

2D Materials Focus Topic Room 15 - Session 2D-TuA

Growth of 2D Materials

Moderator: Taisuke Ohta, Sandia National Laboratories

2:20pm **2D-TuA-1 A New Approach to the Synthesis of High-quality Graphene on Silicon Carbide**, *Piotr Ciochoń, J Kołodziej*, Institute of Physics, Jagiellonian University, Poland

A new approach to the synthesis of high-quality graphene on silicon carbide

One of the most widely used methods of graphene synthesis is the graphitization of the (0001) and (000-1) surfaces of silicon carbide crystal. In order to obtain high quality graphene, it is necessary to slow down the excessive sublimation of silicon, observed at temperatures at which graphene ordering occurs. The most widely used method to accomplish this is carrying out the graphitization process in the presence of atmospheric pressure of inert buffer gases, such as argon.

We propose an alternative approach to solve this issue, which relies on exposing SiC surface during thermal annealing to the high-purity beam of silicon, obtained from an external sublimation source. The proposed solution has two advantages over the buffer-gas method. Firstly, it reduces the amount of impurities present near the surface by several orders of magnitude, as compared to even the purest inert gases at the atmospheric pressure. Secondly, it allows for precise control over the process parameters, leading to the possibility of near-equilibrium graphitization.

We have performed a thorough study of the process, systematically varying the parameters, such as graphitization temperature, process time and the silicon flux density and found that the synthesized graphene is characterized by very high degree of crystallographic ordering, low concentration of defects and large size of monocrystalline domains. Varying the process parameters, we were able to control the number of synthesized graphene layers, without the deterioration of overall graphene quality. Moreover, the process has shown a remarkable reproducibility, allowing for proper standardization of the synthesized material, a step considered crucial for the widespread introduction and use of graphene-based devices.

Our method allows for fast, reproducible synthesis of a very high-quality graphene directly on an insulating surface and is perfectly suited for preparing hybrid heterostructures and intercalation of foreign atoms. We have performed preliminary studies of intercalation with Cr atoms, during the graphitization process, as our approach allows to overcome several problems, resulting in unsuccessful past attempts.

2:40pm **2D-TuA-2 Cation-Eutectic Transition via Sublattice Melting in $\text{CuInP}_2\text{S}_6/\text{In}_{4/3}\text{P}_2\text{S}_6$ van der Waals Layered Crystals**, *M Susner*, Air Force Research Laboratory; *M Chyasnawichyus, Q He, B Conner, D Cullen, P Ganesh, D Shin, J McMurray, A Borisevich, M McGuire*, Oak Ridge National Laboratory; *Y Ren*, Argonne National Laboratory; *Petro Maksymovych*, Oak Ridge National Laboratory

Metal thiophosphate materials family offers a materials toolbox with broad functionality that includes magnetism, ferrielectricity and electron correlations. Here we report on heterostructure engineering of layered ferrielectric CuInP_2S_6 , which controllably introduces 1D and 2D chemical boundaries into the crystal on bulk scale. Single crystals of mixed $\text{Cu}_{1-x}\text{In}_{4/3+x}\text{P}_2\text{S}_6$ spontaneously phase separate into ferrielectric (CuInP_2S_6) and paraelectric ($\text{In}_{4/3}\text{P}_2\text{S}_6$) chemical domains, providing a new route to functional in-plane heterostructures in layered and 2D materials. We used high temperature x-ray diffraction and in-situ electron microscopy to conclusively demonstrate that this material forms a single phase at high temperature, and to identify the mechanism by which the phase separation proceeds upon cooling. Above 500 K $\text{Cu}_{1-x}\text{In}_{4/3+x}\text{P}_2\text{S}_6$ adopts a heavily disordered structure with respect to metal/vacant sites occupying the octahedral sites within a layer, thus indicating high Cu^+ and In^{3+} mobilities. However, the framework of P_2S_6 anions remains invariant across this transition. Considering the results of our detailed measurements of the transition temperature as a function of Cu/In ratio, we propose that this transition can be understood as eutectic melting on the cation sublattice, conceptually similar to intermediate temperature behavior of halide superionic conductors. Such a model suggests that the transition temperature for the melting process is relatively low because it requires only a partial reorganization of the crystal lattice. As a result, varying the

cooling rate through the phase transition controls the lateral extent of chemical domains over several decades in size, forming an intricate mesh of in-layer heterostructures comprised of domains with distinct cation compositions. Heterostructures can be formed, destroyed, and reformed by thermal cycling. Using this mode of lattice manipulation, we demonstrate that the ferroelectric T_c can be both increased to a nearly record level (about 20K higher than the pure bulk CuInP_2S_6 of 305K) and completely suppressed well below room temperature, without changing the physical sample, chemical composition, or loss of reversibility. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

[1] Susner et al., "Metal Thio- and Selenophosphates as Multi-Functional van der Waals Layered Materials", *Advanced Materials*, in press (2017)

[2] Susner et al., Cation-eutectic transition via sublattice melting in $\text{CuInP}_2\text{S}_6/\text{In}_{4/3}\text{P}_2\text{S}_6$ van der Waals layered crystals, *ACS Nano* in review (2017).

