## Novel Materials
## Room Swan BC - Session NM-MoA2

### Chalcogenides
**Moderator: Maria Tamargo**, City College of New York

3:30pm **NM-MoA2-9 Growth of Ultrathin $PtSe_2$ using Molecular Beam Epitaxy**, ***Maria Hilse***, *K. Wang,* The Pennsylvania State University; *R. Engel-Herbert,* Paul-Drude-Institut für Festkörperelektronik, Germany

$PtSe_2$ was recently proposed as promising material for low-power, high-performance, and ultra-thin-body electronic application because of its sizeable band gap up to 1.2 eV, high carrier mobility in the order of 1,000 $cm^2$/Vs, stability in air, and possibility of low-temperature fabrication compatible with CMOS back-end-of-line (BEOL) processing. First experimental values of its high carrier mobility of 210 $cm^2$/Vs, that outperforms other 2-dimensional materials such as black phosphorus, $MoS_2$ and $WSe_2$, demonstrate the great potential of optimizing the deposition process in order to grow high-quality $PtSe_2$ material. This work employed molecular beam epitaxy (MBE) to take advantage of its excellent in-situ control and monitoring capabilities to shine light on the kinetic processes involved and to optimize material properties, a strategy that is proven to produce high-quality and large size layers of various transition metal chalcogenides.

In a first growth approach, we optimized deposition parameters for 3-layer (L), and 3-nm thick Pt layers on c-plane $Al_2O_3$, which we subsequently exposed to a Se flux at medium temperatures to drive a selenization conversion of the Pt film into $PtSe_2$. A detailed investigation of reflection high-energy electron diffraction (RHEED) and Raman spectroscopy revealed that the thickness of the so formed $PtSe_2$ is limited to the mono/few-layer regime regardless of the selenization temperature and the Se flux exposure time. Even for the very thin 3-L thick Pt film, the $PtSe_2$ transformation rate was smaller than 100 %. We conclude that the reason for the observed self-limited selenization process in the MBE environment is the compared to other physical vapor deposition techniques extremely small Se flux accessible within MBE.

In a second growth approach, we deposited Pt and Se simultaneously with the goal to form $PtSe_2$ directly from the gas phase on the $Al_2O_3$ substrate surface. This approach proved unlimited in the film thickness and enabled crystalline $PtSe_2$ formation with a close to ideal wetting behavior, and nucleation starting at the atomic $Al_2O_3$ step edges at 200 °C to 300 °C growth temperature with an optimal Se overpressure of 10 to 15 times the Pt flux judged by atomic force microscopy, RHEED, X-ray diffraction, and Raman investigation. A $PtSe_2$ film conversion from a three- to a two-dimensional layered microstructure alongside with a significant enhancement of the crystallinity of the material was however observed only after a post-growth annealing process in Se atmosphere confirmed by Raman and transmission electron microscopy investigation.

3:45pm **NM-MoA2-10 Ultra-thin $Bi_2Se_3$ Films Grown by Molecular Beam Epitaxy**, ***Saadia Nasir***, *S. Law,* University of Delaware

$Bi_2Se_3$ (BS) is a widely studied 3D topological insulator material which has potential applications in optics, electronics, and spintronics. Below the critical thickness of approximately 6 nm, the bandgap opens and BS transitions into the trivial insulator. Investigation of different optical or electronic phenomenon around the critical thickness can provide us with some interesting information that can be useful for device applications. Growing continuous ultra-thin BS films with a thickness of few nanometers and good morphology is challenging. To obtain good-quality ultra-thin films, we tried growing BS films using a variety of different growth recipes and conditions on sapphire (0001) substrates using a Veeco GENxplor MBE system. We started with the two-step method in which after growing a few nanometers of the film, the rest of the sample is grown at a comparatively higher temperature. Growing directly on un-treated sapphire substrates using a two-step growth method resulted in a fragmented non-coalesced film, and we did not observe the usual triangular domain morphology. We next tried a substrate pre-treatment recipe in which we grew 5nm of BS then heated the substrate to 470°C and kept it there for 30 minutes to thermally decompose the film. Decomposition was confirmed by the reflection high energy electron diffraction pattern that showed only the sapphire Kikuchi lines. We then tried the direct growth and the two-step growth on the pre-treated sapphire substrates using different growth rates and substrate temperatures. The samples grown on sapphire after treatment showed better substrate coverage indicating improvement in domain coalescence. We also explored the effects of substrate temperature and growth rate on the films grown on pre-treated substrates. We observed that for direct growth, higher growth rates resulted in films with an improved RMS surface roughness (SR), whereas for two-step growth the SR stayed comparable for different growth rates. For higher growth temperatures, the bismuth and selenium ions do not wet the substrate well,resulting in a film morphology comprising non-coalesced columns. Decreasing the substrate temperature suppressed the columnar growth which drastically improved the SR for both growth recipes. We also observed that the two-step growth on the pre-treated substrate resulted in the typical triangular domain morphology. Improvement of the SR and the film morphology with higher growth rates and lower substrate temperatures contrasts with what we usually see for the epitaxial growths. Overall, the flatter ultra-thin films with lower surface roughness makes them reliable for thickness-dependent studies.

