Venue: Harris Engineering Center Room 101
University of Central Florida
Orlando, FL 32816

Time: August 21-22, 2015
Steering committee

- Saiful Khondaker, Chair (University of Central Florida)
- Abdelkader Kara, Co-Chair (University of Central Florida)
- Michael Leuenberger, Co-Chair (University of Central Florida)
- Laurene Tetard, Co-Chair (University of Central Florida)
- Jayan Thomas, Co-Chair (University of Central Florida)

Organizing Committee

- Luis Balicas (Florida State University)
- Matthias Batzill (University of South Florida)
- Irene Calizo (Florida International University)
- Humberto Rodriguez Gutierrez (University of Louisville)
- Jing Guo (University of Florida)
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- Michael Leuenberger (University of Central Florida)
- Laurene Tetard (University of Central Florida)
- Jayan Thomas (University of Central Florida)
- Denis Karaiskaj (University of South Florida)
**Scientific Program**

**Friday, August 21, 2015**

**Registration open: 7.30AM**

**Inauguration: 8.12 – 8.30AM**
8.12 - 8.15: Saiful Khondaker, Workshop Chair
8.15-8.20: MJ Soileau, Vice President for Research and Commercialization, UCF
8.20-8.23: Michael Johnson, Dean, College of Sciences, UCF
8.23-8.26: Bahaa Saleh, Dean, College of Optics and Photonics (CREOL), UCF
8.26-8.29: Michael Georgiopoulos, Dean, College of Engineering and Computer Science, UCF

**Session A: Plenary Session I**
Chair: Masa Ishigami (UCF)
A1. 8.30-9.30AM: Mark C. Hersam: Integration Challenges and Opportunities for 2D Materials

**Coffee break: 9.30-9.45AM (sponsored by Thorlabs)**

**Session B: Growth, Synthesis and Characterization**
Chairs: Laurene Tetard (UCF) and Humberto Rodriguez Gutierrez (USF)

B1. 9.45-10.25 AM: Ludwig Bartels: Transition Metal Dichalcogenides: Growth, Characterization and Modification (Invited)
B2. 10.25-11.05 AM: Peter Dowben: The Symmetry-Resolved Surface-Derived Electronic Structure of MoS$_2$ and WSe$_2$ (Invited)
B3. 11.05-11.45 AM: Humberto Terrones. Beyond graphene: Graphene foams and transition metal dichalcogenides (Invited)
B4. 11.45AM-12.15 PM: Kai Wang: Synthesis and Processing of Twisted WSe$_2$/WS$_2$ Type-II Heterobilayers with Strong Interlayer Coupling

**Lunch break: 12.15-1.00 PM, Lunch will be provided (sponsored by Witec)**

**Session C: Plenary Session II**
Chair: Richard Klemm (UCF)
C1. 1.00 – 2.00 PM: Steven G. Louie: Novel Interaction and Correlation Effects in Quasi 2D Materials

**Session D: Theory and modeling**
Chairs: Jing Guo (UF) and Michael Leuenberger (UCF)

D1. 2.00-2.45 PM: David Tománek: Unexpected electronic properties of layered semiconductors beyond graphene (Invited)
D2. 2.45–3.30 PM: Boris Yakobson, From the first principles: On growth, grain boundaries, and electronic consequences for graphene, h-BN, TMDC (Invited)

Coffee break: 3.30-3.45PM (sponsored by Raith Nanofabrication)

D3. 3.45-4.05 PM: Andor Kormányos: Spin-orbit coupling, quantum dots and magnetoconductance oscillations in monolayer transition metal dichalcogenides
D4. 4.05-4.25 PM: Benjamin Revard: Computational Discovery of Novel Two-Dimensional Materials with an Evolutionary Algorithm
D5. 4:25-4.45 PM: Sadegh Mehdi Aghaei: Effects of periodic nanoholes on the energy band gap of armchair silicene nanoribbons: a density functional theory study

Session E: Summary and Discussion of day 1: 4.45-5.30PM
Discussion Leaders: Ludwig Bartels and Boris Yakobson
Discussion Topic: Challenges and opportunities in growth, characterizations and modelling

Session F: Poster and reception: 5.30 - 7.30 PM (sponsored in part by Horiba)
Chairs: Lei Zhai (UCF) and Irene Calizo (FIU)

7.30 PM: Workshop adjourns for Day 1

Saturday, August 22, 2015

Session G: Electronics and devices
Chairs: Luis Balicas (FSU) and Saiful Khondaker (UCF)
G1. 8.00-8.38 AM: Huili Grace Xing: Challenges and Opportunities in 2D Crystals: graphene and beyond (Invited)
G2. 8.38-9.16 AM: Xiangfeng Duan: Electronic and Optoelectronic Devices from Two-Dimensional Materials and their Heterostructures (Invited)
G3. 9.16 -9.54 AM: Eric Vogel: Symmetric 2D Vertical Heterostructure Devices: Simulation and Experiment (Invited)
G4. 9.54-10.32 AM: Emanuel Tutuc: Electron Transport and Tunneling in Graphene-based Heterostructures (Invited)

Coffee break: 10.32-10.45AM (jointly sponsored by MBraun and Nanoscale)

Session H: Optoelectronics and Photonics
Chairs: Abdelkader Kara (UCF) and Denis Karaiskaj (USF)
H1. 10.45 – 11.23 AM: Fengnian Xia: Graphene and Beyond for Nanophotonics (Invited)
H2. 11.23 - 12.01 PM: Han Wang: Bridging the Gap – Rediscovering Black Phosphorus as an Anisotropic Layered Material for Electronics and Optoelectronics (Invited)

Lunch break: 12.01 PM-12.45 PM, Lunch will be provided (sponsored by Nanobase Inc., Korea)
H3. 12.45-1.23 PM: Linyou Cao: Engineering the Light-Matter Interactions at 2D TMDC Materials (Invited)
H4. 1.23-2.00 PM: Dan H Huang: Coupled Model and Theory for Graphene Based Multi-Functional Devices (Invited)

Session J: Energy and Catalysis
Chairs: Jayan Thomas (UCF) and Matthias Batzill (USF)
J1. 2.00-2.40 PM: Peter Sutter: Nanostructures and Heterostructures of 2D Materials (Invited)
J2. 2.40 - 3.20 PM: Talat Rahman: Tailoring properties of single-layer transition metal dichalcogenides: looking beyond graphene (invited)

Coffee break: 3.20-3.35 PM

J3. 3.35 - 4.15 PM Aditya Mohite: Phase engineering of Transition Metal Di-chalcogenides for optoelectronic applications (Invited)
J4. 4.15 - 4.45 PM Shahriar Memaran: Pronounced photovoltaic response from p-n junctions based on multi-layered MoSe2

Session K: Summary and Discussion of Day 2: 4.45-5.30 PM
Discussion leaders: Talat Rahman, Huili Grace Xing and Dan H Huang
Discussion Topic: Challenges and opportunities in electronic, energy and photonic devices

5.30PM: Workshop adjourns
Sponsors:

Office of Research and Commercialization
College of Science
College of Optics and Photonics
College of Engineering and Computer Science
Department of Physics

Nanobase Inc., Korea
Abstracts
Two-dimensional materials have emerged as promising candidates for next-generation electronic and optoelectronic applications. As is common for new materials, much of the early work has focused on measuring and optimizing intrinsic properties on small samples (e.g., micromechanically exfoliated flakes) under idealized conditions (e.g., vacuum and/or cryogenic temperature environments). However, real-world devices and systems inevitably require large-area samples that are integrated with dielectrics, contacts, and other semiconductors at standard temperature and pressure conditions. These requirements are particularly challenging to realize for two-dimensional materials since their properties are highly sensitive to surface chemistry, defects, and the surrounding environment. This talk will thus explore methods for improving the uniformity of solution-processed two-dimensional materials with an eye toward realizing scalable processing of large-area thin-films. For example, density gradient ultracentrifugation allows the solution-based isolation of transition metal dichalcogenides (e.g., MoS2, WS2, MoSe2, and WSe2) and boron nitride with homogeneous thickness down to the single-layer level. Similarly, two-dimensional black phosphorus is isolated in solution with the resulting flakes showing field-effect transistor mobilities and on/off ratios that are comparable to micromechanically exfoliated flakes. In addition to solution processing, this talk will also report on the integration of two-dimensional materials with dielectrics and other semiconductors. In particular, atomic layer deposition of dielectrics on two-dimensional black phosphorus suppresses ambient degradation, thereby preserving electronic properties in field-effect transistors at atmospheric pressure conditions. Finally, p-type semiconducting carbon nanotube thin films are combined with n-type single-layer MoS2 to form p-n heterojunction diodes. The atomically thin nature of single-layer MoS2 implies that an applied gate bias can electrostatically modulate the doping on both sides of the p-n heterojunction concurrently, thereby providing five orders of magnitude gate-tunability over the diode rectification ratio in addition to unprecedented anti-ambipolar behavior when operated as a three-terminal device.
growth processing allows chalcogen exchange towards local change of bandgap. Deposition onto functional substrates - such as ferroelectrics - permits further local modification of the material properties toward device applications.


B2. (Invited) The Symmetry-Resolved Surface-Derived Electronic Structure of MoS2 and WSe2

Takashi Komesu, Iori Tanabe, Duy Le, Quan Ma, Ludwig Bartels, Eike F. Schwier, Yohei Kojima, Mingtian Zheng, Hideaki Iwasawa, Kenya Shimada, Masaki Taniguchi, Talat Rahman, and Peter A. Dowben

The MoS2 and WSe2 monolayers are a direct gap semiconductor and promising for possible 2-dimensional spintronic devices. But symmetry, as well as the nature of the band gap (direct or indirect) matters. While there are both experimental and theoretical studies of the band structure of MoS2(0001) and WSe2(0001), as well as for monolayer MoS2, few (actually none in any significant fashion) have considered the wave vector dependent symmetry and origin of the spectral weights. We have undertaken angle-resolved inverse photoemission and photoemission spectroscopy measurements to identify the wave vector dependent band gap of MoS2(0001) and WSe2(0001) using p- and s-polarization geometry to distinguish the even and odd states. Indeed, these are the first combined angle-resolved photoemission (occupied state) and angle-resolved inverse photoemission (unoccupied state) studies of the transition metal dichalcogenide reported. Fig. 1 shows the wave vector and symmetry dependent band structure of MoS2(0001). Through comparison with the density functional theory (DFT) calculations, the experimental results for p- and s-polarization geometries, can be assigned to a particular symmetry with good agreement. The dispersion of several bands are easily discerned and we find that the symmetry is in fact wave vector dependent due to overlapping wave vector dependent spectral weight contributions.
The top of the valence band is dominated by the Mo 4d or WSe$_2$ states MoS$_2$(0001) and WSe$_2$(0001) respectively and can be perturbed by adsorbates. Indeed, we find that, after Na adsorption, the valence band structure was shifted as much as 0.5 eV away from the Fermi level, which clearly indicates the Na atoms donate electrons to MoS$_2$ [2] or WSe$_2$. Surprisingly, Na adsorption does not significantly perturb the MoS$_2$ or WSe$_2$ band dispersion, and the band shifts are close to rigid. Cobalt is far more strongly interacting with WSe$_2$, but even with very low coverages is seen to be a p-type dopant.

