Thursday Afternoon, October 31, 2013

Graphene and Other 2D Materials Focus Topic
Room: 101 A - Session GR+EM+NS+SS+TF-ThA

Beyond Graphene: Other 2D Electronic Materials and their Heterostructures

Moderator: J.A. Robinson, The Pennsylvania State University, A. Turchanin, University of Bielefeld, Germany

2:00pm **GR+EM+NS+SS+TF-ThA1 Functionalization of MoS_2 Surfaces for High-k Atomic Layer Deposition**, ***S. McDonnell***, *A. Azcatl, C. Buie, N. Lu, J. Kim, C.L. Hinkle, M.J. Kim, R.M. Wallace*, University of Texas at Dallas

The transition metal dichalcogenide (TMD) family of materials are 2-D bulk crystals similar to graphite that can be exfoliated to yield single-layer analogs to graphene. The materials can be metallic or semiconducting with bandgaps that are tunable with thickness. Recent publications have focused on devices fabricated with MoS_2 or WSe_2 channels and the deposition of thick gate oxides was carried out by atomic layer deposition (ALD) without any functionalization suggesting that these surfaces may be more reactive than graphene.[1,2]

Preliminary results have shown that the direct deposition of HfO_2 using tetrakis (dimethylamino) hafnium (TDMA-Hf) and H_2O precursors on MoS_2 is not a scalable process. The deposition of films less than 15 nm in thickness is three-dimensional, with pinholes reaching the MoS_2 surface. Ozone functionalization of graphene, as well as the deposition of seed layers by e-beam, has been previously shown to allow the subsequent uniform growth of high-k materials by ALD.[3,4]

Presented here will be a comparative study of ozone and e-beam seed-layer based functionalization. X-ray photoelectron spectroscopy will be used to probe the interfaces for any chemical reactions. Atomic force microscopy, inelastic ion scattering, and transmission electron microscopy will be used to monitor the film uniformity. The band offsets of the resultant heterostructures will also be presented.

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1 B. Radisavljevic *et al.*, "Single-layer MoS_2 transistors," Nature nanotechnology 6 (3), 147-150 (2011).

2 H. Fang et al., "High-Performance Single Layered WSe_2 p-FETs with Chemically Doped Contacts," Nano letters 12 (7), 3788-3792 (2012).

3 B. Lee et al., "Characteristics of high-k Al_2O_3 dielectric using ozone-based atomic layer deposition for dual-gated graphene devices," Applied Physics Letters 97, 043107 (2010).

4 B. Fallahazad et al., "Dielectric thickness dependence of carrier mobility in graphene with HfO_2 top dielectric," Applied Physics Letters, 97, 123105 (2010).

2:20pm **GR+EM+NS+SS+TF-ThA2 Silicene: From Single Sheets to Multilayers**, ***G. Le Lay***, *A. Resta*, Aix-Marseille University, France

Born in 2012 on a silver plate [1], artificially created by epitaxy on silver (111) substrates since it does not exist in nature, silicene, graphene's silicon cousin, offers many exciting promises. This is due, typically, to its Dirac fermions with trigonal or hexagonal wrapping and very high Fermi velocity, its two-dimensional topological insulator character, a hint for high-temperature superconductivity, and, last but not least, its direct compatibility with current silicon-based electronics.

However, the significant task to isolate free-standing silicene sheets has not yet been achieved. We will present a first step in this endeavor, since we have succeeded in growing silicene multi-layer stacks, which host massless Dirac Fermions, as demonstrated by the cone-like dispersion in Angle-Resolved PhotoElectron Spectroscopy measurements [2]. We could further characterize this novel silicon allotrope by comparing simultaneously acquired nc-AFM and STM observations in conjunction with transport measurements revealing sheet resistance.

In my talk, I will present these last results and draw perspectives for future research and potential applications.

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[1] "Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon" P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. Le Lay, *Phys. Rev. Lett.*, 108, 155501 (2012).

[2] "Evidence of Dirac fermions in multilayer silicene" P. De Padova, P. Vogt, A. Resta, J. Avila, I. Razado-Colambo, C. Quaresima, C. Ottaviani, B. Olivieri, T. Bruhn, T. Hirahara, T. Shirai, S. Hasegawa, M. C. Asensio and G. Le Lay, *Appl. Phys. Lett.*, 102, 163106 (2013).

[3] "Sheet resistance of multilayer silicene" P. Capiod, M. Berthe, A. Resta, P. De Padova, T. Bruhn, P. Vogt, G. Le Lay and B. Grandidier, submitted.