3:00pm **2D-TuA-3 Direct, Real-Time Observation of Layer-by-Layer Growth of a 2D Semiconductor using *In Situ* X-ray Synchrotron Radiation**, *H Bullen, R Nahm, S Vishwanath, G Xing, James Engstrom*, Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. In a number of studies, thin films of these materials are produced by techniques such as exfoliation. While these techniques have been invaluable concerning the measurement of electronic and other important physical properties, growth of thin films of these materials is essential to fully exploit their promise in a variety of devices. In particular, there is a great need to develop an understanding of the growth process such that one can at will deposit an arbitrary number of layers (e.g., 1, 2, 3 etc.) on a variety of possible substrates. Here we report on the metal-organic MBE growth of thin films of WSe_2 on sapphire substrates using $\text{W}(\text{CO})_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $\text{W}(\text{CO})_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence, both *in situ* and in real time. We have examined growth for a variety of conditions, including the flux and incident kinetic energy of the $\text{W}(\text{CO})_6$, and the substrate temperature. After a short incubation time, we observe steady-state epitaxial growth of crystalline WSe_2 thin films. X-ray fluorescence confirms formation of a stoichiometric thin film of WSe_2 . Perhaps most interestingly, during epitaxial growth we observe strong and sustained oscillations at the "anti-Bragg" condition for X-ray scattering, consistent with layer-by-layer growth. These results enable a direct determination of how each successive layer forms^[1], and how these depend on process conditions. Concerning process conditions, we observe a spectacular change in the growth as the incident kinetic energy of the $\text{W}(\text{CO})_6$ is varied. At sufficiently low values of the incident kinetic energy we observe no growth, while at higher values we observed sustained 2D LbL growth. These results point to the importance of incident kinetic energy in driving the dissociative chemisorption of the $\text{W}(\text{CO})_6$ precursor.

[1] See, e.g., A. R. Woll, T. V. Desai and J. R. Engstrom, *Quantitative modeling of in situ x-ray reflectivity during organic molecule thin film growth*, *Phys. Rev. B* **84**, 075479/1-14 (2011).

3:20pm **2D-TuA-4 Crystallization Kinetics of Photonically Annealed 2D Materials**, *N Glavin, R Vila, R Kim, R Rao, M McConney, B Maruyama, L Bissell*, Air Force Research Laboratory; *R Rai*, Air Force Research Laboratory; University of Dayton; *Christopher Muratore*, University of Dayton

Synthesis of flexible electronic devices using low-cost, naturally abundant materials (e.g., MoS_2) directly onto inexpensive polymeric materials promises manufacturing of flexible 2D devices at economically viable scales enabling use of their unique physics in grand challenge areas of energy, healthcare, and national security. Recently-proven approaches for low temperature 2D synthesis suitable for flexible substrates developed by the authors include growth of amorphous materials with subsequent photonic annealing to access crystalline domain sizes up to several microns. This approach has been demonstrated for synthesis of large area ultrathin monolithic layers as well as $\text{MoS}_2/\text{WS}_2/\text{BN}$ multilayers with pristine interfaces, allowing interrogation of intrinsic properties of 2D materials and their heterostructures as they apply to diverse optoelectronic devices. Detailed kinetic studies of crystal formation were accomplished through

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high throughput in-situ Raman spectroscopy at different surface temperatures and ambient conditions. With this technique, heterostructures were formed incorporating multiple TMD layers that were annealed simultaneously, and insights into the role of surface diffusion for metal and chalcogen species, and factors dictating activation energy for two-dimensional crystallization will be discussed.