References:
B4. Synthesis and Processing of Twisted WSe₂/WS₂ Type-II Heterobilayers with Strong Interlayer Coupling
Kai Wang¹, Bing Huang¹, Mengkun Tian², Frank Ceballos³, Ming-Wei Lin¹, Masoud Mahjouri-Samani¹, Alexander A. Puretzky¹, Christopher M. Rouleau¹, Mina Yoon¹, Kai Xiao¹, Hui Zhao³, Gerd Duscher², David B. Geohegan¹
¹.Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 USA
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³. Department of Physics and Astronomy, The university of Kansas, Lawrence, Kansas 66045 USA

Monolayers of 2D crystals are new materials with new emergent properties. Geim etc. proposed stamping these materials to form new heterojunctions for controllable semiconductor heterojunctions, however charge transfer should be expected to depend sensitively on the atomic hybrid orbital interactions at the interface. Here we synthesize individual monolayer 2D crystals of WS₂ and WSe₂ by chemical vapor deposition on sapphire and silicon/silicon oxide substrates, and investigate the charge transfer characteristics between their heterobilayers at different twist angles obtained by removing one material and stamping it on the other. First, the photoluminescence (PL) and Raman spectra were characterized for each as-synthesized monolayer on the respective substrates. Spatial nonuniformities in the PL intensity were noted for the WS₂ on SiO₂/Si in certain conditions, and will be discussed. Next, heterobilayers were fabricated in different orientations by stamping with polymethyl methacrylate and their charge transfer characteristics were investigated using PL and transient absorption spectroscopy. Good interfacial contact was confirmed after annealing by Raman spectroscopy and observation of the appearance of the 311 cm⁻¹ mode that is characteristic of WS₂ multilayers. Strong quenching as well as red shifts of the individual WS₂ and WSe₂ PL peaks at 2.0 and 1.68 eV, respectively, were observed. In addition, a new intermediate PL band at 1.78 eV was observed. The magnitude of the three bands was approximately constant for a variety of twist angles measured between 0° and 60°. Pump-probe transient absorption spectra reveal fast charge transfer (sub-ps) at the interface for all pumping configurations studied. The results are interpreted in the context of a Type II heterojunction model and configuration-dependent DFT band structure calculations. The strong interlayer coupling observed at the heterojunction and its relative insensitivity to orientation appear promising for the stamp-processing of new heterostructured 2D bilayers with controllable properties for ultrathin electronics.

Research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and performed in part as a user project at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

C1. (Plenary) Novel Interaction and Correlation Effects in Quasi 2D Materials
Steven G. Louie
Physics Department, University of California at Berkeley, and Lawrence Berkeley National Lab, Berkeley, California 94720 U.S.A.
Experimental and theoretical studies of atomically thin quasi two-dimensional (2D) materials and their nanostructures have revealed that these systems can exhibit highly unusual behaviors. Owing to their reduced dimensionality, quasi 2D materials present opportunities for manifestation of concepts/phenomena that may not be so prominent or have not been seen in bulk materials. Symmetry, many-body interaction, and substrate screening effects often play a critical role in shaping qualitatively and quantitatively their electronic, transport and optical properties, and thus their potential for applications. In this talk, we present theoretical studies on quasi-2D systems such as monolayer and few-layer transition metal dichalcogenides (e.g., MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$) and metal monochalcogenides (such as GaSe and FeSe) as well as graphene. Several quantum phenomena are discussed, including novel and dominant exciton effects, tunable magnetism, and electron supercollimation by disorder in these materials. We investigate their physical origins and compare theoretical predictions with available experimental data.

**D1. (Invited) Unexpected electronic properties of layered semiconductors beyond graphene**

David Tománek
Physics and Astronomy Department, Michigan State University,
East Lansing, MI 48824, USA ● tomanek@pa.msu.edu

Graphene monolayers, have sparked off unprecedented interest due to their unique electronic structure, but will unlikely replace silicon electronics due to a vanishing fundamental band gap. To still realize the promise of 2D semiconductor electronics, scientists are turning to other layered materials with a nonzero band gap. In this respect, layered structures of group V elements are rapidly attracting interest. Few-layer phosphorus dubbed phosphorene combines high carrier mobility with an unprecedented flexibility to tune the band gap by changing the number of layers or in-layer strain [1-3]. Multiple allotropes of phosphorene, illustrated in Figure 1, may coexist within a monolayer with virtually no energy penalty to form grain boundaries [3]. Similar to graphene, phosphorene may form fullerenes and nanotubes [4]. There are countless possibilities to tile a phosphorene monolayer with different allotropes, providing the possibility of complex electronic structure patterning [5]. Similar intriguing electronic properties as found in phosphorene are postulated also for arsenene, a monolayer of gray arsenic, and isoelectronic IV-VI semiconductors [6]. Computer simulations are a welcome means to gain microscopic insight into the physical properties and possible ways to synthesize these structures, as a guide to experimental efforts.

![Figure 1. Different structural phases of phosphorene (Ref. [3])](image)

D2. (Invited) From the first principles: On growth, grain boundaries, and electronic consequences for graphene, h-BN, TMDC

Boris I. Yakobson
Rice University, Houston, USA

It is of great interest and importance for materials design to uncover, through computational and theoretical modeling, the following relationships: {basic atomic interactions \(\rightarrow\) structure/morphology \(\rightarrow\) functionality (including electronic)}. I will discuss recent examples from low-dimensional materials, where we seem to achieve satisfactory degree of understanding, mostly focusing on 2D graphene [1], transition metal disulfides [2-3], phosphorene [4].


D3. Spin-orbit coupling, quantum dots and magnetoconductance oscillations in monolayer transition metal dichalcogenides

Andor Kormányos,1 and Guido Burkard1
1Department of Physics, University of Konstanz, D-78464 Konstanz, Germany

We have developed a \(\mathbf{k.p}\) theory framework (see [1] and a recent review in [2]) to describe the dispersion of the conduction and valence bands at their extrema (the K, Q, Γ and M points of the hexagonal Brillouin zone) in atomic crystals of semiconducting monolayer transition metal dichalcogenides (TMDCs). We parametrized the essential parts of the \(\mathbf{k.p}\) Hamiltonians for MX2 monolayers (here M={Mo, W} and X={S, Se, Te}) using density functional theory calculations. We use this theory framework to study a variety of problems that are not easy to address by first-principles calculations. We considered the Rashba-type spin-orbit coupling in these materials [3] and found that it consist of two parts. The first one is known from earlier studies on two-dimensional electron gas. In addition, however, there is a second part which is specific of monolayer TMDCs. In contrast to graphene, one can form quantum dots by electrostatic gating in
these materials and we have studied the single-particle spectrum of such quantum dots. We found that in external magnetic field they can serve as simultaneous valley and spin filters. Finally, motivated by recent experimental progress [4,5] in the measurement of magnetoconductance properties of TMDCs, we investigate how the spin-orbit coupling and the broken valley degeneracy of the Landau levels (LL) affect the Shubnikov-de Haas oscillations in TMDCs [6]. To this end we first study the Landau level spectrum. We find that in a wide magnetic field regime the valley degeneracy breaking of the LLs is linear in magnetic field. The effect of the non-parabolicity of the band-dispersion on the LL spectrum is also discussed. We then use the self-consistent Born approximation and the Kubo-formalism to calculate the Shubnikov-de Haas oscillations of the longitudinal conductivity. We point out how the doping level affects the magnetoconductance and compare the results of our theoretical calculations with recent measurements[4].

(a) Schematic of a quantum dot in a monolayer TMDC [3] (b) Shubnikov-de Haas oscillations in the magnetoconductance: measurement (squares) and theory (solid lines) [6]


**D4. Computational Discovery of Novel Two-Dimensional Materials with an Evolutionary Algorithm**

Benjamin Revard, Arunima Singh, Will Tipton, Richard G. Hennig
Cornell University, University of Florida

Two-dimensional materials present a new class of materials that with their ultimate thinness, maximum surface area, and unique properties, have become increasingly attractive for applications ranging from nanoelectronics to energy conversion and storage. In our work, we employ computational tools to predict which 2D materials can form and to characterize their properties for various applications with the goal to identify the most promising 2D materials candidates for synthesis efforts. We have developed a grand-canonical genetic algorithm for structure prediction (GASP) to search for two-dimensional materials. Coupled with accurate quantum mechanical first-
principles methods, we show that the evolutionary algorithm can successfully identify known structures of 2D materials, such as graphene and SnS$_2$, explore the energy landscape of the 2D semiconductor InP and discover several novel low-energy structures for 2D oxides. We currently apply the approach to a number of other promising candidate systems, including group-IV oxides and Al$_2$O$_3$, and will report the findings.

D5. Effects of periodic nanoholes on the energy band gap of armchair silicene nanoribbons: a density functional theory study
Sadegh Mehdi Aghaei$^1$ and Irene Calizo$^{1,2}$
$^1$Department of Electrical and Computer Engineering, Florida International University, Miami, Florida 33174, United States
$^2$Department of Mechanical and Materials Engineering, Florida International University, Miami, Florida 33174, United States
Silicene, a new allotrope of silicon which can be considered as the silicon version of graphene has caught huge attention due to its inherent compatibility with silicon based nanotechnology. Unlike planar graphene, silicon atoms in silicene honeycomb lattice are buckled which lead them to adopt sp$^3$ hybridization over sp$^2$. However, similar to graphene silicene has a zero band gap; therefore, to use it in future nanoelectronics devices, a band gap is necessary. One approach for two-dimensional materials that has drawn attention is through quantum confinement and edge effects found in nanoribbon nanostructures.

Using density functional theory (DFT), we present a systematic study of the electronic properties of armchair silicene nanoribbons perforated with periodic nanoholes (ASiNRPNHs). Electronic properties of armchair silicene nanoribbons (ASiNRs) with mono-hydrogen (:H) terminated edges (sp$^2$ hybridization) are significantly different from ASiNRs with double-hydrogen (:2H) terminated edges (sp$^3$ hybridization). Considering variations in energy band gap of pristine ASiNRs versus nanoribbon width “W”, three distinct family behaviors (W = 3n, W = 3n + 1, and W = 3n + 2, n is a positive integer) can be found. Interestingly, when the hydrogenation varies from (:H) to (:2H), the band structures are affected and the order of band gap values change from “$E_G (3n + 2) < E_G (3n) < E_G (3n + 1)$” to “$E_G (3n + 1) < E_G (3n + 2) < E_G (3n)$”. This study shows that double hydrogenation of silicon edge atoms of W-ASiNRs can cause a band gap that is nearly equal to the band gap of (W−2)-ASiNR with mono-hydrogen terminated edges. We also find that different factors such as nanoribbons width, repeat periodicity of nanoholes, hydrogenation of dangling bonds, and position of nanoholes relative to both edges determine the energy band gap values of ASiNRPNHs because these factors alter the strength of quantum confinement in nanoribbons. Broadly speaking, an even number of repeat periodicity, di-hydrogenation of silicon dangling bonds, and perforating nanoholes near edges of nanoribbons give rise to a larger band gap.

