3R-WSe_2 bilayers.

2D-Contributed On Demand-91 Small Energy Gap Revealed in $CrBr_3$ Using Scanning Tunneling Microscopy and Spectroscopy (STM/S), ***Dinesh Baral,*** *Z. Fu, A. Zadorozhnyi, R. Dulal, A. Wang, N. Shrestha, U. Erugu, J. Tang, Y. Dahnovsky, J. Tian, T. Chien,* University of Wyoming

Exploration of electronic and magnetic properties of 2D materials family is in a good advancement, with the goal of minimizing electronic devices towards atomic level. This family includes a huge range of materials- from insulators, semiconductors, metals to superconductors. In 2017, two independent groups demonstrated stable magnetic ordering in 2D vdW materials (CrI_3 and $Cr_2Ge_2Te_6$) [1,2] bringing in the ferromagnetic materials in 2D family. Since then, 2D magnetism has been discovered in various vdW materials, for example CrX_3 (X= Cl, Br, I) [3,4] among which $CrBr_3$ is the most air stable in CrX_3 family. Magnetic and optical properties of bulk $CrBr_3$ have been studied from 1960s. Despite the great attention in magnetic and optical properties, the electronic properties of $CrBr_3$ are relatively unexplored. Based on the various optical measurements, it is believed that $CrBr_3$ have an energy gap in the range of 1.68 – 2.1 eV[5,6]. Density fluctuation theory (DFT) reports show even higher deviations in the energy gap. These controversial results have indicated that the electronic properties of $CrBr_3$ is not well explored.

In this talk, I will present the result from STM/S of both thin and thick $CrBr_3$ flakes along with density fluctuation theory (DFT) calculations to reveal small energy gap to be 0.57 eV ± 0.04 eV[7]. This uncovering of small energy gap will solve the controversy and is the key to better understand the electronic properties of $CrBr_3$.

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2D-Contributed On Demand-94 Electrical Transport Properties of N- and P- Doped Inse: Bulk Crystals Versus Exfoliated Layers, ***Zheng Sun,*** The George Washington University; *S. Krylyuk,* National Institue of Standards and Technology; *P. Vora,* George Mason University; *M. Zaghloul,* The George Washington University; *A. Davydov,* National Institue of Standards and Technology

Efficient doping of van-der-Waals layered semiconductors, including carrier type, concentration and mobility, is challenging but essential for enabling their future electronic and photonic applications. Indium monoselenide, InSe, is a prime example of such layered materials with promising optoelectronic properties, which can be exfoliated down to few-nanometer-thin layers for device applications. This poster reports on substitutional n- and p- doping of InSe by introducing Sn and Zn dopants, respectively, in the Bridgman bulk crystal growth. Electrical transport properties of undoped vs. n- and p- doped InSe crystals are compared by conducting Hall measurements on the bulk InSe crystals and FET transport measurements on exfoliated thin layers. Undoped InSe is intrinsically n-type in both bulk and thin-film forms, with $[n]\sim 3.5\cdot 10^{14}$ cm^{-3} and m values of up to 1,400 $cm^{2}\cdot V^{-1}\cdot s^{-1}$ for thick layers at 300K. Carrier concentration in Sn-doped thick layers increases approximately two-fold, while the corresponding mobility reduces ~2 times at 300 K. Zn-doped InSe shows p-behavior for bulk InSe with $[p]\sim 7.9\cdot 10^{13}$ cm^{-3} and m ~ 43 $cm^{2}\cdot V^{-1}\cdot s^{-1}$ at 300 K, which reverts to ambipolar or n-type behavior for thin layers in FET devices.

