

# Tuesday Afternoon, November 7, 2023

## 2D Materials Technical Group

### Room C123 - Session 2D+TF-TuA

#### 2D-Materials: Synthesis

**Moderators:** David Johnson, University of Oregon, Peter Liljeroth, Aalto University

#### 2:20pm 2D+TF-TuA-1 High-Order Van Der Waals Superlattices and Artificial Quantum Solid Beyond Mechanical Exfoliation and Restacking, *Xiangfeng Duan*, UCLA **INVITED**

The advent of two-dimensional atomic crystals (2DACs) and van der Waals heterostructures (vdWHs) has inspired a new thinking on heterostructure construction beyond the limits of lattice matching requirement. However, the vdWHs explored to date have been largely limited to relatively simple systems with a small number of building blocks. The preparation of high-order vdW superlattices with a larger number of alternating units is exponentially more challenging due to the limited yield and scalability of the commonly used exfoliation-and-restacking strategy. Here I will discuss strategies to create high-order vdW superlattices (vdWSLs). First, by exploiting a capillary-force-driven rolling-up process, we show a series of synthetic VDWHs can be transformed into high-order vdWSLs with alternating atomic layers of widely variable material compositions, electronic band offset dimensions, chirality and topology. Alternatively, we further discuss a molecular intercalation approach to prepare a new family of hybrid superlattices consisting of alternating layers of covalently bonded 2D atomic layers and self-assembled molecular layers, which opens the door to exploit highly versatile molecular design strategies to tailor solid-state materials, enabling artificial materials with designable structural motifs and tunable electronic properties beyond the reach of conventional crystalline solids. We will particularly highlight a recent example of a new class of chiral molecular intercalation superlattices with robust chiral-induced spin selectivity. The formation of high-order vdW superlattices defines a rich artificial materials platform to unlock previously inaccessible physical limits and enable new device concepts beyond the reach of the existing materials.

#### 3:00pm 2D+TF-TuA-3 Understanding the Sequential Growth of Bilayer MoS<sub>2</sub> on SiO<sub>2</sub> Substrate by Mo Isotope Labeling, *Kai Xiao*, Center for Nanophase and Materials Sciences Oak Ridge National Laboratory; *Y. Yu*, School of Physics and Technology, Wuhan University, China; *J. Hachtel*, Center for Nanophase and Materials Sciences Oak Ridge National Laboratory; *M. Yoon*, Material Science and Technology Division, Oak Ridge National Laboratory; *A. Puzetzyk*, *A. Ievlev*, *C. Rouleau*, *D. Geohagan*, Center for Nanophase and Materials Sciences Oak Ridge National Laboratory

Bilayer 2D materials and heterostructures with different stacking configurations have attracted interest due to their emerging optical and quantum properties. Usually, it can be synthesized by the two-step chemical vapor deposition (CVD) method. Here we utilized isotope labeling method to study the CVD growth of bilayer MoS<sub>2</sub> on SiO<sub>2</sub>/Si substrates. The stacking configuration and growth sequence were characterized by Raman spectroscopy, time-of-flight second ion mass spectroscopy (ToF-SIMS), and scanning transmission electron microscopy (STEM). We found that the growth of bilayer MoS<sub>2</sub> follows a sequential growth process which the second growth layer of MoS<sub>2</sub> goes underneath the first growth layer. The AB and AA stacked bilayer MoS<sub>2</sub> are formed by templating the first growth single crystal MoS<sub>2</sub> layers. The embedded antiphase grain boundaries were characterized by atomic-resolution z-contrast STEM. Density functional theory (DFT) with molecular dynamic (MD) simulation were performed to understand the sequence growth pathway of bilayer MoS<sub>2</sub>. This new understanding of the growth mechanism for bilayer MoS<sub>2</sub> can provide a new strategy for synthesis of 2D materials with controllable layer numbers and stackings.