Finally, ASiNRPNHs could be suggested as a potential material for applications in electronics owing to its probable compatibility with existing silicon technology and its tuning capability of the nanoribbons band gap.

G1. (Invited) Challenges and Opportunities in 2D Crystals: graphene and beyond
Huili Grace Xing
Two-dimensional (2D) crystals such as transition metal dichalcogenides (TMDs) along with other families of layered materials including graphene, SnSe₂, GaSe, BN etc, has attracted intense attention from the scientific community. One monolayer of such materials represent the thinnest “quantum wells”. These layered materials typically possess an in-plane hexagonal crystal structure, and can be stacked together by interlayer van der Waals interactions. Therefore, it is possible to create novel heterostructures by stacking materials with large lattice mismatches and different properties, for instance, superconductors (NbSe₂), metals, semi-metals (graphene), semiconductors (MoS₂) and insulators (BN). Numerous novel material properties and device concepts have been discovered, proposed and demonstrated lately. However, the low internal photoluminescence efficiency (IPE, < 1%) and low carrier mobility observed in the 2D semiconductors suggest strongly that the materials under investigation today most likely suffer from a high concentration of defects.

In this talk, I will share our progress and the challenges we face in terms of preparing, characterizing these 2D crystals as well as pursuing their applications.

**G2. (Invited) Electronic and Optoelectronic Devices from Two-Dimensional Materials and Their Heterostructures**

Xiangfeng Duan  
*Department of Chemistry and Biochemistry, University of California, Los Angeles  
Los Angeles, California 90095 USA, Email: xduan@chem.ucla.edu*

Two-dimensional layered materials (2DLMs), such as graphene or molybdenum disulfide, represent ideal 2D material systems for exploring fundamental chemistry and physics at the limit of single atomic thickness. With *van der Waals* interactions between neighboring layers, different 2DLMs can be flexibly integrated without the limitation of lattice mismatches. This approach therefore opens up vast possibilities for nearly arbitrarily combining multiple materials and integrating distinct properties at the atomic scale, and thus enabling entirely new opportunities beyond the reach of existing materials. Here I will focus my discussion on exploring these 2D materials and their heterostructures as new platforms for the creation of a wide of electronic and optoelectronic devices with unique functions or unprecedented performance. Examples discussed include: ultra-high speed transistors; a new design of vertical transistors for ultra-flexible electronics; and new types of tunable photonic devices.

**G3. (Invited) Symmetric 2D Vertical Heterostructure Devices: Simulation and Experiment**

Eric Vogel  
*Materials Science and Engineering  
Georgia Institute of Technology*

Since the 1970s, resonant tunneling devices have attracted significant attention for their potential in a variety of applications including multi-valued logic, high frequency radar and communication
Vertical heterostructures consisting of two-dimensional (2D) materials such as graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDs) have a variety of properties which can potentially overcome some of the limitations of epitaxial 3D semiconductor heterostructures. In this talk, simulations of 2D heterostructures will first be described including how various properties and parameters impact the predicted current-voltage characteristics. The second part of the talk will describe challenges associated with fabricating heterostructures based on large-area and manufacturable materials focusing on graphene-insulator-graphene (GIG) heterostructures. Overall, the results provide important insights necessary for future, large-scale manufacturing of resonant and other 2D vertical heterostructure devices.

Emanuel Tutuc
Department of Electrical and Computer Engineering
The University of Texas at Austin

Vertical heterostructures consisting of atomic layers separated by insulators can open a window to explore the role of electron interaction in these materials otherwise not accessible in single layer samples, and also to explore device applications.

We describe here the realization of vertical heterostructures consisting of graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides realized using a layer-by-layer transfer. In double bilayer graphene heterostructures separated by hBN dielectric [1], we employ the top layer as a resistively detected Kelvin probe and map the chemical potential of the bottom bilayer graphene as a function of electron density, perpendicular magnetic field, and transverse electric field. At zero magnetic field the chemical potential reveals a strongly non-linear dependence on density, with an electric field induced energy gap at charge neutrality. The data allow a direct measurement of the density-dependent effective mass, the electric field-induced bandgap at zero magnetic field, orbital Landau level energies, and the broken symmetry quantum Hall state gaps at high magnetic fields [1]. In samples where the two layers are rotationally aligned the interlayer tunneling current measured as a function of interlayer bias reveals a gate-tunable negative differential resistance thanks to momentum conserving tunneling [2, 3]. We discuss potential device application based on these experimental observations, and metrics to benchmark their performance.

We also describe the realization and electron transport in graphene-MoS2 heterostructures, which reveal a strong negative compressibility in the MoS2 layer as a result of electron-electron interaction [4].


H1. (Invited) Graphene and Beyond for Nanophotonics
Fengnian Xia, Yale University
15 Prospect St, New Haven CT 06511

Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, has been intensively explored by physicists and engineers due to its unique electronic and photonic properties. In this talk, I will first address the physics of light-graphene interaction within the single-electron framework, followed by a discussion of light excitation of collective oscillations of the carriers, i.e., plasmons in graphene. I will then cover a variety of graphene photonic devices such as high-bandwidth photodetectors and optical modulators. Finally I will talk about other emerging two-dimensional materials such as transition metal dichalcogenides and black phosphorus and their applications in nanophotonics.

H2. (Invited) Bridging the Gap – Rediscovering Black Phosphorus as an Anisotropic Layered Material for Electronics and Optoelectronics
Han Wang, University of Southern California, 3737 Watt Way, Los Angeles, CA 90089, USA

In this talk, I will discuss our recent work in introducing black phosphorus (BP) to the layered-material family as a novel anisotropic 2D material for electronic and optoelectronic applications. Narrow gap BP thin film (0.3 eV in bulk) serendipitously fill the energy space between zero-gap graphene and large-gap TMDCs, making it an promising material for near and mid-infrared optoelectronics. BP thin films show high mobility above 650 cm²/V.s at room temperature along the light effective mass (x) direction, implying its promising potential for high frequency, thin-film electronics. Furthermore, its anisotropic nature within the plane of the layers may allow for the realization of conceptually new electronic and photonic devices impossible in other 2D materials. In the talk, I will also present our work in demonstrating 20 GHz black phosphorus radio-frequency transistors. Our recent progress in characterizing the optical properties of monolayer BP and in achieving large-area synthesis of black phosphorus thin film will also be discussed. I will conclude with remarks on promising future directions of black phosphorus research and how this new material is expected to benefit the next-generation electronics and photonics technologies.

H3. (Invited) Engineering the Light-Matter Interactions at 2D TMDC Materials
Linyou Cao
One of the most appealing applications of two dimensional (2D) transition metal dischalcogenide (TMDC) materials is in photonics, such as LEDs, lasers, photodetectors, and solar cells. In this presentation, I will discuss our recent results on the engineering of light-matter interactions at 2D TMDC materials. We have measured the dielectric function of atomically thin MoS$_2$ films with different layer numbers and discovered an intriguing layer-dependence in the dielectric function, which can be ascribed to the effect of strongly bound excitons. By leveraging on the knowledge of the dielectric function, we have designed strong absorbers (>90%) with atomically thin MoS$_2$ films for either narrow-band or broad-band incidences such as solar radiation. Additionally, I will show our results in improving the quantum efficiency of 2D TMDC materials by one order of magnitude (> 30%) through substrate engineering.

H4. (Invited) Coupled Model and Theory for Graphene Based Multi-Functional Devices

Danhong Huang$^1$, G. Gumbs$^2$, O. Roslyak$^3$

$^1$Air Force Research Laboratory, Space Vehicles Directorate, Kirtland Air Force Base, NM 87117, USA
$^2$Department of Physics and Astronomy, Hunter College of the City University of New York, 695 Park Avenue, New York 10065, USA
$^3$Department of Physics and Engineering Physics, Fordham University, Bronx, NY 10458, USA

In this talk, the microscopic-level models will be introduced for nonlinear transport at high biases, optical transitions with ultrafast carrier scattering and plasmonic near-field optics. Based on these physics models, a bottom-up technical approach is proposed for designing multi-functional semiconductor quantum devices starting from first-principle band-structure calculations up to system control algorithms. Specific attention has been put on nonlinear electron transport in graphene under a high electric field as well as interplay of Coulomb and electromagnetic couplings in gapped graphene.

J1. Nanostructures and Heterostructures of 2D Materials
Peter Sutter
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2D crystals, such as graphene, hexagonal boron nitride, and a family of metal dichalcogenides represent a new class of materials with unique characteristics that are interesting for fundamental research as well as for applications in electronics, energy conversion, sensing, etc. Combining different 2D materials in heterostructures and exploiting carrier confinement in nanostructures are promising strategies for designing materials with engineered properties different from those found in extended, homogeneous 2D crystals.
Here, we discuss recent progress in the bottom-up synthesis of 2D heterostructures and nanostructures. Using in-situ microscopy and spectroscopy, we recently introduced the concept of lateral heteroepitaxy for the integration of 2D materials with sub-100 nm in-plane dimensions. Even smaller structures, suitable for exploiting confinement effects, are produced by atomically precise bottom-up assembly processes using molecular precursors. Extending this approach to achieve both undoped and doped graphene nanoribbons by surface-assisted and solution-phase synthesis, we show that doping can be harnessed to obtain nanoribbon heterostructures and that it can trigger striking hierarchical self-assemblies that produce novel 3D metamaterials with tunable properties.
Our results demonstrate avenues for harnessing vapor phase growth processes and the powerful toolset of organic and polymer chemistry to produce nanoscale 2D materials, heterostructures, and novel 3D metamaterials.

J2. (Invited) Tailoring properties of single-layer transition metal dichalcogenides: looking beyond graphene
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Single-layer Molybdenum disulfide (MoS2) appears to be a promising material for next generation nanoscale applications because of its low-dimensionality and intrinsic direct band-gap of about 1.9 eV. Several experimental groups have reported novel electronic and transport properties of single layer MoS2 and other transition metal dichalcogenides, which may be further tuned through alloying, defects, doping, and coupling to substrate. In this talk I will present results from joint theoretical and experimental investigations [1, 2] which provide a framework for manipulating the functionality of this material. My emphasis will be on evaluation of binding energies of optical excitations (excitons and trions) using a density matrix based time dependent density functional theory method which takes into account long ranged exchange-correlation found necessary to provide reasonable agreement with experimental data. The effect of a monolayer support such as graphene, hexagonal boron nitride and silicene on the electronic structure and characteristics of optical excitations in monolayer transition metal dichalcogenides will be examined. Optical excitations in heterostructures consisting of monolayers of two different transition metal dichalcogenides will also be highlighted. I will also address the issue of tuning catalytic properties
of single layer MoS2 through vacancies and other defects [3]. Possible technological applications of these materials will also be discussed.


