2D Materials Focus Topic
Room 103B - Session 2D+TF-WeM

2D Materials: Growth and Fabrication

Moderator: Masoud Mahjouri-Samani, Oak Ridge National Laboratory

8:00am **2D+TF-WeM1 Synthesis and Characterization of Two-dimensional WSe₂ Grown using Chemical Vapor Deposition***, **Avra S. Bandophadyay**, G.A. Lara Saenz, C. Biswas, A.B. Kaul,* University of Texas at El Paso

Semiconducting Transition Metal Dichalcogenides (TMDCs) have attracted a lot of attention recently, because of their interesting electronic, optical, and mechanical properties [1]. Among large numbers of TMDCs, monolayers of tungsten diselenides (WSe_2) are of particular interest since WSe_2 possesses a direct band gap (~1.6eV) and tunable charge transport behavior, which makes it suitable for a variety of electronic and optoelectronic applications. Direct synthesis of large domains of monolayer WSe_2 and their growth mechanism studies are important steps toward applications of WSe_2. In this work, we have synthesized Tungsten Diselenide via Chemical Vapor Deposition Method using WO_3 powder and Se pellets as the precursors. Selenium was placed at the upstream side of the furnace at a temperature zone of 260-270°C. The temperatures and distances of these two sources were carefully controlled and adjusted. We used silicon with 300 nm thermally grown SiO_2 as the substrate and it was placed at some distance from the WO_3 source. The substrates for growing WSe_2 are put at the downstream side, where the Se and WO_3 vapors were brought to the targeting substrates by an Ar/H_2 (4:1) flowing gas with a flow rate of 120sccm. The pressure was maintained at 5Torr throughout the experiment. The temperatures at the Se source, WO_3 source and Substrates are maintained 260°C, 950°C and 750-850°C respectively. After the growth, the temperature of the furnace was naturally cooled down to room temperature and the samples were taken out for characterization. The size and shape of the as-grown flakes were observed under an Optical Microscope. Raman spectroscopy was used to determine the number of layers by noting the location of the Raman peaks and the relative Raman shift. In this paper we will discuss our work on the synthesis and characterization of 2D WSe_2, where we have also succeeded in forming monolayer structures for electronic device applications.

References:

[1] A. B. Kaul, *Journal of Materials Research*, vol. 29, pp. 348-361, 2014.

[2] H.Sahin et al, Physics Review B, vol. 87, pp. 1654091-1654096, 2013.

8:20am **2D+TF-WeM2 Reduction of Graphene Oxide by a Selective Surface Modification Process via Chemical Route for Achieving Higher Proportion of Graphene***, K. Dave,* CSIR Centre for Cellular and Molecular Biology (CCMB), India*; **KyungHee Park**,* Chonnam National University, Republic of Korea*; M. Dhayal,* CCMB, India

The primary objective of the study was to target the removable of remaining oxygen available as carboxylic acid functionalities from the surface of first level of reduced graphene oxide. Hence, first we describes preparation of highly exfoliated graphene oxide (GO) from graphite which was further reduced by hydrazine and sodium borohydride. Further we used soda lime for removing carboxylic functional group from the surface of reduced GO by decarboxylation. X-ray photoelectron spectroscopic analysis confirm the synthesis of exfoliated graphene oxide by chemically introduced oxygen as -COOH), –OH and C-O-C. A very high % proportion of carbon atoms as carboxylic functionality observed in the synthesized GO whereas the reduction of it with NaBH4 and Hydrazine significantly reduced it. The use of soda lime had further reduced the carboxylic group in both the $NaBH_4$ and N_2H_4 reduced GO. Raman spectroscopic analysis showed two distinct peaks of graphene oxide and reduced graphene in Raman spectra which were correlated with breathing mode of sp^2 atom and graphitic carbonic sp2 of carbon atoms. A strong red shift in the G-band position was observed after oxidation of graphite into GO due to increase in the number of layers of graphene whereas the reduced GO by both reducing agent $NaBH_4$ and N_2H_4 had showed a decrease in the red shift of the D-band. Above finding confirms better conversion of GO into graphene due to increased SP_2 carbon proportion after selective reduction of the GO. In the future we planned to use these materials for biomedical applications.