2D-Contributed On Demand-97 Electronic Characterization Using Scanning Tunneling Microscopy and Spectroscopy of Solution-Synthesized Graphene Nanoribbons With Functional Groups, ***Abigail Berg,*** University of Illinois at Urbana-Champaign; *G. Li, A. Sinitskii,* University of Nebraska - Lincoln; *J. Lyding,* University of Illinois at Urbana-Champaign

We present the electronic characterization of a bottom-up solution-synthesized heterostructure made of the 9-A and chevron graphene nanoribbon (GNR) with $C_{10}H_{21}$ functionalized side chains. Atomically precise graphene nanoribbons with functional side chains have the potential of being connected to DNA origami scaffolding as a method of achieving deterministic GNR length and precursor arrangement. We use the dry-contact transfer (DCT) method to exfoliate the GNRs onto clean Si(100) in a room temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM). The bandgap and density of states are probed using scanning tunneling spectroscopy (STS). We find that there is a semi-transparency effect across the bulk of the GNR most likely due to random C-Si bonds forming at the GNR-substrate interface. There is also an induced doping effect on the substrate next to the GNR which is most pronounced along the top and bottom edges of the GNR.

2D-Contributed On Demand-100 Observation of Electrically Tunable van Hove Singularities in Twisted Bilayer Graphene from NanoARPES*, Ryan Muzzio,* Carnegie Mellon University*; A. Jones, P. Majchrzak, S. Pakdel,* Aarhus University, Denmark*; D. Curcio,* aarhus University, Denmark*; K. Volckaert, D. Biswas,* Aarhus University, Denmark*; J. Gobbo, S. Singh,* Carnegie Mellon University*; J. Robinson,* Naval Research Laboratory*; K. Watanabe, T. Taniguchi,* National Institute for Materials Science, Japan*; T. Kim, C. Cacho,* Diamond Light Source, UK*; N. Lanata, J. Miwa, P. Hofmann, S. Ulstrup,* aarhus University, Denmark*; J. Katoch,* carnegie Mellon University

The possibility of triggering correlated phenomena by placing a singularity of the density of states near the Fermi energy remains an intriguing avenue toward engineering the properties of quantum materials. Twisted bilayer graphene is a key material in this regard because the superlattice produced by the rotated graphene layers introduces a van Hove singularity and flat bands near the Fermi energy that cause the emergence of numerous correlated phases, including superconductivity. Direct demonstration of electrostatic control of the superlattice bands over a wide energy range has, so far, been critically missing. This work examines the effect of electrical doping on the electronic band structure of twisted bilayer graphene using a back-gated device architecture for angle-resolved photoemission measurements with a nano-focused light spot. A twist angle of 12.2° is selected such that the superlattice Brillouin zone is sufficiently large to enable identification of van Hove singularities and flat band segments in momentum space. The doping dependence of these features is extracted over an energy range of 0.4 eV, expanding the combinations of twist angle and doping where they can be placed at the Fermi energy and thereby induce new correlated electronic phases.

2D-Contributed On Demand-103 2020 AVS Graduate Research Awardee: Scanning Tunneling Microscopy Studies of Carbon-Based Nanostructures Grown Through Competing on-Surface Interactions and Chemistry*, Jeremy Schultz,* *N. Jiang,* University of Illinois at Chicago

Intermolecular and molecule-substrate interactions are paramount to on-surface chemistry, where highly localized chemical environments determine physical properties and dynamic processes. Scanning tunneling microscopy (STM) enables the ability to probe individual atoms and molecules, revealing local electronic effects and structure. STM was used to study a common method used to develop two-dimensional nanocarbon structures. The Ullmann-like coupling reaction is induced by a metal substrate, involving the the dissociation of an aromatic carbon-halogen bond which allows for covalent intermolecular coupling. We extend this reaction method to consider the effects of the inclusion of a catalytically active diketonic group within the structure of the precursor molecule. Additionally, the process was found to critically depend on the substrate identity.

On Ag(100), the precursor 3,6-dibromo-phenanthrequinone (DBPQ) molecules were found to self-assemble through hydrogen and halogen interactions, resulting in well-ordered molecular islands which impacted the organometallic structure ultimately formed after reaction. The metal-organic coordination networks that formed following thermal annealing were found to arise from the competition between C⋯Ag⋯C and C=O⋯Ag interactions [1]. On Au(100), two competing intermediate dimers were possible, cis and trans forms. The cis form was preferentially present on the bare Au(100), and the trans form occurred within atomic bromine networks that formed on the surface with total selectivity. The cis dimers were found to terminate at tetramers, as steric hindrance prevented the formation of longer oligomers. While the trans dimers could result in longer polymeric chains. Utilization of increasing coverage resulted in the selective formation of long polymer chains proceeding through the bromine stabilized trans dimers [2]. This work highlights the consequences of the inclusion of functional groups in the precursor molecule, as well as the roles of initial self-assembly, competing fundamental interactions, and leaving groups in steering reaction-based bottom-up assembly.