References

J3. (Invited) Phase engineering of Transition Metal Di-chalcogenides for optoelectronic applications

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Transition metal dichalcogenides (TMDs) represent a family of materials with versatile electronic, optical, and chemical properties. Most TMD bulk crystals are van der Waals solids with strong bonding within the plane but weak interlayer bonding. The individual layers can be readily isolated. Single layer TMDs possess intriguing properties that are ideal for both fundamental and technologically relevant research studies. We review the structure and phases of single and few layered TMDs. We also describe recent progress in phase engineering in TMDs. The ability to tune the chemistry by choosing a unique combination of transition metals and chalcogen atoms along with controlling their properties by phase engineering allows new functionalities to be realized with TMDs. In this talk I will describe our recent efforts to gain access intrinsic electrical and optical properties of TMDs by utilizing phase engineering.

Achieving Ohmic contacts to layered transition metal dichalcogenides (MoS2, WS2, WSe2 and MoSe2) has been a challenge to researchers owing to the Schottky barrier between metal and semiconductor. This has resulted in low on-currents, mobilities and poor sub-threshold slopes in the devices made with these materials. Here we demonstrate a universally applicable to all semiconducting TMDs where we fabricated hybrid transistors, which have 1T phase of the material at the contacts and 2H phase of the material as the channel. The 1T phase significantly reduces the Schottky barrier between the metal and the semiconductor thereby mitigating the high contact resistance issues and allowing for probing the true intrinsic optoelectronic properties of transition metal dichalcogenides. Material synthesis, compositional, optical and electrical characterization results will be discussed in detail. This strategy has implications for several applications in optoelectronics, catalysis, supercapacitors and batteries.
Semiconducting transition metal dichalcogenides (TMDs) are layered solids having indirect band gaps comparable to Si, which can be grown in large area, and whose gap(s) can be tuned by varying composition. The experimental evidence collected so far for exfoliated TMDs single-crystals, composed of a single- or of few-atomic layers, points towards a strong interaction with light. This contrasts with the small photovoltaic efficiencies $\eta \leq 1\%$ reported so far for thin or for bulk crystals. Here, we evaluate the photovoltaic potential of these materials by studying the response of electrostatically gated p-n junctions composed of approximately ten atomic-layers of MoSe$_2$ stacked on the dielectric h-BN. In addition to a nearly ideal diode-like response, these p-n junctions yield, under AM-1.5 illumination, photovoltaic efficiencies $\eta$ exceeding 10.4 % (with fill-factors surpassing $\sim$0.65), under which current bulk Si technologies yield $\eta$ ranging from $\sim$15 to $\sim$25 %. Given the available strategies for increasing $\eta$, such as increasing the crystal thickness (or photon path), tuning the gap, improving the quality of the electrical contacts, or even fabricating tandem cells, our study suggests a remarkable potential for photovoltaics based on translucent TMDs.
F1. Fragmentation and exfoliation of low-dimensional materials: a statistical approach.  
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The exfoliation of a 2D nanosheets (as example, of graphene or boron nitride) from a 3D bulk material is a process spanning from nano- to meso-scale.\(^1\) Exfoliation always yields a poly-dispersed range of nanosheets thickness and lateral size. When characterizing these 2D sheets solutions, their average size and size standard deviation are commonly reported, in this way assuming that their size follows a “Gaussian” (a.k.a. “normal”) distribution. Conversely, the experimental data show that the size distribution of these materials is highly asymmetric and non-Gaussian. Noteworthy, this asymmetry in size distribution is similar to what observed in very different systems such, as example, the distribution of chemical elements in rocks, the species abundance in biology, the lengths of latent periods of infectious diseases in medicine, the distribution of galaxies in astronomy.\(^2\)  

We used automatized image processing of Atomic Force Microscopy (AFM) data to measure, one by one, the exact shape and size of thousands of nanosheets obtained by exfoliation of different 2D-materials (i.e. boron nitride and graphene oxide) performing in this way statistics on all the sheets present on the surfaces, for a total of thousands of sheets, as compared to the tens of sheets analysed by manual TEM statistics typically used for this task. Being the resolution of AFM much larger than the average sheet size, analysis could be performed directly at the nanoscale, and at single sheet level. Combining AFM data with electron microscopy and optical microscopy images we monitored the exfoliation process from macro- to nano-scale spanning 3 orders of magnitude, from 100 microns to 100 nm scale. Different statistical functions were then used to model the asymmetric distribution of nanosheets sizes typically obtained, providing insight into the different fragmentation processes that influence sheet size at different scales.  

![Fig.1](image-url) a) SEM image of the pristine BN flakes used for exfoliation. b) Exfoliated solutions of BN in isopropanol, showing strong scattering due to the dispersed flakes. c) AFM image of BN nanosheets spin coated on silicon oxide substrates. d) Zoom-in of a single nanosheet, showing the typical, non-exact way to estimate of its length and width. e) Histogram distribution of sheet size obtained instead measuring precisely the area of each sheet.  

References  
F2. Pristine and intercalated transition dichalcogenide superconductors
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Transition metal dichalcogenides (TMDs) are quasi-two-dimensional layered compounds that exhibit strongly competing effects of charge-density wave (CDW) formation and superconductivity (SC). The weak van der Waals interlayer bonding between hexagonal layers of octahedral or trigonal prismatic TMD building blocks allows many polytypes to form. In the single layer $1T$ polytype materials, one or more CDW states can form, but the pristine TMDs are not superconducting. The $2H$ polytypes have two or more Fermi surfaces and saddle bands, allowing for dual ordering, which can be coexisting CDW and SC ordering, two SC gaps as in MgB$_2$, two CDW gaps, and possibly even pseudogaps above the onset $T_{\text{CDW}}$ of CDW orderings. Higher order polytypes allow for multiple CDW gaps and at least one superconducting gap. The CDW transitions $T_{\text{CDW}}$ usually greatly exceed the superconducting transitions at their low $T_c$ values, their orbital order parameters (OPs) are generally highly anisotropic and can even contain nodes, and the SC OPs can be greatly affected by their simultaneous presence. The properties of the CDWs ubiquitously seen in TMDs are remarkably similar to those of the pseudogaps seen in the high-Tc cuprates. In $2H$-NbSe$_2$, for example, the CDW renders its general $s$-wave SC OP orbital symmetry to be highly anisotropic and strongly reduces its Josephson coupling strength ($IcR_n$) with the conventional SC, Pb. Hence, the pristine TMDs are highly ‘‘unconventional’’ in comparison with Pb, but are much more ‘‘conventional’’ than are the ferromagnetic superconductors such as URhGe. Applied pressure and intercalation generally suppress the TMD CDWs, allowing for enhanced SC formation, even in the $1T$ polytype materials. The misfit intercalation compound (LaSe)$_{1.14}$(NbSe$_2$) and many $2H$-TMDs intercalated with organic Lewis base molecules, such as TaS$_2$(pyridine)$_{1/2}$, have completely incoherent $c$-axis transport, dimensional-crossover effects, and behave as stacks of intrinsic Josephson junctions. Except for the anomalously large apparent violation of the Pauli limit of the upper critical field of (LaSe)$_{1.14}$(NbSe$_2$), these normal state and superconducting properties of these intercalation compounds are very similar to those seen in the high-$T_c$ superconductor Br$_2$Sr$_2$CaCu$_2$O$_{8+}$ and in the organic layered superconductor $(\text{ET})_2\text{Cu[N(CN)$_2$]Br}$, where ET is bis(ethylenedithio)tetrathiofulvalene. Electrolytic intercalation of TMDs with water and metallic ions leads to compounds with very similar properties to cobaltates such as Na$_{x}$CoO$_2$$\cdot$yH$_2$O.

Prefer oral session
High quality graphene can be grown on several transition metals by chemical vapor deposition in vacuum. For many investigations and modifications of graphene it would be desirable to decouple the graphene from the metal support. This may be accomplished by intercalation and subsequent oxidation of a reactive element. However to maintain the properties of graphene it is also important that the oxide layer is well-ordered and does not exhibit a high density of defects that may couple to the graphene. FeO is known to form a 2D-oxide monolayer on Pt(111), exhibiting a moiré superstructure characteristic for 2D materials on metals (see Fig. (a)). We have demonstrated that this 2D-FeO layer can also be formed in between graphene and Pt(111) by Fe-intercalation and subsequent oxidation at 40 Torr O\textsubscript{2} in high pressure cell at \( \sim 230 \, ^\circ\text{C} \) [1]. Fig. (b) shows an STM image of graphene on top of the FeO-moiré/Pt(111) structure. In order to facilitate space-averaging investigations it would be desirable for this approach to also work on metal substrates that facilitate the formation of a single graphene domain. For example Ir(111) is a substrate on which single crystal graphene can be grown. However, there exist no reports that Ir also supports the growth of 2D-FeO. Here we demonstrate that 2D-FeO/Ir(111) can be indeed prepared by room temperature Fe deposition on Ir(111) and subsequent exposure to 10\textsuperscript{-6} Torr oxygen for about two minutes at \( \sim 600\, ^\circ\text{C} \). Atomic-resolution STM of the moiré-FeO/Ir(111) is shown in the Fig. (c). Thus the formation of graphene/2D-FeO/Ir(111) appears to be possible goal.

Figure: (a) model of hex-FeO layer on Pt(111) (red-grid lines) indicating the origin of the moiré structure due to various adsorption sites of the Fe-atoms with respect to the Pt substrate atoms. (b) Graphene layer on top of an interfacial 2D-FeO-layer, i.e. a graphene/2D-FeO/Pt(111) heterostructure. The long-range modulation is from the underlying 2D-FeO moiré structure while the superimposed hexagonal structure is the graphene lattice. (c) Preliminary results for 2D-FeO layer on Ir(111). The long-range hexagonal structure is the moiré structure. In addition atomic resolution of the 2D-FeO is observed.

CVD-grown graphene on Cu-foil can be transferred onto other materials. Here we investigate the quality and properties of such transferred graphene and their interfaces by scanning tunneling microscopy (STM) and angle resolved photoemission spectroscopy (ARPES). Generally STM indicates that clean interfaces are possible by vacuum annealing of the transferred graphene on Nb-doped SrTiO$_3$ [1] and on MoS$_2$ [2-4]. For graphene/Nb-SrTiO$_3$(001) STM resolves the modulation of the underlying reconstruction of the SrTiO$_3$(001) reconstruction while for graphene on MoS$_2$ a weak moiré structure is observed due to lattice rotation and mismatch. Detailed investigations of the electronic structure of the graphene/MoS$_2$ van der Waals heterostructure were performed by nano-ARPES and spin-resolved ARPES at the SOLEIL synchrotron. While the Dirac-cone of graphene was maintained, hybridization-gaps were observed in the graphene π-band where the band overlapped with the MoS$_2$ bands that exhibit out of plane orbital character. This indicates some chemical interaction between the layers even for van der Waals heterostructures [3]. Furthermore, the MoS$_2$ band structure is modified by the graphene leading to a band gap narrowing of \(\sim 0.1\) eV due to an upward shift of the valence band maximum at the Γ-point. Carrier screening in MoS$_2$ due to the conduction electrons in graphene may induce this band renormalization. This may be general phenomenon for MoS$_2$/metal interfaces. Finally spin polarized measurements show that the spin-orbit split bands at the K-points (valleys) of p-doped MoS$_2$ become spin polarized at the graphene/MoS$_2$ interface. This is tentatively explained by a symmetry breaking of MoS$_2$ in the graphene induced space charge region a schematically shown in the figure.