4:00pm **NM-MoA2-11 Molecular Beam Epitaxy Growth of Site-determined Wavelength-tunable Quantum Emitters in Atomically-thin Semiconductors**, ***Mingyu Yu***, *S. Law,* University of Delaware

Two-dimensional (2D) van der Waals (vdW) materials have emerged as a promising platform to develop quantum photonics technology, where site-controlled localized quantum emitters (QEs) can be created at a wafer-scale. The weak interlayer vdW interaction along the c-axis allows various materials to be stacked together or transferred to different substrates. The strain-induced QEs on vdW materials have the advantage of long coherence time and position-controllability. $Ga_2Se_2$ is an advanced vdW material with exceptional bandgap tunability and favorable synthesis conditions. We aim to obtain an atomically-thin $Ga_2Se_2$ film to create strain-localized QEs.

A QEs system based on 2D vdW materials is a highly anticipated but immature technology because most existing fabrication methods for 2D material devices are hard to employ at the wafer-scale. We use molecular beam epitaxy in a Veeco GENxplor system to obtain extremely-high sample quality at the wafer scale. The first challenge is to obtain a flat, single-orientation $Ga_2Se_2$ monolayer (ML) with minimal twin boundaries. The Se overpressure, growth rate, and growth temperature are critical factors affecting the film quality.

To date, we have optimized the growth window for bulk $Ga_2Se_2$ film (30 nm thickness). The sample scan shows a root mean square roughness as low as 1.83 nm with a (002)-oriented crystal structure (Fig.S1). The growth rate is found to significantly affect the Se overpressure. A slow growth needs a substantially reduced Se flux, otherwise the excess Se will lead to $Ga_2Se_3$ (Fig.S2). Contrary to expectation, a higher growth rate caused better crystallinity (Fig.S3). We are now focusing on the growth of MLs. Since Ga and $Ga_2Se_2$ do not wet sapphire well, films tend to show 3D features instead of a flat, continuous film when the film is thin. A 2-step growth mode is proposed as a potential solution. Step 1 is to deposit an initial $Ga_xSe_y$ film, then thermally decompose it at high temperature, aiming to improve film wettability by changing the substrate surface chemistry. We expect that this is achieved via atomic substitution at the substrate surface and/or by forming a reaction interlayer. Step 2 is to grow a $Ga_2Se_2$ film on the reacted substrate. A streaky reflection high energy electron diffraction pattern and characteristic X-ray diffraction peaks both confirm a much-improved film crystallinity compared to the sample grown directly, and the atomic force microscopy image shows a continuous film (Fig.S4). Further study will focus on this 2-step growth method and further improvement of film quality.

4:15pm **NM-MoA2-12 Epitaxial Growth of PbSnSe Ternary Alloys on III-V Substrates**, ***Pooja Reddy***, Stanford University; *B. Haidet,* Univesity of California Santa Barbara; *K. Mukherjee, L. Nordin,* Stanford University

The IV-VI semiconductor family of PbSe-SnSe alloys is a rich system to explore for electronic and optoelectronic applications. It spans narrow direct bandgap materials and topological crystalline insulators in the Pb-rich cubic rocksalt phase, and indirect bandgap semiconductors with useful thermoelectric and optoelectronic properties in the Sn-rich layered orthorhombic phase [1,2,3]. Importantly, this layered phase is only a slightly distorted rocksalt structure, making the study of structural phase transitions between the two systems very interested towards the end of harnessing contrasts in the electronic properties between the two phases. Heteroepitaxy of PbSe-SnSe materials provides a route to access these diverse set of properties for a range of thin film devices. In our work, we describe the growth of PbSnSe alloys in both the cubic and layered phases on technologically relevant (001) GaAs substrates by molecular beam epitaxy.