8:40am **2D+TF-WeM3 Scalabale Production of Molybdenum Disulfide-based Biosensors***, **A.T. Charlie Johnson**,* University of Pennsylvania **INVITED**

We demonstrate biosensor arrays based on CVD-grown molybdenum disulfide (MoS_2) field effect transistors (FETs) coupled to a computationally-redesigned soluble variant of the μ-opioid receptor (MOR). By transferring dense films of monolayer MoS_2 crystals onto prefabricated electrode arrays, we obtain clean, high-quality FETs that allow reproducible protein attachment. The yield of MoS_2 FETs and biosensors exceeds 95%, with average mobility of 2.0 $cm^2V^{-1}s^{-1}$ (36 $cm^2V^{-1}s^{-1}$) under ambient (in vacuum). An atomic length linker chemistry enables target binding very close to the MoS_2 surface to maximize sensitivity. The biosensor calibration curve for a synthetic opioid peptide target indicates binding affinity that matches values determined using traditional techniques and a limit of detection ~ 3 nM. The combination of scalable array fabrication and rapid readout enabled by MoS_2 transistors offer the prospect of a solid-state drug testing platform for rapid readout of the interactions between novel drugs and their intended protein targets.

9:20am **2D+TF-WeM5 Growth of Graphene on Cubic Silicon Carbide on Silicon Substrates***, **Mehdi Rezaee**, G.L. Harris, J. Griffin, C. Taylor,* Howard University*; E. Hu, D. Bell,* Harvard University

Graphene is a two-dimensional sheet of sp^2 carbon atoms with extraordinary high mobility and quantum properties that makes it a promising candidate for future electronics. Large-scale production of graphene is paramount for the development of graphene-based electronics. This thesis focused on the synthesis and characterization of graphene layers. Two methods were used to grow graphene films. First, graphene films were epitaxially grown on silicon carbide substrates by thermal decomposition of SiC at high temperatures and low pressures. An in-house built reactor consisting of an induction furnace was used to form epitaxial films for electronic applications. Second, chemical vapor deposition was used for direct graphene synthesis on 3C-SiC using copper as a catalyst. In the thermal CVD processes, hydrogen and methane gases were used as precursors. Methane acts as a carbon source, while annealing and cooling were done in a hydrogen environment. Different polytypes of silicon carbide (6H-SiC and 3C-SiC) and their crystal orientations were exploited as substrates to form epitaxial graphene. A hetero-epitaxial 3C-SiC epilayer was first deposited on Si substrate using the chemical vapor deposition technique in the cold wall, low-pressure horizontal CVD reactor. The reactor temperature, argon pressure, flow rate and concentration of different gases (propane, silane, hydrogen and argon) was investigated to control the growth of 3C-SiC and graphene sublimation rate. The resulting graphene films were confirmed using Raman spectroscopy. Further, graphene films have been characterized with the tools of atomic force microscopy (AFM) and scanning electron microscopy (SEM). Mobility, electrical resistivity and carrier density measurements were taken using Hall effect measurements.

This work was supported by the STC Center for Integrated Quantum Materials, NSF Grant No. DMR-1231319 and the PREM NSF Program.DMR-1205608 grant.