ARPES and spin resolved ARPES (SARPES) measurements for the spin-orbit split bands at the K-point. For the graphene-covered surface the bands are \(\sim 20\%\) spin polarized, which is explained by a contact potential induced polarization of the MoS$_2$ surface causing a symmetry breaking in the MoS$_2$.

F5. Growth of MoTe2 monolayers by molecular beam epitaxy (MBE) on MoS2(0001) single crystals: Evidence of valence band maximum localization

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Heterostructures of van der Waals materials in particular transition metal dichalcogenides (TMDs) are promising new materials and devices for potential electric and optoelectronic applications.1,2 Molecular beam epitaxy (MBE), in principle, enables superior control over composition and layer-control. Growth of TMDs heterostructures are however challenging due to the high vapor pressure of chalcogens. Here we investigate the conditions for growing monolayer MoTe2 on MoS2(0001) substrates and characterize the thermal as well as chemical stability of the grown films by photoemission spectroscopy and scanning probe microscopy.3

One especially important aspect of this study is the modification of the electronic structure of the MoTe2 monolayer due to the interaction with the MoS2 substrate. For TMDs a transition from indirect to direct band gap from bulk-materials to monolayers is well established. This transition is due to interlayer orbital interaction and thus may also occur in between layers of heterostructures. However, the different lattice constants of the materials give rise to a moiré structure with locally varying interlayer coordination within the moiré unit cell. As shown in the figure, we observe in scanning tunneling spectroscopy that the valence band maximum and thus the band gap is modified by 0.14 eV within the moiré structure leading to a periodic modification of the VBM with the 2.6 nm periodicity of the moiré structure. This band gap modification is attributed to the locally varying interlayer orbital interactions.4

Fig.: Local variation of the band gap within the moiré superstructure of MoTe2. In (a) the STS map of the tunneling current at -0.95V bias voltage is shown. This STS map reproduces the moiré periodicity that is seen in the simultaneously acquired STM image shown in (b). The differential conductance (dI/dV), averaged over 50 data points from two regions in the moiré unit cells, indicated in (a), are shown in (c).

While the position of the conduction band minimum is approximately the same for both regions the valence band maximum varies by ~0.14 eV, indicating a local valence band maximum localization within region 1 of the moiré structure.

References
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4 H. Coy Diaz, R. Chaghi, Y. Ma, M. Batzill; Valence band maximum localization in moiré pattern of the MBE-grown van der Waals heterostructure MoTe2/MoS2. Submitted
Transition metal dichalcogenides (TMDs) have been shown to exhibit excellent optoelectronics properties due to their sizable and tunable band gaps whose magnitudes are strongly dependent on the number of atomic layers. Recently, rhenium sulphide (ReS\textsubscript{2}), which in contrast to other semiconducting TMDs does not crystallize in a trigonal prismatic but in a distorted octahedral coordination, was found to be a direct band-gap semiconductor with a gap of 1.5 eV. Here, we report the temperature dependent field-effect mobility of few-layered ReS\textsubscript{2} field-effect transistors (FETs) mechanically exfoliated onto Si/SiO\textsubscript{2} substrates. ReS\textsubscript{2} FETs perform as a n-type, direct band gap semiconductor with an average room temperature two-terminal mobility surpassing ~30 cm\textsuperscript{2}/V\textcdot s, which increases sharply as the temperature decreases to 100 K. The highest observed field-effect mobility, measured in a four terminal configuration, approaches $\mu_{\text{FE}} \sim 250$ cm\textsuperscript{2}/V\textcdot s at $T = 20$ K. At high electron densities, the four-terminal conductivity increases by a factor of ~3 upon cooling from 300 to 20 K, and as expected for a metallic system. This contrasts with the activated behavior observed at negative back-gate voltages, indicating a gate-voltage induced crossover from a semiconducting to a metallic state. Raman scattering reveal a strong anisotropy, i.e., a strong dependence on the angle between the polarization of the incident light and the crystallographic axes. We index the peaks observed in the Raman spectra based on density functional theory calculations and the point group symmetry of ReS\textsubscript{2} finding that all Raman modes are of $A_\text{g}$ type. A direct band-gap in ReS\textsubscript{2} could open interesting prospects for optoelectronic applications with improvements in carrier mobility.
F7. Optical signatures of states bound to vacancy defects in monolayer MoS2

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Abstract: The electron states in pristine MoS2 single layer (SL) form classes of states that are even and odd with respect to reflections about the central Mo plane. Apart from the well-known bandgap of $E_{g\parallel} = 1.9 \text{ eV}$ in the optical in-plane susceptibility $\chi_{\parallel}$ due to the $\sigma$ transition between the even valence band (VB) and the even conduction band (CB), we show that $\pi$ transitions between the even VB and the odd CB+1 band gives rise to a bandgap of $E_{g\perp} = 3.2\text{ eV}$ for the optical out-of-plane susceptibility $\chi_{\perp}$. In particular, we show that the presence of odd states bound to vacancy defects (VDs) leads to the formation of resonances in $\chi_{\perp}$ inside $E_{g\perp}$ in MoS2 SL with VDs.

We use density functional theory, the tight-binding model, and the Dirac equation to study MoS2 SL with three types of VDs: (i) Mo-vacancy, (ii) S2-vacancy, and (iii) 3×MoS2 quantum antidot. The resulting optical signatures not only provide the possibility to identify the type but also the concentration of VDs, thereby paving the way to quantifying the purity of defected SLs of transition metal dichalcogenides containing VDs.


Figure:

(a) Bandstructure of MoS2 SL, showing the out-of-plane bandgap $E_{g\perp} = 3.2\text{ eV}$ determined by the transition $T_0$. The Fermi level is set at $\varepsilon_F = 0 \text{ eV}$. (b) Mo-vacancy in 7x7 supercell, (c) S2-vacancy consisting of a pair of S atoms removed in 7x7 supercell, (d) hexagonal 3×MoS2 QAD in 8x8 supercell.
F8. **Gold-doped graphene as a cost-effective, highly stable and active electrocatalyst for the oxygen reduction reaction: prediction from first principles**

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One of the main obstacles hindering large scale practical application of hydrogen fuel cells is a prohibitive high cost of Pt (or Pt-based) catalysts for the oxygen reduction reaction (ORR) on the fuel cell cathode. In this work, we consider Au-doped graphene as an inexpensive alternative to Pt for facilitating ORR [1]. Our first-principles calculations show that Au atoms incorporated into graphene di-vacancies form a thermodynamically stable structure. Furthermore, calculation of the binding energies of the ORR intermediates reveals that Au-C bonding makes the C atoms neighboring to Au optimally reactive for ORR. The calculated ORR free energy diagrams suggest that the Au-graphene structures have an ORR onset potential as high as that of Pt. Importantly, our calculations suggest that electrochemical stability of this structure is much higher than that of Pt. We also demonstrate that the linear relation among the binding energy of the reaction intermediates assumed in a number of works on computational high-throughput material screening does not hold, at least for this non-purely transition-metal material.


F9. **Piezospectroscopic surface sensing and characterization of hybrid carbon fiber composites**

Quentin Fouliard, Aline Faria Da Silva, Nicholas Benenati, Imad Hanhan, Declan Carolan, Yangyang Qiao, Ambrose Taylor, Seetha Raghavan  
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Emerging materials such as alumina embedded carbon fiber composites have promising applications not only in structural development due to their improved mechanical properties, but also in advanced sensing and characterization of composites. Alumina nanoparticles provide stress-sensitive photo-luminescent properties that can be captured through 2D surface mapping. This laser based non-contact technique, known as piezospectroscopy, can be used to characterize the properties and mechanical response of the hybrid carbon fiber composites. Mechanical tests combined with photo-luminescent collection enabled measurements of in-situ spectral shifts to be captured for the characterization presented in this work. Digital image correlation was used to validate and develop the piezospectroscopic results, shedding light on 2D mechanical properties, such as the micromechanical response. This work has significant potential for future development as non-invasive damage detection in aerospace structures.

F10. High temperature 2D coatings for reusable spacecraft characterized under extreme conditions

Valentina Villegas, Brooke Sarley, Albert Manero, Katia Artzt, Janine Wischek, Stefan Hackemann, John Okasinski, Jonathan Almer, Anette M. Karlsson, Marion Bartsch, and Seetha Raghavan

Ceramics and ceramic composites as 2D coatings provide highly sought-after capabilities that have the potential to withstand extreme temperatures and heat fluxes; severe oxidation and high mechanical stresses associated with next generation re-entry environments. The complexity of these extreme operational conditions demands stringent tolerances on failure initiation and consequently an extension of the boundaries of current characterization capabilities for 2D materials. This work presents a real-time approach to elucidating the evolution of mechanical and structural properties of these materials under load at ultrahigh temperatures using synchrotron x-ray diffraction and tomography that will pave the way to much-needed significant advances in thermo-mechanical performance of 2D materials for reusable spacecraft.

Reference:
Real-time synchrotron measurements of ceramic 2D coatings for hypersonic applications.

**F11. Graphene Guided Assembly of Conjugated Polymers**  
Lei Zhai, Saiful Khondaker, Matthew McInnis, Chen Shen, Narae Kang

\(\pi\)-bonded surfaces of graphene are ideal for guiding the assembly of conjugated polymers (CPs) and providing optimum CP/electrode interfaces for efficient charge injection. In addition, extraordinary electronic and mechanical properties of graphene increases their utility for applications as electrodes in organic electronic devices. This presentation reports the investigation graphene guided assembly of conjugated polymers including the effect of molecular weight on assembly structures, the fabrication of graphene/CP based field-effect transistors and the impact of the interfacial properties on device performance.
The ability to tailor the properties of a material is essential to optimize device functionality. Recently, attention has been focused to tailor the properties of two dimensional molybdenum disulfide (MoS$_2$), not only by controlling the number of layers but also by means of external controls. In this talk, I will present evidence that the electrical and optical properties of monolayer and few layers MoS$_2$ can be tuned by controlled exposure of the samples to oxygen plasma [1-2] or by deposition of metal nanostructures [3].