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2D-Contributed On Demand-106 Band Structure and Electronic Properties of Edge-Functionalized Germanene Nanoribbons*, Alexander Goldstone,* *Q. Li,* George Mason University

In the wake of the discovery of graphene, the search for new and remarkable 2D materials with astounding electronic and mechanical properties has led to the fabrication of germanene, a 2D germanium allotrope similar to silicene. Unlike the planar structure of the graphene lattice, germanene has a buckled honeycomb structure with two vertically displaced sublattices. Free-standing germanene is a semimetal, where the electrons behave as massless relativistic particles leading to enhanced carrier mobility. Indeed, recent studies have shown germanene to have an intrinsic carrier mobility on the order of $6\text{x}10^5$ cm^{2}V^{-1}s^{-1}[1], an order of magnitude greater than graphene's. Another advantage over graphene is germanene's larger spin-orbit gap (23 meV)[2], which when compared to graphene's (<0.05 meV) makes germanene a superior candidate to exhibit the quantum spin Hall effect at experimentally viable temperatures. Lastly, the germanene lattice allows for an opening of the band gap via an applied electric field or adsorption of foreign atoms, enabling the creation of germanene based field-effect devices. In this study we analyze the effect of edge passivating species H, C, N, P, As, O, S, Se, Te, F, Cl, Br, and I on the electronic and spin-orbit properties of germanene armchair and zigzag nanoribbons. For each species, the effect of width and strain on the band structure is examined, as well as the magnetic moment and spin orbit gap of the nanoribbons to explore potential applications for spintronic devices. We found that for each passivating species, the armchair nanoribbons transition between semiconductor and semimetal in a cyclical pattern depending on width. The bandgap of the nanoribbon, as well as the semimetal point, are tunable through width, passivation species, and mechanical strain. In the case of zigzag germanene nanoribbons, the material remains a semimetal regardless of width, but the nature of the band structure varies significantly among different passivation species with some displaying potential superconducting properties. The different passivation species reveal distinct groups showing similarities in both the geometric structure and band structure of the nanoribbons over various widths. Using machine learning we attempt to classify these passivation species into distinct groups that generate nanoribbons with similar physical and electronic properties.

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2D-Contributed On Demand-109 Non-Enzymatic Electrochemical Sensing of H_2O_2 Based on 2d Tellurene*, Netanya Dennis,* *F. Yan, M. Garcia Cervantes, B. Chitara,* North Carolina Central University

2D tellurene (Te) nanosheets have recently emerged as promising building blocks for nanoscale high-performance electronic and optoelectronic devices due to their unique electrical and optical properties. Here, we report the synthesis of large-area, high-quality 2D Te nanosheets using a facile one-pot hydrothermal approach, and demonstrate for the first time their use for electrochemical detection of hydrogen peroxide (H_2O_2) with micromolar sensitivity. The as-synthesized 2D Te nanosheets were characterized by Raman spectroscopy, scanning electron microscopy, and atomic force microscopy. The electrochemical performance of 2D Te nanosheets was examined by cyclic voltammetry and amperometry. The 2D Te nanosheets-based sensor shows selective detection of H_2O_2 in the presence of higher concentrations of common interfering substances in human sweat, including NaCl, ascorbic acid, uric acid, and dopamine. An exploration of the feasibility of this methodology for glucose detection in artificial human sweat is currently underway. The findings reported here shed new light on the development of a new generation of flexible and wearable glucose sensors based on 2D materials.