9:40am **2D+TF-WeM6 Growth of Graphene on Cu Single Crystal Substrates***, **Tyler Mowll**,* University at Albany-SUNY*; Z.R. Robinson,* College at Brockport-SUNY*; C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Copper foils are frequently used to grow single-layer graphene by chemical vapor deposition (CVD). The primary reasons for this are the low costs of the Cu foils, the low solubility of carbon in Cu, and the relatively low cost of the equipment needed to grow the films. However, the polycrystalline nature of Cu foils can lead to numerous crystalline defects in the graphene, resulting in a reduction in the transport properties. To provide a systematic study of the CVD graphene growth process, a study of the growth of graphene on single crystal Cu substrates, with terminations along the (100), (110), and (111) planes, was performed. Synthesis was performed in an ultra-high vacuum (UHV) chamber using a modified setup to allow growth at pressures as high as 1 Torr. Ethylene was used as the precursor gas. To control Cu sublimation at the elevated growth temperatures, an Ar overpressure was used. This arrangement allowed for the preparation of clean Cu surfaces by sputtering and annealing the Cu crystals in UHV, followed by graphene growth at low pressure, and analysis with low energy electron diffraction in UHV without breaking vacuum. This avoided exposure of the crystal to atmospheric contaminants. It was found that surface termination plays a strong role in the rotational alignment of the nucleating graphene grains and the decomposition rate of the ethylene. It was observed that single-domain epitaxy is possible on Cu(111) when the ethylene pressure is 5 mTorr or less. However, growth on both Cu(100) and Cu(110) result in a minimum of two domains. In addition, ex-situ EELS is currently being performed on well-ordered epitaxial graphene films grown on Cu(111) and Cu(100) to determine the effect of the graphene-Cu interaction on the electronic properties of the graphene.

11:00am **2D+TF-WeM10 Atomic Layered Large Area Growth of 2D Monolayers Over Different Substrates***, **Joseph Waters**, S. Garg, S. Balci, S. Kim, P. Kung,* University of Alabama

Atomically-thin transition metal dichalcogenides (TMDCs) such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) are of great interest because of their unique semiconducting and optical properties. For example, unlike graphene, MoS_2 is a semiconductor whose band gap changes from indirect (~1.2 eV) to direct (~1.85 eV) as the material thickness reduces from bulk to a monolayer state. This makes MoS_2 promising for numerous optoelectronic and biosensing applications. TMDC monolayers have originally been realized through exfoliation. However, the ability to synthesize monolayers over larger areas than those achievable with exfoliation requires scalable techniques such as chemical vapor deposition.

Here, we report the large area growth of monolayer thin films of TMDCs, such as MoS_2 and WS_2, by low-pressure chemical vapor deposition in an oxygen-free inert argon atmosphere. The growth of these materials has been compared on various substrates, such as basal plane sapphire, (001) SiO_2/Si, and GaN/sapphire substrates. The effects of growth conditions, including growth temperature, on the characteristics of the resulting material have been studied. The physical properties of the monolayers have been characterized using electron microscopy and atomic force microscopy to study their topology over the various substrates, in conjunction with confocal micro-Raman and micro-photoluminescence spectroscopy to correlatively assess their optical characteristics. The terahertz time domain spectroscopy of MoS_2 and WS_2 monolayer thin films will also be presented. We will further discuss the impact of these monolayer materials for robust optoelectronic device applications.

11:20am **2D+TF-WeM11 Growth of Doped Graphene from Fullerene Precursors***, X. Fei, J. Neilson, V. Lopez,* California State University Northridge*; H.J. Gao,* Chinese Academy of Sciences, People's Republic of China*; L. Gan,* Peking University, People's Republic of China*; **Li Gao**,* California State University Northridge

Heteroatom-doped graphene materials have potential applications in electronic devices, energy storage and conversion systems, and gas storage. Chemical doping with various heteroatoms is an effective strategy for tuning the properties of graphene in order to expand its applications. Toward the practical applications as well as fundamental studies of doped graphene materials, it is an urgent task to explore effective approaches to synthesize these materials with a high level of control over their doping properties. In this talk, we will discuss the synthesis of heteroatom-doped graphene materials from fullerene precursors. Initial success has been achieved on the iridium and ruthenium surfaces. The growth process and the properties of grown doped graphene materials are characterized by using scanning tunneling microscopy on the atomic scale. We will discuss how the growth process and the properties of grown doped graphene depend on precursor/metal systems and experimental conditions. This new synthesis approach is an important complement to the existing strategies for the preparation of heteroatom-doped graphene.