When single layer and multilayered MoS$_2$ samples were exposed to oxygen plasma, we found that the mobility, on-current and resistance of samples vary exponentially by up to four orders of magnitude with respect to the plasma exposure time. Photoluminescence (PL) study show a decrease of PL intensity leading a complete quenching. Raman studies conducted before and after plasma treatment show a significant decrease of intensity of MoS$_2$ peaks with the creation of new oxidation induced peak, while X-ray photoelectron spectroscopy (XPS) study show peaks associated with MoO$_3$ after plasma exposure. Our study suggest that that during exposure to oxygen plasma, the energetic oxygen molecules interact with MoS$_2$ and create MoO$_3$ rich defect regions that acts as a tunnel barrier for the injected conduction electrons, giving rise to the exponential increase in resistivity as a function of plasma exposure time.

By depositing nanostructures of Au on MoS$_2$, we investigate the electronic structure of the resulting hybrid systems. We found strong evidence of PL quenching of MoS$_2$ as a result of charge transfer from MoS$_2$ to Au: p-doping of MoS$_2$. This was also confirmed from the charge transport study where we observe a positive shift in threshold voltage in the transfer characteristics of the MoS$_2$ FET upon deposition of Au nanostructure.

F13. Excitations and ultrafast response in double-layer transition-metal dichalcogenides

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We analyze possibility of plasmon and exciton states in two-layer MoS₂, MoSe₂ and WS₂ systems by applying time-dependent density-functional theory and many-body theory approaches. In particular, we demonstrate that in addition to the standard plasmon mode, the systems may demonstrate an extra plasmon excitation with charge oscillations perpendicular to the layers. The doped systems may have another type of collective excitation – Mahan exciton, a coupled electron-hole state. We show that similar to the undoped case, the binding energy of the Mahan exciton can be quite large, 20-30meV. In addition, we analyze a possibility of the ultrafast electron-hole separation in the undoped bilayer system of MoS₂-WS₂ through the inter-layer hole transfer, and show that such a possibility takes place, in agreement with experimental observations. We discuss possible application of the results in optoelectronic technologies.

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F14. Manipulating band structure of single layer MoS₂ via adsorbates and defects

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The influence of sodium on the band structure of single layer MoS₂ was investigated using density functional theory simulations. We will show that Na-adsorption leads to charge transfer to the MoS₂ surface causing an effect similar to n-type doping of a semiconductor. Moreover, we will show results of our simulations indicating that the hybridization of electronic states of Na and that of MoS₂ causes narrowing of the bandgap. At 1 monolayer (1ML) coverage of Na on MoS₂, the system becomes metallic with a parabolic band that disperses from valance band to conduction band. Details of the effect on electronic band structure MoS₂ of Na will be discussed and compared to the effect of Co and vacancy defects.

*This work is supported in part by the U.S. Department of Energy under grant DE-FG02-07ER15842
F15. Methanol synthesis on defect-laden single-layer MoS2 supported on Cu(111): A first principles study
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Despite being found to be the preferred structure in single layer MoS2, the sulfur-vacancy row does not facilitate alcohol synthesis from syngas [1] because its narrow size limits the adsorption, diffusion, and formation of involving species. On Cu(111), strong interactions between MoS2 and Cu are expected to reduce the corrugations caused by sulfur-vacancy rows, resulting in a larger exposure of sulfur vacancies to adsorbates which promisingly enhances the catalytic activity of the row structure towards alcohol synthesis from syngas. Based on our ab-initio calculations performed using density functional theory utilizing the DFT-D3 correction for accounting the van der Waals interactions, we show (1) that there is a significant charge transfer from the Cu(111) surface to MoS2, enhancing its catalytic properties, (2) that the binding energies of CO and dissociated H2 increase by 0.3 eV in comparison to that on unsupported MoS2, indicating stronger interactions, and (3) that the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS2. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syngas on single-layer MoS2 with a vacancy row. We will also present the energetic pathways for the formation of other possible products such as methane, formaldehyde, and water, as well as that of (reverse) water gas-shift reaction.
*This work is supported in part by the U.S. Department of Energy under grant DE-FG02-07ER15842

F16. Title: Some New Non-Cryogenic Rocket Fuels
Presentation author: ILIA TOLI
Abstract. In this poster, 2D nitrogen allotropes are proposed as rocket fuels and plant fertilizers, a solution to the nitrogen fixation problem. It is proven with ab initio methods that 2D nitrogen allotropes exist as bucky balls and as nano sheets. Thermodynamic estimations are made that show that they are excellent solid fuels for rocket propulsion.

F17. The use of 2D graphene as computer chip. I have published a paper in the topic.
Presentation author: ILIA TOLI
A data storage chip made of a single layer Fg (fluorographene) sheet is proposed. It stores 0.5 Petabyte per cm2 data. This is 500,000 GB/cm2. In stand alone it is tear resistant and stable for up to 24 hours in temperatures up to 400 C. On a support surface at room temperature it is stable indefinitely. Various methods for writing and reading are proposed. The Fg sheet may be placed on a support surface, typically a single-crystal silicon sheet. The support and the Fg sheet can be stacked up in 3D. This dramatically increases the density of information storage. No stereochemical rearrangements are expected to occur because of the tight arrangements of carbon in graphene. Stereochemical deformations should be minimal, local and not problematic, furthermore minimized
by the van der Waals forces of the support sheet. The Fg sheet is kept firm into place on all of its borders, and maybe also at a few places across it, as needed. The problem of radicals is solved with a proper mathematical model of encoding.

**F18. Preparation, hydroxylation, and permeability of ultra-thin two-dimensional silicate films**

**Presenting Author:** William E. Kaden

**Abstract:** This presentation will cover a brief overview of preparation conditions leading to an array of monolayer and bilayer silicate films as a function of support, loading, heating and environmental conditions. Such films act as atomically well-defined models of a wide-range of materials, like glasses, zeolites, and various clay-like minerals, with applications in fields ranging from electronics, to catalysis, and geology. A comparison of Mo, Ru, and Pd supports will show a correlation between the silicate structures forming and the oxygen affinity and lattice parameter of the underlying materials. Those materials with greater oxygen affinities lead to increased preference of monolayer structures with vertical Si-O-M linkages to the support, while those with weaker affinities lead to a greater likelihood of forming decoupled physisorbed bilayer structures. In intermediate cases (Ru), both structures are possible depending on Si coverage. Film crystallinity is also affected by preparation conditions, and will be discussed as well. The main focus of the presentation will be the elucidation of the fundamental silicate hydroxylation mechanisms within UHV (with and without electron-bombardment mediation) and liquid environments using bilayer SiO2/Ru(0001). In UHV, the hydrophobic, fully saturated, SiO2 structure shows only small amounts of defect-mediated hydroxylation upon exposure to water vapor under a wide-range of conditions, but this may be tuned using recently developed electron bombardment protocols. Atomic-level mechanisms for the hydroxylation process will be compared with liquid based dissolution studies and previous geological studies, which will show a preference for OH attack at Si sites in the absence of defects. Using Pd and Au permeation and nucleation effects will be explored as a function of film structure and hydroxylation, with Au showing a preference for permeation through vitreous domains, and physisorbed water, but not direct hydroxyl interaction, showing a pore-blocking effect in both cases. In the case of Pd, comparisons will also be made to liquid-based adsorption and nucleation techniques commonly applied in more applied research, and used
to better understand the various processes leading to the creation of activated metal sites following oxidation, reduction, and annealing procedures.

**F19. Adsorption of pentacene on vicinal surfaces: role of coordination, surface chemistry and vdWs effects**

Jeronimo Matos, Abdelkader Kara  
University of Central Florida

In contrast to low miller index surfaces, vicinal surfaces are characterized by steps and step edges that not only present an interesting atomic landscape for the adsorption organic molecules, but also a unique electronic structure resulting in part from the low coordinated atoms at the step edges. The adsorption of pentacene on the stepped (511), (221), (911) surfaces (respectively 3, 4 and 5-atom wide terraces) of Cu and Ag (coinage transition metals); Pt (reactive transition metal); and Ni (reactive, magnetic transition metal) are studied using density functional theory, in order to investigate the support effects arising from differing surface chemistry. We compare the adsorption energy, adsorption geometry and electronic structure predicted by the PBE functional with those obtained from one of the optimized vdW-DF methods: optB88-vdW.

**F20. Experimental realization of new topological phases of matter beyond topological insulators**

Madhab Neupane  
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A three-dimensional (3D) $Z_2$ topological insulator (TI) is a crystalline solid, which is an insulator in the bulk but features spin-polarized Dirac electron states on its surface. In 2007, the first 3D TI was discovered in a bismuth-based compound. The discovery of the first TI tremendously accelerated research into phases of matter characterized by non-trivial topological invariants. Not only did the 3D $Z_2$ TI itself attract great research interest, it also inspired the prediction of a range of new topological phases of matter. The primary examples are the topological Kondo insulator, the topological 3D Dirac and Weyl semimetals, the topological crystalline insulator and the topological superconductor. Each of these phases was predicted to exhibit surface states with unique properties protected by a non-trivial topological invariant. In this talk, I will discuss the experimental realization of these new phases of matter in real materials by momentum and time-resolved photoemission spectroscopy. The unusual properties of the protected topological surface states can lead to future applications in spintronics and quantum computation, which hold promise to revolutionize our electronics and energy industries.
MoS₂, which has similar energy gap to the semiconductor silicon, has attracted attention due to its superior electrical, optical and mechanical properties. Synthesis of single crystal MoS₂ thin film has faced technological difficulties including poor control over doping. Recent success at growing single crystal MoS₂ film was achieved in a sealed evacuated tube, but this method is unsuitable for manufacturing and poorly controls the sulfurization process. Our approach is using chemical vapor deposition in a tube furnace with flowing gas. We report an investigation of doping with different elements. The objective is to boost MoS₂ electrical conductivity and optical absorption without degrading the crystal structure with application to solar energy generation.

A simple and fast detection of organic pollutants including polycyclic aromatic hydrocarbons (PAHs) in soil, water, and air is increasingly important for real-time environmental monitoring and associated environmental impact assessments to aid in natural anthropogenic hazard responses and soil remediation. Among many hydrophobic organic compounds, PAHs are of great concern because of their carcinogenic and mutagenic properties. The determination of PAHs in environmental samples can be accomplished by conventional analytical methods such as HPLC or GC-MS; however, these methods are time consuming and require invasive collection of samples in the field and transportation to centralized laboratories for analysis. Electrochemical methods...
are often complementary to the aforementioned techniques, allowing the possibility for inexpensive and portable instruments; however, there are only a few applications of electrochemical sensors for monitoring organic pollutants in water\textsuperscript{3}.

According to previous research of graphene properties, graphene shows potential for the sensing of PAHs by interacting with aromatic molecules through dispersion forces\textsuperscript{4}. Graphene’s conductance will increase with the absorption of aromatic molecules as a result of intermolecular $\pi$ electron delocalization\textsuperscript{5, 6} making this study the first to experimentally demonstrate monolayer graphene sensor for toluene detection in aqueous environment, a first step effort to PAH detection in water environments. This concept significantly simplifies the fabrication process by avoiding the use of a functionalized graphene and using dry process for graphene synthesis and transfer instead of drop-casting. This makes the whole process compatible to batch microfabrication, scalable and less prone to performance variation. Based on this, a graphene-based nanosensor was developed for \textit{in situ} monitoring of PAHs in aqueous solutions.