Synthesis science was supported by the U.S. Dept. of Energy, Office of Science, Materials Science and Engineering Division. This work was performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

#### 4:20pm 2D+TF-TuA-7 The Transformation from Dendritic to Triangular WS<sub>2</sub> Growth via NaCl-Assisted Low-Pressure Chemical Vapor Deposition, *Himal Pokhrel*, *J. Duncan*, *S. Pollard*, The University of Memphis

Monolayer tungsten disulfide (WS<sub>2</sub>) is one of the promising two-dimensional materials in the transition metal dichalcogenide family due to its remarkable optical, electronic, and electrocatalytic behavior. However, the structure of this material varies significantly with growth conditions. In this work, we use the salt-assisted low-pressure chemical vapor deposition

(LPCVD) method to grow monolayer WS<sub>2</sub> crystals reaching over 50 μm in size on the SiO<sub>2</sub>/Si substrates. We observe a transition from large, dendritic to triangular growth by systematically varying the amount of promoter material (NaCl), growth temperature, and source-substrate distance. The synthesized material is characterized by Raman spectroscopy, scanning electron microscopy, and X-ray photoemission spectroscopy in order to understand the role of each parameter during the growth process. The results of this work provide a framework for the synthesis of large-area WS<sub>2</sub> growth with variable morphology through salt-assisted LP-CVD.

Key words: Chemical vapor deposition, dendrites, WS<sub>2</sub>

#### 4:40pm 2D+TF-TuA-8 Hybrid Pulsed Laser Deposition Growth of Layered Chalcogenides, *Mythili Surendran*, *H. Chen*, *J. Ravichandran*, University of Southern California

Mythili Surendran<sup>1</sup>, Huandong Chen<sup>1</sup>, Shantanu Singh<sup>1</sup>, Boyang Zhao<sup>1</sup> and Jayakanth Ravichandran<sup>1</sup>

1. Mork Family Department of Chemical Engineering and Materials Science, University of Southern California

Chalcogenides, especially layered transition metal dichalcogenides, have emerged as an exciting class of materials that host several novel physical phenomena suitable for a broad range of electronic and photonic applications. High-quality thin film growth of these chalcogenides is critical to enable investigations into their fundamental properties and also for device applications. The thin films of layered chalcogenides are mostly grown using chemical vapor deposition, although molecular beam epitaxy, metal-organic vapor deposition, pulsed laser deposition (PLD) and several other techniques have been exploited. However, large area and high-quality growth with precise and uniform thickness control and low defect densities still remain a challenge due to a large cation-chalcogen vapor pressure mismatch, corrosive and reactive nature of most chalcogen precursors, high synthesis temperatures and the propensity to oxidize easily in the presence of oxygen at these high temperatures. In case of metal disulfides, most growth techniques utilize H<sub>2</sub>S as the sulfur source. However, H<sub>2</sub>S is a toxic, hazardous, and flammable gas and require high temperatures for efficient decomposition and sulfurization, resulting in high defect densities.

Here, we report an alternative hybrid PLD approach wherein we employed organo-sulfur precursors as sulfur source to grow chalcogenide thin films. This novel method enables low temperature growth (~500°C) of chalcogenides as the precursors decompose at a lower temperature (~250-400°C) to provide dissociated sulfur species. To demonstrate the efficacy of this approach, we have demonstrated large area epitaxial growth of Group IV 2D chalcogenides such as TiS<sub>2</sub> (metallic), ZrS<sub>2</sub> and HfS<sub>2</sub> (semiconducting). Structural and electrical characterization, along with low temperature transport studies reveal low defect densities and high carrier mobilities in these thin films. These results emphasize the importance of development of low temperature growth techniques for high mobility refractory metal-based chalcogenides for electronic applications, especially with back-end-of-line (BEOL) compatibility. The potential of these chalcogenides as suitable candidates for transparent and conducting layers in chalcogenide-based optoelectronic devices will be discussed. Further, we will also briefly discuss about the epitaxial growth of a variety of other chalcogenides such as 3D metal chalcogenides, chalcogenide perovskites, thus establishing the versatility of this novel method to grow chalcogenides for next-generation electronics and photonics.

#### 5:00pm 2D+TF-TuA-9 Effect of Several Growth Parameters on Graphene Growth on Four Types of Supported Cu Films Using Cold Wall Cvd and Perspective on Growth Mechanism of Graphene from Scaling Functions of Graphene Island Size Distribution, *Shantanu Das*, Intel Corporation

Graphene growth was explored on solid electrodeposited, recrystallized, sputter deposited and liquid Cu films supported on W or Mo refractory substrates under ambient pressure using Ar, H<sub>2</sub> and CH<sub>4</sub> mixtures using a custom-automated LabVIEW controlled graphene growth method in a custom-modified multi-chamber UHV chamber transformed into a cold wall CVD system. Among these films, electrodeposited Cu film was chosen to study the effect of total flow rate, CH<sub>4</sub>:H<sub>2</sub> ratio and dilution of the CH<sub>4</sub>/H<sub>2</sub> mixture by Ar at a fixed substrate temperature of 1000 °C and total pressure of 700 Torr, on the nucleation density and average size of graphene crystallites. The resulting morphological changes correspond with those that would be expected if the precursor deposition rate was varied at a fixed substrate temperature for physical deposition using thermal evaporation. The evolution of graphene crystallite boundary morphology

