PCSI
Room Ballroom South - Session PCSI-3TuM
2D Materials and Heterostructure Growth

Moderator: Susanne Stemmer, University of California, Santa Barbara

11:00am **PCSI-3TuM-31 Chemically and Atomically Ordered States in 2D Crystal Alloys**, ***Nasim Alem,*** Penn State University **INVITED**

Alloying and doping are considered versatile strategies for tuning charge and heat transport in nanostructures. Whether the resulting alloy structure is random or ordered can have a profound impact on the macroscale electronic, optoelectronic, vibrational, and transport properties of the material. In this talk, we present structural and chemical ordering[1, 2] as a mechanism to design anisotropy in the family of 2D transition metal dichalcogenides (TMDs) alloys (Fig. 1). Leveraging recent advancements in atomic resolution scanning/transmission electron microscopy (S/TEM) imaging and spectroscopy, we show the formation of chemically ordered states and vacancy/dopant coupling that leads to unusual relaxation effects around dopant-vacancy complexes leading to local strain and symmetry breaking around individual dopant sites. In addition, we will further uncover the defect structure, i.e. grain boundaries and anti-phase boundaries, and their stability and dynamics in monolayer TMD crystals and their alloys. This understanding can have a strong impact on the synthesis and functionality of novel nanostructure alloys and provides the key to properly design devices for heat dissipation applications, energy storage, electronics, optoelectronics, and thermoelectrics.

1. Azizi, A.; Wang, Y.; Stone, G.; Elias, A. L.; Lin, Z.; Terrones, M.; Crespi, V. H.; Alem, N. Defect Coupling and Sub-Angstrom Structural Distortions in W1–xMoxS2 Monolayers. Nano Lett 2017, 17, 2802-2808.

2. Azizi, A.; Wang, Y. X.; Lin, Z.; Wang, K.; Elias, A. L.; Terrones, M.; Crespi, V. H.; Alem, N. Spontaneous Formation of Atomically Thin Stripes in Transition Metal Dichalcogenide Monolayers. Nano Lett 2016, 16, 6982-6987.

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11:30am **PCSI-3TuM-37 Defect-Assisted Heteroepitaxial Growth of Monolayer Tungsten Diselenide Films with Preferential Orientation on Hexagonal Boron Nitride**, ***Xiaotian Zhang,*** *F Zhang, Y Wang, D Schulman, T Zhang, A Bansal, N Alem, S Das, V Crespi, M Terrones, J Redwing,* The Pennsylvania State University

The rapid development of device technologies based on 2D transition metal dichalcogenides (TMDs) causes increasing demand for synthesis of high quality large area monolayer and few layer films. Our previous work demonstrated epitaxial growth of large area monolayer WSe_2 films on c-plane sapphire using gas source chemical vapor deposition (CVD). However, the optical and electrical properties of coalesced monolayer films grown on sapphire are negatively impacted by the existence of anti-phase boundaries (APBs) as well as non-uniformities arising from steps and charge-induced doping associated with the sapphire surface. Prior studies demonstrated a preferred domain orientation for TMDs grown on hBN and first-principle calculations suggest this phenomenon originates from single atom vacancies on the hBN surface that act as nucleation sites. In this study, we further investigate the mechanism of defect-assisted domain alignment of 2D TMDs on hBN and demonstrate the growth of fully-coalesced WSe_2 films on hBN with a reduced density of APBs and improved optical and electrical properties compared to films grown on sapphire.

Wse_2 monolayer films were grown by gas source CVD at 800°C using $W(CO)_6$ and H_2Se in a H_2 carrier gas employing a multi-step process to separately control nucleation density and lateral growth and coalescence of domains. Single crystal hBN flakes exfoliated from bulk crystals and transferred onto c-plane sapphire were used as substrates. He plasma treatment and NH_3 annealing were used to modify the surface defect density of hBN. Detailed studies of Wse_2 deposition on hBN as a function of growth conditions and substrate pre-treatment confirm that domain nucleation is controlled by the surface defect density rather than the precursor concentration. Over 90% of Wse_2 domains have consistent orientation via the defect-assisted growth. Through careful control of nucleation and extended lateral growth time, fully coalesced Wse_2 monolayer films on hBN were produced for subsequent characterization. High resolution scanning transmission electron microscopy (S/TEM) analysis demonstrates the absence of APBs in coalesced regions formed by the merging of 0° oriented domains. Temperature-dependent photoluminescence measurements show sharp and enhanced exciton and trion emission peaks, with no defect-related bound exciton emission from monolayer Wse_2/hBN down to 80K. Backgated FET devices fabricated on Wse_2/hBN films transferred to SiO_2/Si substrates show an order of magnitude increase in room temperature carrier mobility (~5 cm^2/V-s) compared to similar devices fabricated using monolayer Wse_2 films transferred from sapphire.