2:40pm **GR+EM+NS+SS+TF-ThA3 Topological Valleytronics in Monolayers of Group-VI Dichalcogenides**, ***D. Xiao***, Carnegie Mellon University **INVITED**

In many crystals the Bloch bands have inequivalent but degenerate energy extrema in the momentum space, known as valleys. The valley index constitutes a well-defined discrete degree of freedom for low-energy carriers that may be used to encode information. This has led to the concept of valleytronics, a new type of electronics based on manipulating the valley index of carriers. In this talk, we show that, when inversion symmetry is broken, a pair of valleys which are equivalent by time-reversal are distinguishable by their magnetic moment and Berry curvature. These quantities give rise to valley Hall effect and circularly-polarized valley optical selection rule both in graphene and in monolayer group-VI transition metal dichalcogenides. Moreover, in monolayer dichalcogenides, we find that the electrons and holes at the band edges are described by massive Dirac Fermions with strong spin-valley coupling, which further results in valley and spin dependent optical selection rule, and coexistence of valley Hall and spin Hall effects. These phenomena pave the way towards dynamic control of valley and spin by electric and optical means for device applications in monolayer dichalcogenides. We will report photoluminescence studies on dichalcogenide thin films, which show the first evidence on valley optical selection rule and optical valley pumping.

3:40pm **GR+EM+NS+SS+TF-ThA6 Controlled Scalable Synthesis of Uniform High-quality Monolayer and Fewlayer MoS_2 Films**, ***L. Cao***, North Carolina State University **INVITED**

Two dimensional (2D) materials with a monolayer of atoms represent an ultimate control of material dimension in the vertical direction. Molybdenum sulfide (MoS_2) monolayers, with a direct bandgap of 1.8 eV, offer an unprecedented prospect of miniaturizing semiconductor science and technology down to a truly atomic scale. Recent studies have indeed demonstrated the promise of 2D MoS_2 in fields including field effect transistors, low power switches, optoelectronics, and spintronics. However, device development with 2D MoS_2has been delayed by the lack of capabilities to produce large-area, uniform, and high-quality MoS_2 monolayers. Here we present a self-limiting approach that can grow high quality monolayer and few-layer MoS_2 films over an area of centimeters with unprecedented uniformity and controllability. This approach is compatible with the standard fabrication process in semiconductor industry. It can pave the way for the development of practical devices with 2D MoS_2 and opens up new avenues for fundamental research.

4:20pm **GR+EM+NS+SS+TF-ThA8 Electronic and Optical Properties of MoS_2 at Monolayer Thickness**, ***T.F. Heinz***, Columbia University **INVITED**

Inspired by the fascinating properties and application potential of graphene, interest within the community has extended to a broader class of stable, atomically thin materials. In this paper, we will discuss recent advances in the study of atomically thin layers of MoS_2 as representatives of the class transition metal dichalcogenides. Although the structure of the monolayer of MoS_2 is similar to that of graphene, the A and B sublattice are occupied either by Mo atoms or by a pair of S atoms, rather than just by C atoms. This difference in symmetry allows MoS_2 to be a semiconductor with a significant band gap. Through characterization of the optical properties of the material as a function of thickness, we show that quantum confinement effects lead to a crossover in MoS_2 from an indirect gap semiconductor in the bulk to a direct gap semiconductor at monolayer thickness.

As expected for lower-dimensional materials, excitonic effects are very strong in monolayer MoS_2. This allows for the existence of charged exciton with binding energies sufficient to produce stable states even at room temperature. Another distinctive feature of this material is the possibility of creating long-lived valley polarization in which one of the two inequivalent, but energetically degenerate K and K' valleys is populated in preference to the other. We demonstrate how this can be achieved using optical excitation with circularly polarized radiation and monitored through the retention of

the polarization in fluorescence emission. The pronounced change in symmetry from the non-centrosymmetric monolayer to the centrosymmetric bilayer has also been examined through its influence on the production of valley polarization and of optical second-harmonic radiation.

5:00pm **GR+EM+NS+SS+TF-ThA10 Low Energy Ion Scattering Studies of the Surface Termination and Structure of Bismuth Selenide**, *W. Zhou, X. He, Z.Y. Wang, J. Shi,* ***J.A. Yarmoff***, University of California, Riverside

Topological insulator (TI) materials are electrically conductive through unique two-dimensional surface states that are characterized by a Dirac cone, while they are insulators in the bulk. TI's have garnered great attention because of their potential use in next generation electronic devices. One of the concerns with TI's, however, is that their surface transport can degrade over time, which has been dubbed the "aging" effect. The transport is dependent on the detailed surface structure and how it changes over time, but this is not completely understood.