11:40am **2D+TF-WeM12 Evaluation of Precursor Chemistry for Controllable Growth of Molybdenum Disulfide by Pulsed Chemical Vapor Deposition***, **Berc Kalanyan**, J.E. Maslar, W.A. Kimes, B.A. Sperling, E. Garratt, B. Nikoobakht, R. Beams, S.J. Stranick, A.V. Davydov,* National Institute of Standards and Technology (NIST)

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs), e.g., MoS_2, are of increasing interest for next-generation nanoelectronic and optoelectronic devices due to their thickness dependent optical and electrical properties. For many applications, high volume manufacturing of devices based on TMDs will require deposition techniques that are capable of reproducibly growing wafer-scale films with monolayer control. To date, TMD deposition processes largely rely on powder vaporization and transport, with minimal control over precursor fluxes and chemistry. A detailed understanding of metal and chalcogen precursor chemistry in relation to film properties remains an important step toward the design of highly-controllable deposition processes suitable for large-scale 2D synthesis.

We aim to identify promising chemistries for chemical vapor deposition (CVD) processes for TMDs. We focus on MoS_2 CVD using organometallic and organosulfur compounds in a research grade single-wafer deposition system equipped with *in situ* optical diagnostics. The precursor flux is measured using optical mass flow meters installed on the delivery lines while deposition chemistry is characterized in the reactor volume above the deposition surface using *in situ* Fourier transform infrared (FTIR) spectroscopy. As-deposited and annealed films are characterized with *ex situ* techniques, including Raman and photoluminescence spectroscopy, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy.

Large-area thin films of MoS_2 were prepared from (η^5-ethylcyclopentadienyl)-dicarbonylnitrosyl molybdenum, cycloheptatriene tricarbonyl molybdenum, bis(ethylbenzene) molybdenum, 1-propane thiol, and diethyl disulfide sources. Film composition and growth rates on SiO_2 and c-plane Al_2O_3 were characterized for each compound as a function of precursor exposure time. Gas phase reaction chemistry and thermal stability of precursors were evaluated using FTIR spectroscopy. The full-width at half-maximum values for in-plane (E_{2g}^1) and out-of-plane (A_{1g}) Raman modes for MoS_2 were used as indicators of film quality. By relating film properties to gas-phase chemistry for various metal precursors, we will highlight precursor design and process conditions that lead to high quality CVD films.

12:00pm **2D+TF-WeM13 *In-situ* Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of hexagonal Boron Nitride Monolayers on Pd(111)***, **Pedro Arias**, A. Ebnonnasir, F. Fankhauser,* University of California at Los Angeles*; C. Ciobanu,* Colorado School of Mines*; S. Kodambaka,* University of California Los Angeles

Using *in-situ* ultra-high vacuum variable-temperature scanning tunneling microscopy (STM), we investigate the chemical vapor deposition kinetics of hexagonal boron nitride (hBN) monolayer growth on Pd(111) substrates as a function of substrate temperature, borazine flux, and deposition time. All of the experiments were carried out on sputter-deposited Pd(111)/Al_2O_3(0001) thin films. In each experiment, STM images were acquired while resistively heating the Pd(111) samples on the STM stage at temperatures between 300 K and 773 K and in the presence of borazine (10^{-7} ~ 10^{-6} Torr) for times between 60 s and 2500 s. We observe the nucleation and growth of chemisorbed (and presumably partially dissociated) borazine islands on the Pd surfaces. From the STM images, we measured the island density and size as a function of time, temperature, and borazine flux. We find that both the island density and size increase with increasing borazine flux and deposition time. We also find that borazine islands form on Pd(111) ‘up-steps.’ After achieving monolayer coverage of borazine, the samples are annealed in ultra-high vacuum at 1020 K for 60 seconds to form hBN monolayers. We then determined of the number density of rotational domains in the hBN layers, based upon which we identify the deposition parameters critical to the growth of single-domain hBN layers on Pd(111).

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