The sensor was fabricated using photolithography and etching of Au/Ti film on a silicon wafer followed by the transfer of a single graphene layer which was prepared separately by chemical vapor deposition (CVD). The performance of the graphene nanosensor was characterized using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The graphene-based sensor demonstrated a fast (< 10 sec) and linear response to toluene (0 to 17 ppm) at +400 mV vs. Ag/AgCl when measured amperometrically. The novelty can be found in utilizing high affinity of graphene to PAHs and intermolecular electron delocalization at the interface of graphene and a benzene ring for toluene detection in water. The developed sensor is the first to use monolayer graphene for the detection of toluene in contaminated water with a good sensitivity and is applicable to many contaminated water bodies or engineered systems due to its reduced sensing cost, portability, and ease of use.

\textbf{F23. Growth of CVD graphene and CVD MoS$_2$ for 2D Heterostructures}

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\textbf{Abstract}

Two-dimensional materials such as graphene and MoS$_2$ show great potential for the development of novel electronic devices on flexible substrates.. Graphene is a single layer sheet of sp$^2$ carbon bonds with high mobility and low resistivity of $10^{-6}$ $\Omega$ cm. However graphene has no band gap and therefore by itself it is not good for device applications that would require a band gap. Single layer MoS$_2$ has a structure similar to graphene, with the sp$^2$ bonds connecting molybdenum and sulfur, but it has a direct band gap of 1.83eV, therefore it is suitable for transistors and

The two materials can be combined to form ultrathin heterostructured devices. In the past most devices made from MoS\textsubscript{2} and graphene required extensive exfoliation of bulk material with little yield. This is not optimal for mass production of devices. Here we use chemical vapor deposition (CVD) method to grow films or large area flakes of MoS\textsubscript{2} and test transfer techniques to stack them on top of CVD grown graphene to create heterostructured devices for photovoltaic applications.

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**References**

**F24. Thermal Transport in Single-Layer MoS\textsubscript{2} and Black Phosphorus Transistors**
Leitao Liu, Zhipeng Dong and Jing Guo, *Senior Member, IEEE*
Department of Electrical and Computer Engineering, University of Florida

We calculate the ballistic thermal conductance in single-layer MoS\textsubscript{2} and black phosphorus based on the phonon dispersion. The ballistic thermal conductance of single-layer MoS\textsubscript{2} is almost isotropic with a value of 0.7 W/mK; meanwhile, in single-layer black phosphorus (BP), the in-plane ballistic thermal conductance is anisotropic with a value of 0.72 W/mK in the zigzag direction and 0.40 W/mK in the armchair direction. Fig.1 gives the direction dependent ballistic thermal conductance single-layer MoS\textsubscript{2} and black phosphorus at $T = 300K$. Also, we investigate the thermal transport behaviors at steady state in double-gated MOSFET-like transistors with single-layer MoS\textsubscript{2} and BP used as the channel material. The conventional Fourier’s law with contact temperatures as the boundary conditions and modified boundary conditions [1] which can capture quasi-ballistic phonon transport effects are used. Fig.2 shows the steady-state temperature profiles in single-layer MoS\textsubscript{2} and BP based transistors with $L_{Ct}= 30$nm, which is comparable to the phonon mean free path $\lambda$. The transport direction is in the zigzag direction. The simulation results show that Fourier’s law with contact temperatures as the boundary conditions underestimates the peak temperature rise both in single-layer MoS\textsubscript{2} and monolayer black phosphorus transistors. Fig.3 presents the anisotropy of thermal transport in in single-layer black phosphorus. And higher in-plane thermal conductivity and ballistic thermal conductance lead to higher temperature rise in the armchair direction than that in the zigzag direction. This shows that there is less self-heating in zigzag direction, though carrier transport is preferred in armchair direction [2].
Fig. 1. Direction dependent ballistic thermal conductance in single-layer MoS$_2$ and black phosphorus.

Fig. 2. Steady-state temperature profiles in transistors with single-layer MoS$_2$ and black phosphorus (BP) used as the channel materials at $L_{CH}=30\text{nm}$. Both Fourier’s law with contact temperatures as the boundary conditions (CB) and modified boundary conditions (MB) are simulated. The insertion is heat generation rate profile.

Fig. 3. Steady-state temperature profiles in single-layer black phosphorus (BP) transistors along the zigzag and armchair directions with modified boundary conditions at $L_{CH} = 30\text{nm}$.


F25. Patterned 2D Heterostructures Based on Transition Metal Dichalcogenide.

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Isolated single-layers of transition metal dichalcogenides (TMD) are 2D crystals with novel physical properties that differ from their bulk layered counterparts. The electronic structure, phonon modes and crystal symmetry changes with the number of layers and affect the physical behavior of these 2D materials. From the structural viewpoint, layered bulk TMDs are composed of vertically stacked tri-atomic layers (X-M-X) of the same chemical compound MX$_2$ [where, for instance, M=(W,
Mo, and X=(S, Se, Te)], that only interact through van der Waals forces. Modifying the stacking sequence by alternating layers of different compounds as well as locally controlling the chemistry of TMDs, could open new possibilities for a large variety of material with artificially engineered properties and functionalities. In this work, a multi-step method was used to synthesize continuous large-area polycrystalline films of TMDs heterostructures. The two-dimensional films contain arrays of stacked TMDs hetero-layers interconnected by a single-layer of a different TMD. The synthesis approach combines shadow masks, high-vacuum thermal evaporation and chalcogenization in a chemical vapor deposition system. Transmission electron microscopy and Raman mapping were used to study the chemical composition distribution of the films. Depending on the chalcogenization sequence, different levels of alloying were observed in the sections containing hetero-layers. A variety of TMDs heterostructures in which both the metal and/or chalcogen atoms are exchanged from one region to another, were fabricated and studied. Figure1. (a-c) Different TMD patterns created by the multistep method proposed in this work. (d) and (e) are the intensity maps for the E_{12g} Raman mode corresponding to the regions in a TMD heterostructure containing WSe2 and MoSe2, respectively. (f) Raman spectra for spots 1 and 2 in (d) and (e), following two different procedures (labeled series A and B).

F26. Interlayer Shear Vibrations in Bilayer and Few-Layer Graphene: A non-local van der Waals DFT study
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The lattice vibration of graphene has been an important aspect of graphene research due to the role played by the strong electron-phonon interaction in its physical properties. While high-energy phonon bands have been intensely studied and well understood, the knowledge on the low-energy phonons is more limited [1]. Motivated by recent time-resolved pump-probe experiments [1], we report results of a computational study ---density functional theory (DFT) using a non-local van der Waals (vdW-DF) density functional--- of the lowest-energy inter-planar optical phonon, the shearing mode, of few layers of graphite, whose frequency can help determine the number of graphene layers in the slab. The shearing-mode frequency has been found to decrease dramatically when the layer thickness of graphite approaches the bilayer limit. The substrate has been found to have insignificant influence on the shearing vibration. This is well explained by a simple model of coupled harmonic oscillators and previous calculations ignoring the non-local van-der-Waals forces and the relaxation of the interlayer distance. However, our state-of-the art DFT calculations suggest that the interaction of the substrate is sufficiently strong so as to immobilize the contact layer.

F27. Raman spectroscopy of double-side hydrogenated graphene: towards graphane-based electronics
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Recent success in using the Birch reduction for hydrogenating graphene provides a possible avenue towards synthesis of graphane, an sp³ analogue of graphene. Graphane is expected to have a large band gap and can be used to fabricate field effect transistors with high on-off ratios. Here, we have hydrogenated both sides of graphene by exposing suspended graphene to the Birch reduction. We will present the Raman spectra of double-side hydrogenated graphene and compare them to the expected spectra of graphane.

F28. Electronic properties of fluorinated MoS₂
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We have investigated the structural and electronic properties of fluorinated (via plasma processing) molydisulfide using scanning tunneling microscopy, x-ray photoelectron spectroscopy, photoluminescence and ultraviolet photoelectron spectroscopy. Fluorine atoms are strongly bound on molydisulfide and the binding leads to p-doping. As such, fluorination can be useful for chemical doping of molydisulfide.

F29. Tuning of Properties of MoS₂ by Metallic Nanoislands Deposition
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Although the discovery of unique properties of two dimensional (2D) transition metal dichalcogenides (TMDs) in their monolayer form has pushed the boundaries of semiconductor research, the ability to tune their optical and electrical properties by introducing local interactions with the surface offers even greater perspective. Here we will discuss how the properties of MoS₂ monolayer can be tuned by introducing local metal-semiconductor interfaces by depositing metallic nanoislands such as gold (Au), nickel (Ni) and platinum (Pt) onto the MoS₂ surface. We will investigate the local variations of morphology and opto-mechanical properties including photoluminescence (PL) and Raman signatures, in the metal-MoS₂ structures. We will present evidence that PL variations, related to charge transfer between MoS₂ and the metal deposited, can
be used to tune the functionalities of the system. In addition, we will study the evolution of the characteristic Raman peaks to understand the stress exerted on the material. The results suggest new avenues for 2D nanoelectronics, energy application and sensors.

F30. Anisotropic Quantum Transport in Black Phosphorus Field Effect Transistors
Runlai Wan, Xi Cao, and Jing Guo
Department of Electrical and Computer Engineering, University of Florida

We present self-consistent multiscale quantum transport simulations of both phosphorene Schottky-barrier (SB) FETs and MOSFETs. Our results indicate that by properly choosing transport direction, we can optimize the performance of FETs. We obtain the following general results: (1) For phosphorene SBFETs, it is shown that scaling down the gate oxide thickness results in pronounced ambipolar I-V characteristics and significant increase of the minimal leakage current, which, however, can be effectively suppressed by reducing phosphorene to mono or bilayer. (2) Phosphorene MOSFETs is more scalable than SBFET since MOSFET structure can effectively suppress the ambipolar conduction and decrease the leakage current. (3) The highly anisotropic band structure plays a critical role in determining the performance of phosphorene transistors. For SBFETs, ON-current and contact resistance decrease monotonically as the transport direction varies from armchair direction to zigzag direction. For MOSFETs, on the other hand, the optimal transport direction is different when channel length ($L_{CH}$) is greater or less than 10 nm. When $L_{CH} < 10$ nm the optimal transport direction is between armchair direction and zigzag direction while when $L_{CH} > 10$ nm the armchair direction is optimal direction, as shown in figure 1. With the optimum choice of the transport direction, both n- and p-type phosphorene MOSFETs meet the International Technology Roadmap for Semiconductor (ITRS) target at the 5-nm technology node.