In order to grow PbSnSe alloys on GaAs, we used a PbSe buffer layer [4]. The structural similarity between the cubic and orthorhombic phases

allows for quasi-van der Waals epitaxial growth of SnSe and PbSnSe alloys on PbSe. A Riber Compact 21 MBE system with compound PbSe and SnSe cells was used to grow films. (001)-oriented semi-insulating GaAs substrates were prepared either by a regrowth and arsenic capping process, or by desorbing the oxide under a Se overpressure. Once the arsenic cap or oxide layer was thermally desorbed, the GaAs substrate was dosed with a PbSe flux at 400 °C, transforming the (2 x 4) reconstruction to a (2 x 1) reconstruction. A thin nucleation layer of PbSe was then grown at 330 °C which templates the sample for single-oriented growth resulting in a (1 x 1) reconstruction [4]. The PbSnSe alloy or SnSe was grown at temperatures ranging from 200-300 °C, where the composition was determined by the relative fluxes of the PbSe and SnSe compound cells. The structural quality of SnSe and the PbSnSe alloys clearly improved with the PbSe dosing and nucleation growth steps.

While the properties of cubic PbSnSe in the bulk and thin film limits are better known, here we will present electronic property trends as a function of composition for the orthorhombic phase of PbSnSe thin films. We will also explore the effect that PbSe dosing and nucleation has on these trends, thus discerning the role structure has to play on such properties.

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[2]L. Zhao et al. ... M. Kanatzidis, Nature, **508,** 373, (2014).

[3]Y. Jhon et al. ... J. Lee, Adv. Optical Mater., **7,** 1801745 (2019).

[4]B. Haidet et al. ... K. Mukherjee, Phys. Rev. Mater., **4,** 033402 (2020).

4:30pm **NM-MoA2-13 $Bi_2Se_3$ Growth on III-V Substrates**, ***Yongchen Liu***, *W. Acuna,* University of Delaware*; H. Zhang,* National Institute for Science and Technology (NIST)*; D. Ho, R. Hu, Z. Wang, A. Janotti,* University of Delaware*; G. Bryant, A. Davydov,* National Institute for Science and Technology (NIST)*; J. Zide, S. Law,* University of Delaware

Terahertz (THz) technologies have been in the spotlight for several decades due to the variety of applications in this frequency range. Although significant research regarding THz applications has been conducted, combining different THz components into one device for a THz integrated system has not yet been achieved. In this paper, we will present the van der Waals (vdW) epitaxy of the topological insulator $Bi_2Se_3$, which can serve as a THz plasmonic waveguide, on the technologically-important GaAs (001) substrate using a variety of substrate pretreatment conditions in order to understand how to best combine vdW materials with traditional semiconductor substrates.

We conducted the following pre-treatments and growth in a dual Veeco GENxplor system. Three pre-treatments have been used before the synthesis of 50nm $Bi_2Se_3$ films on (001)-oriented GaAs substrates: GaAs oxide desorption under a Se-overpressure, GaAs oxide desorption under an As-overpressure, or a 100nm GaAs/AlAs smoothing superlattice (SL) and a 50nm GaAs buffer layer grown on it. After growth, scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), x-ray diffraction (XRD), and room-temperature Hall effect measurements were used to characterize the samples. STEM shows two different orientations of $Bi_2Se_3$ grains in the Se-desorbed and As-desorbed samples: the desired (0001) and the undesired (10-15) orientation. As opposed to these two samples, a smooth $Bi_2Se_3$/GaAs interface was attained in the SL sample. AFM scans show similar morphology in all three samples; the root mean square roughness of the SL sample is smaller than the others. The XRD scans confirm the presence of the undesired (10-15) orientation in the Se-desorbed and As-desorbed samples. From the AFM images, we also observed antiphase domains: two sets of domains rotated 60 degrees with respect to each other. We performed x-ray pole scans to quantify the ratio of the antiphase domains. The SL sample has a slightly better antiphase domain ratio compared with the other two samples. Finally, DFT calculations determined that a Se-terminated interface is most likely, which is consistent with previous experimental analyses. In summary, this work demonstrates the importance of substrate pretreatment for the growth of the van der Waals material $Bi_2Se_3$ on a GaAs (001) substrate, which lays a concrete foundation for future THz integrated devices.

