2D Materials Focus Topic
Room 201B - Session 2D+EM+MI+NS+TF-MoM

2D Materials Growth and Fabrication
Moderator: Jing Xia, University of California Irvine

8:20am 2D+EM+MI+NS+TF-MoM1 Wafer Scale Epitaxial Growth of Monolayer and Few-Layer WS₂ by Gas Source Chemical Vapor Deposition, *Mikhail Chubarov, T.H. Choudhury, J.M. Redwing,* The Pennsylvania State University

Tungsten disulfide (WS_2) has been widely investigated due to its outstanding properties compared to other 2D TMD including a bandgap of 2 eV, relatively high theoretical electron mobility, valley spin polarization, among others. Commonly, the films are grown on amorphous substrates like SiO_2 and, consequently, consist of high angle grain boundaries after coalescence due to the random orientation of domains. These can act as scattering and recombination centers for charge carriers limiting device performance. To avoid this, a crystalline substrate and epitaxial growth is typically employed for general thin film deposition although this approach has not been extensively investigated for 2D TMD monolayers. Large area growth is also crucial to show technological feasibility of the material for wafer-scale device fabrication.

In this work, we employ cold wall gas source chemical vapor deposition for the growth of WS_2 films on 2" (0001) α-Al_2O_3. To achieve coalesced monolayer growth over the entire substrate, we implemented a multi-step growth process modulating the metal precursor concentration during each of the steps. $W(CO)_6$ and H_2S were used as precursors in H_2 carrier gas. The deposition experiments were conducted over the temperature range from 750 °C to 1000 °C at a pressure of 50 Torr. Characterization of resulting samples was conducted using atomic force microscopy (AFM), in-plane X-ray diffraction (XRD) and room temperature Raman and photoluminescence (PL) measurements.

Initial studies showed that the WS_2 films exhibit multiple crystal orientations which evolve with growth temperature. At lower deposition temperature (750 °C), two orientations rotated 30° one from another were observed. At the high deposition temperature (1000 °C), five different crystal orientations were present. Among others, orientation with epitaxial relation of (10-10)WS_2//(10-10)α-Al_2O_3 was present at all temperatures. It was established that the unwanted orientations can be suppressed by increasing the H_2S concentration. Further adjustment of the growth and use of the multi-step growth process led to the formation of a coalesced epitaxial monolayer WS_2 on α-Al_2O_3 with XRD FWHM of 10-10 peak in ω being 0.09°. This value suggests well in-plane oriented domains with low edge dislocation density. A high intensity, narrow (FWHM=40 meV) PL peak positioned at 2.01 eV was observed for WS_2 films. Monolayer formation was confirmed from the AFM height profile (D =0.9 nm) and Raman measurements by observing spectral region where layer breathing and shear modes would appear. A fully coalesced, monolayer film was achieved using the multi-step growth process in a total time of 80 minutes.

8:40am 2D+EM+MI+NS+TF-MoM2 Wafer Scale Deposition of Monolayer Transition Metal Dichalcogenides, *Kortney Almeida, M. Wurch, G. Stecklein, L. Bartels,* University of California, Riverside

Monolayer transition metal dichalcogenide (TMD) films are promising materials in the continuing development of nanoscale devices. Methods to produce wafer-scale monolayer TMD films have included tube-furnace chemical vapor deposition (CVD), liquid-phase exfoliation, and metal-organic CVD. These methods suffer from issues with particulate contamination, pyrophoric precursors, and high cost. Here we demonstrate the growth of homogeneous wafer-scale monolayer molybdenum disulfide (MoS_2) using solid inorganic and liquid organic precursors in a high-vacuum environment. These results are achieved using an amorphous SiO_2 substrate and without any powder or metal-organic precursors. Growth proceeds by the decomposition of carbon disulfide at a hot molybdenum filament, which yields volatile MoS_x precursors that precipitate onto a heated wafer. The continuous and homogeneous single-layer film of MoS_2 is deposited at wafer scale with a total growth time of fifty minutes. Various thicknesses of the thin films are also demonstrated by the manipulation of the filament power. Optical and electrical characterization indicates performance comparable to or better than MoS_2 film grown by other wafer-scale growth techniques. Our method provides a scalable process to deposit thin TMD films in a high vacuum environment.

9:00am 2D+EM+MI+NS+TF-MoM3 Crystal Growth of 2D Materials: From Model Systems to Integrated Manufacturing, *Stephan Hofmann,* University of Cambridge, UK **INVITED**

In order to serve the industrial demand for "electronic-grade" 2D materials, we focus on chemical vapour deposition (CVD), and in this talk I will review our recent progress in scalable CVD [1] and device integration approaches of highly crystalline graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenide films. The systematic use of in-situ metrology, ranging from high-pressure XPS to environmental electron microscopy, allows us to reveal some of the key growth mechanisms for these 2D materials that dictate crystal phase, micro-structure, defects, and heterogeneous integration control at industrially relevant conditions [2,3]. I will focus on tailored CVD processes to achieve large monolayer h-BN domains with lateral sizes exceeding 0.5 mm. Importantly we show that depending on the process catalyst as-grown h-BN mono-layers can be easily and cleanly transferred using an entirely exfoliation-based approach.[4] We demonstrate sequential h-BN pick-up, opening a pathway to integrate CVD films in high quality 2D material heterostructures. Progress in growth reached a level where adequate characterisation of such 2D crystal layers over large areas has become a key challenge. Hence we also explore new non-contact characterisation methods [5,6]. We work on applications ranging from magentic tunnel junctions [7] to sensing and single molecule analysis [8,9], and the talk will focus on some of the diverse yet connected integration challenges for CVD 2D films that present a key bottleneck towards reliable scale-up manufacturing and commercialisation.