2D Materials

Room On Demand - Session 2D-Invited On Demand

2D Materials Invited On Demand Session

2D-Invited On Demand-7 Tuning Energy Levels and Energy Flow in Nanomaterials Using the External Environment*, Archana Raja,* Lawrence Berkeley National Laboratory **INVITED**

The interaction between charge carriers in atomically thin, quasi-two-dimensional (2D) materials is strongly influenced by the local environment. I will discuss how tuning the external dielectric screening can modify the band gap and exciton energies in 2D transition metal dichalcogenides, allowing the formation of lateral heterojunctions without modifying the material itself [1]. Furthermore, using a combination of optical and angle resolved photoemission spectroscopies with microscopic spatial resolution, we show that the band structure rigidly shifts in response to the change in local dielectric screening [2]. This environmental sensitivity can also lead to a new type of disorder that leads to spatially inhomogeneous band gap and exciton energies as a consequence of spatial variations in the external dielectric screening rather than any material imperfections [3]. I will also briefly discuss new experimental approaches to the study of interfacial phenomena in 2D heterostructures and the associated ultrafast dynamics. In addition to the intrinsic scientific interest in understanding materials in this distinctive regime, such control offers a non-invasive approach to engineer material properties by tuning the local environment rather than the material itself, yielding a new paradigm for nanoscale devices.

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2D-Invited On Demand-13 Atomic-Scale Study and Engineering of Low-Dimensional Materials*, Jani Kotakoski,* University of Vienna, Austria **INVITED**

Despite the great promise of two-dimensional materials due to their exciting properties, they are not always directly suitable for applications. One way to tune the material properties is to manipulate the atomic structure using particle irradiation. However, as one might expect, this is challenging to do in the case of extremely thin materials, where careful control over the irradiation energy and solid understanding of the underlying atomic-scale phenomena are required. Despite the challenges, electron and ion irradiation have recently evolved into powerful techniques to manipulation the atomic structure of two-dimensional materials. At the same time, the recent advancements in aberration-corrected transmission electron microscopy both provide means to directly image the manipulated structures but also to fine tune them by inducing local structural changes and even to move defects and impurity atoms.In this presentation, I will show that low-dimensional materials change shape due to van der Waals interaction within heterostructures, describe the advances in manipulating low-dimensional materials with electron irradiation, including nanometer-range chemical etching and directed diffusion of impurity atoms, and provide an overview of our latest results in using ion irradiation at a large energy scale to modify 2D materials via introduction of foreign atoms and nanopores. Finally, I will also demonstrate that transmission electron microscopy can be incorporated as an integral part of a ultra-high vacuum setup with different possibilities for experimentation before, during and after atomic-resolution microscopy, including the growth of novel 2D materials using free-standing graphene as the substrate.

2D-Invited On Demand-19 Electronic Structures of Two-Dimensional Topological Materials*, Sung-Kwan Mo,* Lawrence Berkeley National Laboratory **INVITED**

Due to the quantum confinement and changes in the symmetry, electrical and topological properties of atomically-thin two-dimensional (2D) materials are often largely different from those of their bulk counterparts. In this talk, I will focus on the changes in topological properties in 2D layers, which is explored by combining bottom-up growth using molecular beam epitaxy (MBE), in situ angle-resolved photoemission (ARPES), scanning tunneling microscopy/spectroscopy (STM/STS), and first principle calculations. We have found that the topological properties of 2D materials can be tuned by thickness, lateral interface, strain, and electric field. The material systems under discussion include 1T'-WTe_2 [1], 1T'-WSe_2 [2], alpha-Sn [3] and Na_3Bi [4].

[1] S. Tang et al., Nat. Phys. **13**, 683 (2017). [2] M. M. Ugeda et al., Nat. Commun. **9**, 3401 (2018). [3] C.-Z. Xu et al., Phys. Rev. Lett. **118**, 146402 (2017); Phys. Rev. B **97**, 035122 (2018). [4] J. L. Collins et al., Nature **564**, 390 (2018).