4:20pm 2D-TuA-7 Intercalation Then Ordering of Oxygen Leading to Isolation Then Etching of Monolayer *h*-BN on Copper, *C Ma, J Park*, Oak Ridge National Laboratory; *L Liu*, University of Tennessee; *Y Kim, M Yoon, Arthur Baddorf*, Oak Ridge National Laboratory; *G Gu*, University of Tennessee; *A Li*, Oak Ridge National Laboratory

The interaction of *h*-BN, the thinnest 2D insulating material, with oxygen is important technologically, but has proven complex. *h*-BN has strong covalent bonds that exhibit great stability and multilayers have been recommended as an oxidation resistant barrier for both metal and graphene substrates. At the same time, oxygen is predicted to form adsorbed chains and then to cut *h*-BN sheets along the chains. We have exposed monolayer *h*-BN on copper substrates to air and then examined the surface with scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) after annealing to 600°C in ultrahigh vacuum. The active adsorbent is identified as oxygen, as expected. More surprising is evidence that oxygen is intercalated between the *h*-BN and copper and forms both quasi-1D and 2D ordered patterns on the predominantly (100) oriented substrate. STM images display double rows of O in hollow sites forming quasi-1D chains preferably along the moiré patterns and, in areas of higher coverage nucleated by steps, a p(2×2)-O superstructure. Efficient O diffusion along moiré channels is supported by first-principles density functional theory (DFT). Despite searches, a p(2×2)O structure on clean Cu(100) has not been observed; instead, higher density c(2×2)O islands are created there. XPS intensities here are consistent with the lower coverage p(2×2)O stabilized by the *h*-BN layer. Intercalated O increases the *h*-BN to Cu distance thereby decreasing the van der Waals interaction. Both STM dI/dV and DFT reflect this increased isolation by a 1.7 eV increase in the monolayer band gap, governed by a decrease in the contribution of the Cu surface to the density of states.

Intercalated oxygen is ultimately not stable and extended annealing at 600°C etches away the *h*-BN. In contrast to previous models, *h*-BN is removed by oxygen found underneath rather than adsorbed on the surface. Etching occurs along *h*-BN zig-zag edges and leads to finally to complete removal of the film. These new mechanisms observed for oxygen introduction, organization, and etching offer opportunities to better understand the stability of *h*-BN monolayers and to exploit the addition of oxygen to modify electronic properties or for formation of nanoscale structures.

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

4:40pm 2D-TuA-8 Polished Nickel Substrates for Large-area Multilayer Graphene Films, *Stefan Lehnardt, J Rowley, K Larsen*, Brigham Young University; *J Abbott, Moxtek; R Vanfleet, R Davis*, Brigham Young University
We show that the roughness of polycrystalline nickel has a significant effect upon the homogeneity of large-area multilayer graphene films grown via chemical vapor deposition. Nickel foil serves as a substrate/catalyst for this multilayer graphene growth. By mechanical polishing nickel foils and reducing roughness from ~100 nm to ~10 nm, we have obtained graphene films with fewer defects and greater thickness uniformity. Mechanical properties were determined by bulge testing and bending measurements on microscale cantilevers. Films from polished foils are thinner and show higher burst pressures.

5:00pm 2D-TuA-9 Heterostructures of Carbon Nanomembranes and Graphene as a Platform for Electrochemical Sensing, *D Kaiser, A Winter, C Neumann*, Friedrich Schiller University Jena, Germany; *A Centeno, A Zurutuza*, Graphenea, Spain; *T Weimann*, Physikalisches Institut, Friedrich Schiller University Jena, Germany

Chemical functionalization of single-layer graphene (SLG) is of key importance for applications in functional electronic devices such as, e.g., field-effect transistor (FET) based nanosensors. However, the electronic structure of graphene is typically degraded after the functionalization, which significantly restricts the applications. Here, we employ a route to non-destructive chemical functionalization of graphene with amino terminated 1 nm thick carbon nanomembranes¹ (NH₂-CNM) generated via electron beam induced crosslinking of aromatic self-assembled

monolayers. The electrical response of the NH₂-CNM/SLG heterostructures in electrolyte-gated FETs shows their high electrical capacitance enabling for effective sensor applications. The electrochemical performance of CNM/graphene FETs for detection of pH-values was studied in parallel with their in detail surface science characterization. We show that the high electronic performance of pristine SLG is preserved in the developed amino-terminated hybrids and demonstrate the pH-sensing with excellent sensitivity and reproducibility. Finally, we discuss the perspectives for highly selective biological sensing with the developed device concepts.