Low energy ion scattering (LEIS), which can measure the composition and atomic structure at the surface of a solid, was used to show that the surface termination can change after *in situ* cleaving, which might be related to aging effect [1]. LEIS spectra were collected from Bi_2Se_3, the prototypical TI material, after cleaving a bulk single crystal in ultra-high vacuum. Bi_2Se_3 has a layered structure with a fundamental quintuple layer (QL) unit composed of five atomic layers ordered as Se-Bi-Se-Bi-Se. While the atoms within each QL are covalently bonded, the QLs are attached to each other by relatively weak van der Waals forces. It has thus been assumed that the material cleaves between QLs resulting in a Se-terminated surface. Surprisingly, however, spectra collected at room temperature using 3 keV Na^+ ions in a double-alignment orientation, which is sensitive only to the outermost atomic layer, show scattering from Bi and none from Se. It was thus hypothesized that the material initially cleaves between QLs, but a thermally activated process induces a termination change. When cleaved at low temperature (80 K), the process is slowed and LEIS measurements are able to monitor the termination change in real time, consistent with the hypothesis.

We will discuss conditions that lead to the termination change, the stability of the Bi-terminated structure and the mechanisms involved. To quantitatively ascertain the atomic structure of the top few atomic layers, additional LEIS spectra were collected as a function of orientation and compared to the results of simulations.

[1] X. He, W. Zhou, Z. Y. Wang, Y. N. Zhang, J. Shi, R. Q. Wu and J. A. Yarmoff, Phys. Rev. Lett. **110**, 156101 (2013).

5:20pm **GR+EM+NS+SS+TF-ThA11 Electronic Activity of Silicene Boundaries, Edges, and Defects**, *A.J. Mannix, B.T. Kiraly, M.C. Hersam,* Northwestern University, ***N.P. Guisinger***, Argonne National Laboratory

Recent experimental evidence suggests that silicene, the silicon analog to graphene, exhibits a Dirac cone band structure[1,3], low temperature superconductivity[2], and Dirac Fermion chirality[3]. These discoveries highlight silicene's potential as a platform for novel electronics and physical phenomena. Depending on the growth parameters, silicon deposition on Ag(111) produces several distinct monolayer silicene phases corresponding to different silicon buckling configurations. Although these phases are well documented, their defect structure remains uninvestigated. Using ultra-high vacuum scanning tunneling microscopy (UHV STM), the structural and electronic properties of edges and defects within these various silicene phases were probed. Several highly-bucked phases are shown to exhibit electronically active domain boundaries, edges, and/or point defects, but do not show evidence of scattering. On the other hand, the lightly buckled honeycomb phase demonstrates clear, bias-dependent electronic scattering from edges and point defects. These contrasting behaviors suggest fundamental differences in charge transport properties that are of great interest to further silicene development. Additional insight is derived from the structure and electronic characteristics of the 0D and 1D defects, which often play a dominant role in determining material properties.

[1] Vogt, P., De Padova, P., Quaresima, C., Avila, J., Frantzeskakis, E., Asensio, M., … Le Lay, G. (2012). Silicene: Compelling Experimental Evidence for Graphene-like Two-Dimensional Silicon. *Physical Review Letters*, *108*(15), 155501. doi:10.1103/PhysRevLett.108.155501

[2] Chen, L., Feng, B., & Wu, K. (2013). Observation of a possible superconducting gap in silicene on Ag(111) surface. *Applied Physics Letters*, *102*(8), 081602. doi:10.1063/1.4793998

[3] Feng, B., Li, H., Liu, C., Shao, T.-N., Cheng, P., Yao, Y., Wu, K. (2013). Observation of Dirac Cone Warping and Chirality Effects in Silicene. *ACS Nano*. doi:10.1021/nn403661h

5:40pm **GR+EM+NS+SS+TF-ThA12 A Large Scale Epitaxial Growth of h-BN and Graphene Hybrid Structures (BNCs) on 6H-SiC (0001) Controlled a Ratio of h-BN and Graphene by Annealing Temperature**, ***H.-C. Shin***, *S.J. Ahn, B.G. Shin, J.-R. Ahn,* Sungkyunkwan University, Republic of Korea

Since the hexagonal boron nitride (h-BN) and graphene lateral hybrid structures (BNCs) were successfully fabricated on Cu foil, methods of BNCs synthesis were studied due to theoretically expected interesting electronic, magnetic and transport properties of BNCs, especially on metallic surfaces. However, for device application, it is required to transfer from metallic surfaces to insulating surface. We demonstrate direct growth of large scale epitaxial BNCs controlled a ratio of h-BN and graphene from perfect h-BN to perfect graphene by annealing temperature on 6H-SiC (0001) wafer. the electronic structures and the growth mechanism of BNCs on SiC were investigated by using low energy electron diffraction (LEED), angle resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM). We found that grown graphene domains gradually replaced initially grown h-BN domains and increased by h-BN decomposition and silicon sublimation at above 1150 degree Celsius. Interestingly, although graphene conventionally grown on 6H-SiC (0001) rotate 30 degrees from substrate, BNCs included both initially grown h-BN and finally grown graphene have 0 degree rotation angle from SiC. Therefore, h-BN and graphene are connected at an atomic scale.

Authors Index

Bold page numbers indicate the presenter