2D-Invited On Demand-25 2020 AVS Medard W. Welch Award Lecture: Chemically Tailoring Interfaces in Two-Dimensional Heterostructures*, Mark Hersam*[1]*,* Northwestern University **INVITED**

As a result of their unique electronic, optical, and physical properties, two-dimensional (2D) materials are actively being explored for applications in next-generation computing [1], quantum information science [2], and energy technologies [3]. With exceptionally high surface-to-volume ratios, 2D materials are highly sensitive to their environment, resulting in a strong dependence of their properties on substrate effects, extrinsic adsorbates, and interfacial defects. Furthermore, the integration of 2D materials into heterostructure devices introduces further demands for controlling interfaces with atomic precision. With this motivation, this talk will explore emerging efforts to understand and utilize interfacial chemical functionalization to influence the properties of 2D heterostructures. For example, organic adlayers can tailor chemical reactivity to enable conformal atomic layer deposition of pinhole-free encapsulation layers that mitigate the deleterious effects of ambient exposure, particularly for ambient-unstable 2D materials such as black phosphorus and monochalcogenides [4]. The integration of organic self-assembled monolayers with 2D semiconductors also allows for tailoring of electronic and optical properties such as photoinduced charge separation in fullerene/InSe heterojunctions [5] and mixed-dimensional excitonic states in phthalocyanine/MoS_2 heterojunctions [6]. By exploiting spatially inhomogeneous surface chemistry, seamless lateral 2D heterostructures can also be realized including perylene/borophene [7] and graphene/borophene [8] heterostructures, each of which show atomically sharp electronic interfaces as confirmed by ultrahigh vacuum scanning tunneling microscopy and spectroscopy. Overall, by providing substantial tailoring of interfaces, chemical functionalization presents opportunities for improved functionality in 2D heterostructure devices.

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2D-Invited On Demand-31 First-Principles Calculations of 2D Materials for Gas Sensing Applications*, Udo Schwingenschlogl,* KAUST, Saudi Arabia **INVITED**

We study the potential of material simulations based on first-principles methods to predict gas sensing properties of 2D materials. This emerging class of materials is of particular interest to gas sensing applications due to high surface-to-volume ratios and chemical stability. We discuss in detail results of electron transport calculations within the Landauer-Büttiker formalism and compare the conclusions to analyses in terms of adsorption energies, charge transfers, and work functions. Specific examples include the effects of the interlayer interaction in bilayer MoS_2 and WS_2 on the gas sensing performance and the consequence of the presence of reactive Si in Si_2BN. We also address the properties of C_3N and para/meta-C_3Si. Potential of very sensitive gas sensing is demonstrated for para-C_3Si and is explained by the susceptibility of Dirac states to symmetry breaking distortions rather than by a mechanism based on charge transfer. Finally, the enhanced gas sensing performance of monovacant C_6BN is studied and it is shown that the work function changes of both pristine and monovacant C_6BN during gas adsorption do not correlate with the changes observed in the I-V characteristics.

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[1] **AVS 2020 Medard W. Welch Awardee**

2D-Invited On Demand-37 Modeling the Growth of 2D Crystals: Analytical, Phase-Field and Machine Learning Methods*, Vivek Shenoy,* University of Pennsylvania **INVITED**

Vertical stacking of monolayers *via* van der Waals (vdW) interaction opens promising routes toward engineering physical properties of two-dimensional (2D) materials and designing atomically thin devices. Increasingly, the bottleneck in this field is the controlled synthesis of these materials through methods such as chemical etching and chemical vapor deposition (CVD). In this talk, I will present insights into synthesis and growth of 2D materials developed from analytical, phase-field, and machine learning models. First, we adapt the state-of-the-art positive and unlabeled (PU) machine learning framework to predict which theoretically proposed 2D materials in the MXene family have the highest likelihood of being successfully synthesized. By considering both the MXenes and their precursors, we identify 18 MXene compounds that are highly promising candidates for synthesis. Next, we develop a general multiscale model for scalable CVD growth of layered materials and predict the necessary growth conditions for vertical (initial + subsequent layers) *versus* in-plane lateral (monolayer) growth. An analytic thermodynamic criterion is established for multilayer growth that depends on the sizes of both layers, the vdW interaction energies, and the edge energy of 2D layers. We connect the model to experimental controls and find that temperature and adatom flux from vapor are the primary criteria affecting the self-assembled growth. This model agrees with experimental observations of various monolayer and bilayer transition metal dichalcogenides grown by CVD. Finally, we consider CVD synthesizable transition metal dichalcogenide heterostructures as a robust platform for engineering quantum confinement of Dirac fermions using a multiscale model for electronic properties.

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