[1] A. Turchanin and A. Götzhäuser, Carbon Nanomembranes, *Adv. Mater.* 28 (2016) 5075

5:20pm 2D-TuA-10 Nucleation of 2D WS₂ by Plasma Enhanced Atomic Layer Deposition from WF₆, H₂ Plasma and H₂S – Impact on Grain Size and Charge Transport, *Benjamin Groven, A Nalin Mehta*, University of Leuven, Belgium; *Q Smets, T Schram, H Bender, W Vandervorst, I Radu, M Caymax, M Heyns, A Delabie*, IMEC, Belgium

To exploit the semiconductor properties of two-dimensional (2D) transition metal dichalcogenides in ultra-scaled nano-electronic devices across large area substrates, these materials need to be deposited with a highly crystalline structure and a controlled number of monolayers by manufacturable deposition techniques. Where the majority of the 2D materials in literature are grown by Chemical Vapor deposition (CVD), Atomic Layer Deposition (ALD) is investigated here as an alternative deposition technique. In ALD, (sub-)monolayer growth control is possible as the deposition is based on self-limiting surface reactions. In addition, due to the relatively low deposition temperature, the 2D materials can be grown directly on temperature sensitive structures at Back-End-Of-Line (BEOL) compatible deposition temperatures. As such, a material transfer from the growth to the target substrate can be avoided.

In Atomic Layer Deposition (ALD), the structure of 2D materials is determined by the nucleation mechanisms. However, the nucleation mechanisms of 2D materials by ALD have so far not yet been investigated. In this work, we investigate the nucleation behavior of WS₂ from a recently reported Plasma-Enhanced (PE)ALD process from WF₆, H₂S and H₂ plasma [1]. We show how the crystallinity and domain size of these layers depends on the starting substrate and the deposition temperature, and how they influence the semiconductor properties of WS₂. WS₂ is grown on 300 mm Si substrates covered with either 30 nm amorphous Al₂O₃ or 90 nm thermally grown SiO₂.

At 300 °C, the growth of WS₂ is strongly enhanced on the Al₂O₃ surface. The high nucleation density of $(2.2 \pm 0.1) \cdot 10^{14} / \text{cm}^2$ promotes fast closure of the first WS₂ layer. On the other hand, the combination of the high nucleation density with lateral and vertical growth contributions limits the crystal domain size to 5-30 nm. By choosing a substrate that has a lower reactivity towards the PEALD precursors, e.g. SiO₂, the nucleation density decreases to $(2.0 \pm 0.1) \cdot 10^{11} / \text{cm}^2$. An even lower nucleation density of $(6 \pm 1) \cdot 10^{10} / \text{cm}^2$ is obtained on SiO₂ by increasing the deposition temperature to 450 °C due to the increasing mobility of the ad-atoms on the surface. By lowering the reactivity of the H₂ plasma to further delay nucleation, the WS₂ crystals grow primarily in a lateral direction, which further increases the crystal grain size to 250 nm. Despite the low deposition temperatures, the WS₂ behaves as a semiconductor in back-gated transistors, that show an $I_{\text{max}}/I_{\text{min}}$ ratio of at least 10⁵ [2].

[1] B. Groven et al., *Chem. Mater.*, 2017, 29 (7), pp 2927–2938

[2] T. Schram, Q. Smets et al. VLSI satellite workshop 2017 (accepted)

5:40pm 2D-TuA-11 Surface Intercalation of Two Disparate Metals in Graphite: Copper and Dysprosium, *Ann Li-Rosales¹, P Thiel*, Iowa State University and Ames Laboratory

In this study, we use STM to investigate the intercalation of atomic metals, copper (Cu) and dysprosium (Dy), in the *surface* of graphite that is pre-treated with Ar⁺ bombardment.

Surface intercalated Dy rafts have a characteristic height of 0.61 ± 0.03 nm, with structured moiré patterns atop faceted rafts. DFT calculations on intercalated Dy rafts support our experimental observation: instead of a *dilute*, ($\sqrt{3} \times \sqrt{3}$)R30° arrangement of Dy atoms as in the well-known stage-1 Dy graphite intercalation compound (GIC), our Dy rafts are *dense* and are composed of three contiguous layers of Dy sandwiched between graphitic layers.

In the case of Cu, for which no *bulk* GIC's are known, we achieve *surface* intercalation of Cu in ion-bombarded graphite. Spanning temperatures of

¹ NSTD Student Award Finalist

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600 – 900 K, the morphology of intercalated Cu responds sensitively. At 600 – 800 K, intercalated Cu forms faceted islands that are variable in heights, ranging from 1.7 nm to as tall as 35 nm. At 850 K, intercalated Cu no longer forms faceted islands; instead, round clusters ranging from ~0.3 nm to 10 nm tall are present. At 900 K, small and round features ~0.3 nm tall prevail. Larger clusters are presumably removed by desorption. High resolution imaging atop a Cu island sheds light on the number of carbon overlayers and shifting in the stacking sequence of carbon lattice, potentially due to strain as a result of intercalation.

Relative to known *bulk* GIC's, our work shows that metals on graphite *surfaces* adopt configurations that are different in two ways. First, the metals form dense intercalated surface islands; and second, metals which do not intercalate in the bulk can do so on the surface. *Surface* intercalation of other metals can be envisioned.

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