# Tuesday Afternoon, November 7, 2023

with decreasing effective C deposition rate indicates the role of edge diffusion of C atoms along the crystallite boundaries, in addition to H<sub>2</sub> etching on graphene crystallite shape. The results indicate that graphene grown on Cu films using cold wall CVD follows a classical two-dimensional nucleation and growth mechanism. Following nucleation at the earliest growth stages, isolated crystallites grow, impinge and coalesce to form a continuous layer. During the pre-coalescence growth regime, the size distributions of graphene crystallites exhibit scaling which is a function of island area, graphene coverage, average island area and areal density. For graphene grown on Cu surfaces that have been annealed in a reducing Ar+H<sub>2</sub> ambient, excellent data collapse onto a monotonically decreasing universal Avrami scaling function is observed irrespective of graphene coverage, surface roughness or Cu grain size. This result is interpreted to indicate attachment limited growth and desorption of C-containing species. Graphene grown on Cu surfaces that were annealed in a nonreducing environment exhibits a qualitatively different bimodal scaling function indicating diffusion-limited growth with a lower attachment barrier combined with C detachment from the graphene edges. Graphene growth on molten Cu films supported on custom-designed Mo substrates demonstrate a similar 2D nucleation and growth mechanism. The roles of temperature gradient, chamber pressure and rapid thermal heating in C precursor-rich environment on graphene growth morphology on thin sputtered Cu films are explained. I anticipate that applying the study of pre-coalescence size distribution method to other 2D material systems may be useful for elucidating atomistic mechanisms of film growth that are otherwise difficult to obtain.

5:20pm **2D+TF-TuA-10 Decoupling of Graphene from Metal Substrate via Interface Epitaxy**, *Abdullah Al-Mahboob, J. Sadowski*, Center for Functional Nanomaterials, Brookhaven National Laboratory

The research on two-dimensional quantum materials (2DQM) received significant attention in both, theoretical and experimental physics. Among 2DQM systems, graphene (Gr) remains a material of special interest since its discovery three decades ago. The interest in 2DQM research further evolved beyond Gr and its analogs (called Xenex) as these materials have potential for technological applications including quantum computing and quantum information.

The interest on Gr originated not only from well-known Gr stability in ambient conditions, massless Dirac carrier characteristics and feasibility of roll-to-roll production, but also successful use of Gr as a template for other 2DQMs. Despite the interest in Xenex other than Gr, such as silicene, antimonene, borophene, these materials are generally unstable at ambient conditions. In order to protect reactive Xenex and stabilizing their structure, Gr can also be used as a protective inert coating. In the present study we explored a method of interfacial 2D growth under the inert overlayer, graphene.

We employed in-situ real-time low-energy electron/photoemission electron microscopy (LEEM/PEEM), micro-beam LEED, XPS/UPS and micro-spot ARPES for the study of interface chemistry of silicon allotropes and 2D silica structures grown at the Gr/Ru interface.

In this report, we show how the Si interface epitaxy can decouple Gr electronically from the catalyst Ru substrate, and a successful scalable synthesis of Gr/V<sub>3</sub>-Silicene and Gr/Si/SiO<sub>2</sub> heterostructures can be realized. Tuning the growth conditions also provided means to control the growth of 2DQM at large scale. The strategy of interface epitaxy could be more general and opens the avenue of growing and stabilizing other atomically thin 2D materials.

Research was carried out at the Center for Functional Nanomaterials and the National Synchrotron Light Source II at Brookhaven National Laboratory under Contract No. DE-SC0012704.