Fig. 1. ON-current ($I_{ON}$) for both phosphorene nMOS and pMOS with different transport direction at channel length (a) 20 nm and (b) 5 nm. $I_{ON}$ is defined at a common specified $I_{OFF}$ of 100 nA/μm and the power supply voltage of 0.5 V. θ=0 is corresponding to armchair direction and θ=90 zigzag direction. $I_{ON}$ for MoS₂ (band structure is nearly isotropic) MOSFETs (red dashed lines) are also plotted for comparison.
F31. Recognition of DNA sequencing through binding of nucleobases to defected-graphene
Valentina Zaffino, Jeronimo Matos and Abdelkader Kara
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Graphene is one of the most promising materials in nanotechnology. Its large surface to volume ratio, high conductivity and electron mobility at room temperature are outstanding properties for use in DNA sensors. For this study, we use Density Functional Theory (DFT), with and without the self-consistent inclusion of van der Waals (vdW) interactions, to investigate the adsorption characteristics of nucleobases (cytosine, guanine, adenine, thymine, and uracil) on pristine graphene and graphene with defects (Divacancy and Stone-Wales). We investigated the performance of two types of vdW-DF functional (optB86b-vdW and rPW86-vdW), as well as the PBE functional, and their description of the adsorption geometry and electronic structure of the nucleobase-graphene systems. We found that the presence of defects results in an increase in binding energy, closer adsorption of the molecule to graphene and greater buckling in both the graphene structure and nucleobases. The adsorption hierarchy with and without defects will be discussed as well as the role of vdWs interactions.

F32. Edge functionalized Band gap tuning of germanene nanoribbon
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Abstract
Extremely high mobility, massless fermions behavior of charge carriers, strong spin-orbit coupling properties of buckled two dimensional germanene structure has attracted intense research interest for high performance devices. A low structural stability and lack of intrinsic band gap makes them less suitable for logic and switching devices. A band gap could be opened in germanene by the application of a perpendicular electric field, surface adsorption, confined into a armchair nanoribbon, and edge functionalization by hydrogen or halogens. In this work, we passivate the edge atoms of armchair germanene nanoribbons (AGeNRs) by hydrogen (-H and -2H) or halogen (- F, -Cl, -Br, -I, -2F, -2Cl, -2br, -2I) atoms. Density functional theory calculations were performed to determine the band gap and stability of the AGeNRs. It was found that double atom edge functionalization of W-AGeNRs (W, ribbon width) resulted in almost the same band gap as compared to one atom edge functionalization of (W-2)-AGeNRs. Fluorine functionalization of AGeNR produced the most stable structure. Edge functionalization of AGeNRs opened up a band gap as small as 0.012 eV when functionalized by -2H and as high as 0.7 eV with -2I. Edge functionalized band gap tuning of AGeNRs may be a route towards the integration of germanene in logic and high performance switching devices.

F33. Observation of friction between gold nanocrystals and graphene using a quartz crystal microbalance
Brandon Blue, Michael Lodge, and Masa Ishigami
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A simple phenomenological formula, \( F = \mu N \), where \( \mu \) is the coefficient of friction and \( N \) is the normal force, governs macroscopic friction. Nanoscale contacts between surface asperities are assumed to determine \( \mu \), but the fundamental science of friction at the nanoscale is still in its infancy. From an engineering standpoint nanoscopic friction at speeds between 1 mm/s and 1 m/s are most technologically relevant. However, existing experimental methods are limited to slower speeds, and theoretical methods are limited to systems that are too small to realize experimentally at these speeds [1].

Our recent results using quartz crystal microbalances (QCM) show that experimental measurements of nanoscale friction at speeds up to 1 m/s are possible [2]. QCMs are thin quartz crystal disks that oscillate in shear mode when an oscillating voltage is applied across them. Surfaces of QCMs can reach peak velocities of m/s with amplitudes in the range of 1-10 nm. QCMs are extremely sensitive to mass adsorption and changes in dissipation at the surface because of their high quality factors. We used the QCM technique to measure the friction of monodisperse gold nanocrystals on graphene, which acts as a model system, to enable simulations that precisely match experimental parameters. We measure that the sliding nanocrystals exhibit viscous friction behavior with a drag coefficient of \( \zeta = 3\times10^{-13} \) kg/s.

References

**F34. The Effect of Defect Density on the Mechanical Properties of Graphene**

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Department of Physics, University of South Florida

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

**F35. Layer-dependent electronic and vibrational properties of SnSe$_2$ and SnS$_2$ 2D materials**

Joseph Gonzalez, Rudy Schlaf and Ivan Oleynik
University of South Florida

Layered metal chalcogenides possess a wide range of unique electronic properties, which are currently explored for applications as novel two-dimensional electronic materials. SnS$_2$ and SnSe$_2$ layered materials consist of covalently bonded S-Sn-S (Se-Sn-Se) sheets bonded together by weak van der Waals interactions. The atomic, electronic and vibrational properties of SnS$_2$ and SnSe$_2$ thin films are investigated using first-principles density functional theory (DFT). The accurate prediction of electronic properties of SnS$_2$ and SnSe$_2$ layered 2D materials is achieved by applying state of the art many-body perturbation theory in GW approximation. The evolution of the thickness-dependent band structure, optical and Raman spectra are discussed.

**F36. Optical coherence in atomic monolayer transition metal dichalcogenides limited by electron-phonon interactions**


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Understanding light mater interactions in nanomaterials is of crucial importance for a variety of applications ranging from optoelectronics to quantum computing. Transition metal dichalcogenides (TMDs) have been recently discovered as two-dimensional materials suitable for numerous applications. We systematically investigate the excitonic dephasing of three representative TMDs, namely MoS$_2$, MoSe$_2$ and WSe$_2$ as monoatomic thick layer and bulk crystals, in order to gain proper understanding on the factors that determine the optical coherence present in these materials. Coherent nonlinear optical spectroscopy in one and two dimensions, temperature dependent absorption combined with \textit{ab initio} theoretical calculations of the phonon spectra, indicate electron-phonon interactions to be the limiting factor. The strong confinement leads to strong electron-phonon coupling and as a result, to very rapid dephasing. Surprisingly, the excitonic dephasing differs slightly between atomic monolayers and high quality bulk crystals, which indicates that material imperfections are not the limiting factor in atomically thin monolayer samples. The temperature dependence of the electronic band gap and excitonic linewidth in bulk crystals reveal strong interaction with the $E'$ and $E''$ phonon modes.
Excitation induced dephasing is observed in both atomic thick monolayers and bulk crystals leading to a residual homogeneous linewidth of 4.5 meV for MoS2 determined by electron-phonon interactions. Finally, ‘ab initio’ calculations of the phonon energies and the phonon density of state reveal only minor differences between the phonon spectra in atomic monolayer TMDs and bulk crystals, which suggests the strong interaction of excitons with the E’ and E” phonon modes in particular is the limiting factor of excitonic dephasing in monolayer TMDs.

II. *ELECTRONIC ADDRESS: KARAISKAJ@USF.EDU*

**F37. Optical limiting in exfoliated Molybdenum disulphide nanoflakes.**
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We studied the absorption characteristics of Molybdenum disulphide (MoS2) nanoflakes dispersion in 1-Methyl-2-pyrrolidinone by Optical Z scan (OZ-scan) and Photo-acoustic Z scan (PAZ-scan) using a 532nm nanosecond laser. A changeover from saturable absorption to optical limiting behavior was observed with increasing input fluence in a conventional OZ-scan measurement. This suggests that different nonlinear processes like nonlinear scattering or excited state absorption might govern this changeover. PAZ-scan measurements, however, showed similar behavior eliminating the possibility of nonlinear scattering and confirming the excited state absorption. To reconfirm the PAZ scan, similar measurements were performed on Tungsten disulphide (WS2) dispersions which showed saturable absorption at all input energies.

**F38. High Photoresponsivity and Short Photo Response Times in Few-Layered WSe2 Transistors**
Qiong Zhou, Nihar R. Pradhan, Jonathan Ludwig, Zhengguang Lu, Daniel Rhodes, Michael Bishop, Komalavalli Thirunavukkarasu, Stephen A. McGill, Dmitry Smirnov, and Luis Balicas
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Here, we report the photoconducting response of field-effect transistors based on three atomic layers of chemical vapor transport grown WSe2 crystals mechanically exfoliated onto SiO2. We find that trilayered WSe2 field-effect transistors, built with the simplest possible architecture, can display high hole mobilities ranging from 350 cm2/(V s) at room temperature (saturating at a value of ~500 cm2/(V s) below 50 K) displaying a strong photocurrent response, which leads to exceptionally high photoresponsivities up to 7 A/W under white light illumination of the entire channel for power densities p < 102 W/m2. Under a fixed wavelength of λ = 532 nm and a laser spot size smaller than the conducting channel area, we extract photoresponsivities approaching 100 mA/W with concomitantly high external quantum efficiencies up to ~40% at room temperature. These values surpass values recently reported from more complex architectures, such as graphene and transition metal dichalcogenides based heterostructures. Also, trilayered WSe2
phototransistors display photoresponse times on the order of 10 μs. Our results indicate that the addition of a few atomic layers considerably decreases the photoresponse times, probably by minimizing the interaction with the substrates, while maintaining a very high photoresponsivity.

F39. Enabling 2D material with direct write lithography

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More and more researchers are turning to 2D materials as a solution for future electronic devices and sensors. Many of these 2D materials are supplied by transferring flakes onto a substrate or growing islands of CVD materials. These techniques can lead to a non-uniform material distribution and thus a challenge to standard lithography mask based processes. At the Nanoscale Research Facility at the University of Florida, we have been able to take advantage of our ion beam lithography tool to assist in the fabrication of non-uniform substrate materials. Our tool set includes the Raith ionLine (ion beam lithography), Raith 150 (electron beam lithography), and the Heidelberg DWL66 (laser lithography) and when employed in concert, we are able to mill, map, and process randomly distributed 2D materials into functional devices.

Starting with a substrate that includes randomly placed 2D materials we can employ the ionLiNE to mill fiducial marks. Both global and local marks can be design, via GDSII, and precisely milled with nm accuracy to odd samples up to 100mm in diameter. The unique tool is equipped with a 2nm stage control, 20-40kV column acceleration and a GDSII editor. Its metal alloy source can currently mill with either Au or Si ion. This greatly increases the flexibility of the instrument to employ non-Ga ions for milling (for fiducial placement or 2D material shaping/isolation), implantation and imaging. For non-conductive substrates, proven sample passivation methods have been developed.

Once alignment marks are in place with a known GDS design file, we transfer both substrate and GDS to the Raith 150 e-beam/SEM tool. With its 2nm resolution laser interferometer stage the tool is capable to systematically map and acquire high resolution SEM images of sections or entire substrate. The array of images is later combined and overlaid over the existing GDS file containing original fiducial marks. This then facilitates design and accurate placement of pads and wires over existing 2D materials. Using standard ebeam lithography techniques and/or plasma etching, pads and wires up to 100nm thick can be processed.

This process has been demonstrated on insulating substrates such as sapphire and thick SiO2. Substrate dimensions can be up to 100mm diameter and standard wafer thickness. Thicker samples can be processed within certain limits. The poster will illustrate these techniques and subsequent results.