References

1. Hofmann et al., J. Phys. Chem. Lett. 6, 2714 (2015).

2. Weatherup et al., Nano Lett. 16, 6196 (2016).

3. Caneva et al. Nano Lett. 16, 1250 (2016).

4. Wang et al., in progress (2018).

5. Lin et al., Sci. Rep. 7, 10625 (2017).

6. Feng et al., Nano Lett. 18, 1739 (2018).

7. Piquemal-Banci et al., ACS Nano (2018).

8. Dahmke et al., ACS Nano 11, 11108 (2017).

9. Walker et al., ACS Nano 11, 1340 (2017).

9:40am 2D+EM+MI+NS+TF-MoM5 Understanding the Edge-Controlled Growth and Etching in Two-Dimensional Materials, *Kai Xiao, X. Li, X. Sang,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *W. Zhao, J. Dong,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; *A. Purektzy,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *C. Rouleau,* Center for Functional Nanomaterials Brookhaven National Laboratory; *F. Ding,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan,44919, South Korea; *R.R. Unocic, D.B. Geohegan,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Understanding the atomistic mechanisms governing the growth and etching of two-dimensional (2D) materials is of great importance in guiding the synthesis of large area, single-crystalline, high quality 2D crystals and heterostructures. In this talk, the growth-etching-regrowth process of monolayer 2D crystals by a CVD method will be discussed. We found that switching from growth to etching formed pores with various shapes in the single crystal domains which can be explained by edge-structure dependent growth process. In addition, combined with first principles theory, and ab initio simulations, in situ STEM imaging was used to understand the evolution of edge structure around pores in monolayers as a function of temperature and Mo chemical potential. Our results demonstrate that by varying the local chemical environment, we can trigger formation of 2D monolayer nanostructures terminated by different edge reconstructions during in situ heating and electron beam irradiation and form edge structures with metallic and/or magnetic properties. The ability to synthesize 2D nanostructures with metastable NW edges having predictable atomic structures opens the door to a wide range of novel 2D materials and heterosturctures with electrical and magnetic properties as revealed by DFT, which could potentially act as functional building blocks for next-generation nano-devices.

References:

[1] X. Li, J. Dong, J. C. Idrobo, A. A. Puretzky, C. M. Rouleau, D. B. Geohegan, F. Ding, K. Xiao, J. Am. Chem. Soc. 139, 482 (2017).

[2] X. Sang, X. Li, W. Zhao, J. Dong, C. M. Rouleau, D. B. Geohegan, F. Ding, K. Xiao, R. R. Unocic, Nature Comm. Accepted (2018).

10:00am **2D+EM+MI+NS+TF-MoM6 Synthesis and Characterization of 1T, 1T', and 2H MoTe$_2$ Thin Films**, *Thomas Empante,* University of California, Riverside; *Y. Zhou,* Stanford University; *S.A. Naghibi Alvillar,* El Camino College; *E.J. Reed,* Stanford University; *L. Bartels,* University of California, Riverside

Transition metal dichalcogenides (TMDs) have been of interest over the past few decades for their intriguing structural, electronic, and optoelectronic properties, particularly when scaled down to thin films. One of the most interesting TMD materials is molybdenum ditelluride (MoTe$_2$) because of its relative ease to attain multiple phases at room temperature, namely the metallic 1T' phase and the semiconducting 2H phase. Here we show a facile chemical vapor deposition process to synthesis not only the aforementioned phases but the elusive unreconstructed 1T phase by regulating the cooling rate and the addition of carbon dioxide during the reaction. Our experimental Raman spectroscopy results were compared to theoretical density functional theory calculations which verify the synthesis of all three phases. Electronic transport measurements were also used to characterize the films and show that the newly synthesized 1T phase is in good agreement with theoretical models depicting semi-metallicity as the material shows increased conductivity with elevated temperatures. In addition to the pure phase materials, mixed phase materials, such as 2H/1T, can be synthesized with slight alterations to the parameters leading to enhancements of the 2H phases' conductivity.

11:20am **2D+EM+MI+NS+TF-MoM10 Low-Defect, High-Uniformity Transfer-Free Graphene on SiO$_2$ by Thermal Chemical Vapor Deposition**, *Leslie Chan, D.S. Tsai, Z. Wang, C. Carraro, R. Maboudian,* University of California, Berkeley

Chemical vapor deposition (CVD) has emerged as the customary approach for scalable, controllable production of graphene for integrated devices. Standard CVD graphene must be transferred from a generic metal growth substrate onto the desired substrate (*e.g.*, SiO$_2$), but this extra transfer often leads to wrinkles, contamination, and breakage that ultimately result in poor device performance. Several groups have demonstrated metal-catalyzed direct CVD-graphene growth on insulating substrates, but the final graphene products are deficient in quality and uniformity. This work details an expansion of the parameter space that enables lower-defect, higher-uniformity graphene than previously reported using nickel and copper catalysts, respectively. We introduce a mechanism based on carbon permeability that provides deeper insight into the growth process. Ultimately, these studies seek to inform the judicious choice of process parameters that will lead to large-area, high-quality, layer-controlled graphene directly on target substrates.

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