5:40pm **2D+TF-TuA-11 Wafer-Scale, Phase-Selective Growth of Two-Dimensional Indium Selenides by Metal-Organic Chemical Vapor Deposition**, *Seunguk Song, S. Jeon, M. Rahaman, J. Lynch, D. Rhee, P. Kumar, S. Chakravarthi, G. Kim, X. Du*, University of Pennsylvania; *E. Blanton*, KBR Inc.; *K. Kisslinger*, Brookhaven National Laboratory; *M. Snure*, Air Force Research Laboratory, Sensors Directorate; *N. Glavin*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *E. Stach, R. Olsson III, D. Jariwala*, University of Pennsylvania

The two-dimensional (2D) indium selenides (InSe and In<sub>2</sub>Se<sub>3</sub>) have garnered attention as a highly desirable ultrathin III-VI semiconductor, possessing favorable qualities akin to III-V semiconductors and 2D van der Waals transition metal dichalcogenides. However, due to the complexity of the In-Se system and challenges related to promoting lateral growth, large-area, *Tuesday Afternoon, November 7, 2023*

phase-selective synthesis of 2D InSe and In<sub>2</sub>Se<sub>3</sub> has proved difficult. Here, our work presents a successful method for the growth of high-quality and thickness-controlled 2D InSe and In<sub>2</sub>Se<sub>3</sub> thin films using vertical, cold-walled metal-organic chemical vapor deposition. By interrupting the Se source periodically, we create an environment deficient in Se that favors the nucleation of InSe over In<sub>2</sub>Se<sub>3</sub>. Additionally, pulsing the Se precursor promotes lateral growth of InSe at low temperatures (360-500 °C), allowing us to produce highly stoichiometric, crystalline thin films on 2-inch sapphire substrates. Importantly, these growth temperatures are compatible with back-end-of-line integration in Si microelectronics. The resulting 2D domains are oriented along the crystal structure of the substrate, and the thickness can be controlled by growth time. We also demonstrate the fabrication of few-layer InSe transistors with high on-to-off current ratios (~10<sup>4</sup>-10<sup>5</sup>) and field-effect mobility (~2.8 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) comparable to that of mechanically exfoliated single crystals of InSe. In the case of a few-layer In<sub>2</sub>Se<sub>3</sub>, its inherent ferroelectric nature allows us to evaluate its potential as a ferroelectric semiconductor field-effect transistor with non-volatile memory. Our work offers a promising approach for creating phase-pure 2D InSe and In<sub>2</sub>Se<sub>3</sub> films at the wafer scale, which can be adapted for other material systems with multiple polymorphs.

## Author Index

**Bold page numbers indicate presenter**

— A —

Al-Mahboob, A.: 2D+TF-TuA-10, **2**

— B —

Blanton, E.: 2D+TF-TuA-11, **2**

— C —

Chakravarthi, S.: 2D+TF-TuA-11, **2**

Chen, H.: 2D+TF-TuA-8, **1**

— D —

Das, S.: 2D+TF-TuA-9, **1**

Du, X.: 2D+TF-TuA-11, **2**

Duan, X.: 2D+TF-TuA-1, **1**

Duncan, J.: 2D+TF-TuA-7, **1**

— G —

Geohegan, D.: 2D+TF-TuA-3, **1**

Glavin, N.: 2D+TF-TuA-11, **2**

— H —

Hachtel, J.: 2D+TF-TuA-3, **1**

— I —

Ievlev, A.: 2D+TF-TuA-3, **1**

— J —

Jariwala, D.: 2D+TF-TuA-11, **2**

Jeon, S.: 2D+TF-TuA-11, **2**

— K —

Kim, G.: 2D+TF-TuA-11, **2**

Kisslinger, K.: 2D+TF-TuA-11, **2**

Kumar, P.: 2D+TF-TuA-11, **2**

— L —

Lynch, J.: 2D+TF-TuA-11, **2**

— O —

Olsson III, R.: 2D+TF-TuA-11, **2**

— P —

Pokhrel, H.: 2D+TF-TuA-7, **1**

Pollard, S.: 2D+TF-TuA-7, **1**

Puretzky, A.: 2D+TF-TuA-3, **1**

— R —

Rahaman, M.: 2D+TF-TuA-11, **2**

Ravichandran, J.: 2D+TF-TuA-8, **1**

Rhee, D.: 2D+TF-TuA-11, **2**

Rouleau, C.: 2D+TF-TuA-3, **1**

— S —

Sadowski, J.: 2D+TF-TuA-10, **2**

Snure, M.: 2D+TF-TuA-11, **2**

Song, S.: 2D+TF-TuA-11, **2**

Stach, E.: 2D+TF-TuA-11, **2**

Surendran, M.: 2D+TF-TuA-8, **1**

— X —

Xiao, K.: 2D+TF-TuA-3, **1**

— Y —

Yoon, M.: 2D+TF-TuA-3, **1**

Yu, Y.: 2D+TF-TuA-3, **1**