11:35am **PCSI-3TuM-38 Novel Sulfide Heterostructures from Designed Precursors**, *D Roberts,* University of Colorado at Boulder; ***Sage Bauers,*** *J Perkins,* National Renewable Energy Laboratory; *C Stoldt,* University of Colorado at Boulder; *A Zakutayev,* National Renewable Energy Laboratory

Composite 2D material systems present not only unique structural and electrical phenomenon but can be intentionally designed to elicit properties desirable for a specific application. Existing reports of chalcogenide heterostructures have shown the ways in which varying thicknesses of constituent layers from monolayer to bulk-like affects the resistivity, [1] transport properties, [2] and overarching band structure [3] of such systems. To date, systems in this vein are limited to selenides and tellurides. Extension to sulfide systems is important to harness properties of emerging 2D materials such as MoS_2 and WS_2

In this work we demonstrate the synthesis of multilayer sulfide heterostructures crystallized from amorphous precursors viasputter deposition. We utilize a combinatorial approach to depositions in order to reduce time and specificity needed in calibrating the time needed to deposit constituent components of such structures. A schematic of this setup can be seen in Fig. 1. Here we will focus on spatially resolved structural characterization of these combinatorial samples with respect to changes in long range ordering indicative of improved crystallinity. Additionally, we investigate the role of off-stoichiometry in as-deposited precursors on the structure and quality of our crystalline end product. Challenges inherent in sulfur-based depositions are also addressed.

11:40am **PCSI-3TuM-39 Rotational Alignment of Epitaxially-grown hBN on Macrostepped Graphene/SiC(0001) Single-Crystal Substrates**, ***Daniel Pennachio,*** University of California, Santa Barbara; *C Ornelas-Skarin,* University of California, Irvine; *N Wilson, E Young, A McFadden, T Brown-Heft,* University of California, Santa Barbara; *K Daniels, R Myers-Ward, K Gaskill, C Eddy, Jr.,* U.S. Naval Research Laboratory; *C Palmstrom,* University of California, Santa Barbara

Many of the intriguing properties of 2D devices rely on the relative rotational alignment between layers. For instance in the graphene/hBN system, band structure modulation can occur at specific alignments [1], but a misalignment may be beneficial if innate graphene properties are to be examined. To allow for scalable graphene/hBN heterostructure formation, this work investigates hBN growth on single-crystal epitaxial graphene (EG) on macrostepped SiC(0001) substrates. The presented results suggest these macrosteps may influence the hBN epitaxial relation such that a metastable, 30° in-plane hBN/EG alignment is more favorable with certain growth conditions than the direct 0° alignment between hBN/graphene, despite their similar crystal structures.

Plasma-enhanced chemical beam epitaxy (PE-CBE), an ultra-high vacuum (UHV) compatible process, was utilized to provide a clean environment for examination of the hBN structural, electrical, and chemical properties via *in-situ* and *in-vacuo* characterization methods. To determine the effect of substrate macrostep morphology, EG on SiC (0001) substrates with no offcut and with a 4° offcut toward $<11\text{-}20>_{SiC}$ were tested. The alignment of the hBN/EG/SiC(0001) heterostructure was studied by relating *in situ* electron diffraction to nuclei edge directions. In addition, cross-sectional transmission electron microscopy (TEM) confirmed registry of the hBN to the EG/SiC substrate, while plan-view TEM showed in-plane alignment and uniformity. The macrostep-directed epitaxy of hBN on EG highlighted in this work highlights the possibility of various rotational alignment during van der Waals epitaxy, a promising feature for direct growth of 2D heterostructures.

[1] M. Yankowitz, *et al.*, Nat. Phys. **8**, 382 (2012).

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