4:45pm **NM-MoA2-14 Structural and Optical Properties of CdSe Grown on InAs**, ***Zheng Ju***, *S. Schaefer, A. McMinn, X. Qi, D. Smith, Y. Zhang,* Arizona State University*; S. Grover,* First Solar, Inc.

**Structural and Optical Properties of CdSe Grown on InAs**

**Zheng Ju** [2] **, Stephen Schaefer** [1] **, Allison McMinn** [1] **, Xin Qi** [1] **, David Smith** [2] **, Sachit Grover** [3] **and Yong-Hang Zhang** [1]

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CdSe is an ideal candidate material for the top cell in tandem applications with a Si bottom cell. Its bandgap energies are 1.68 eV and 1.71 eV in the zincblende (ZB) and wurtzite (WZ) structures, respectively, enabling a theoretical power conversion efficiency of the tandem cell as high as 40%. The ZB InAs (111) crystal plane has an in-plane lattice constant of 4.28 Å, offering a suitable substrate for the epitaxial growth of monocrystalline WZ CdSe with lattice constant a = 4.30 Å. However, the growth of single-phase monocrystalline CdSe with perfect crystallinity, high electron mobility and long carrier lifetimes remains challenging. This abstract reports the molecular beam epitaxial growth of CdSe bulk thin films on InAs substrates for solar cell applications.

Bulk CdSe layers have been grown on (100)-, (111)A- and (111)B-oriented InAs substrates indium-mounted to Si wafers in a dual-chamber III-V and II-VI MBE system at different growth temperatures, Cd/Se flux ratios, and growth rates. InAs buffer growth is carried out in the III-V chamber first, followed by transferring under UHV to the II-VI chamber for CdSe overgrowth. RHEED patterns for the growths on (100) show steaky 2×1 surface reconstruction, while on (111)-oriented substrates show a transition from a streaky 1×1 surface reconstruction with four-fold symmetry to a spotty 1× reconstruction with six-fold symmetry, which indicates growth of WZ CdSe. XRD and PL measurements indicate that CdSe films grown on InAs (100) substrates consist primarily of the ZB phase, while CdSe films grown on (111) substrates exhibit characteristics of mixed ZB and WZ phases. SEM images provide additional clues about the mixed-phase nature of CdSe layers grown on (111) substrates, with some preliminary evidence of a transition from ZB to WZ phase as growth progresses on top of the ZB InAs (111) substrate. TRPL experiments of unpassivated bulk CdSe indicate minority carrier lifetimes of 1-5 ns, with ZB material exhibiting longer lifetime than WZ material. It is anticipated that proper or novel control of the growth conditions will yield desired single-phase CdSe thin films, which are necessary for device applications.

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5:00pm **NM-MoA2-15 Measuring and Then Eliminating Twin Domains in SnSe Thin Films Using a Fast Optical Metrology and Molecular Beam Epitaxy**, ***Wouter Mortelmans***, MIT*; M. Hilse,* Penn State University*; Q. Song, S. Jo, K. Ye,* MIT*; D. Liu, N. Samarth,* Penn State University*; R. Jaramillo,* MIT

Van der Waals (vdW) layered chalcogenides have strongly direction-dependent properties that make them interesting for certain photonic and optoelectronic applications. Orthorhombic tin selenide (α-SnSe) is a triaxial vdW material with strong optical anisotropy within layer planes, which has motivated studies of optical phase and domain switching. As with every vdW material, controlling the orientation of crystal domains during growth is key to reliably making wafer-scale, high-quality thin films, free from twin boundaries. Here, we demonstrate a fast and easy optical method to quantify domain orientation in SnSe thin films made by molecular beam epitaxy (MBE). The in-plane optical anisotropy results in white-light being reflected into distinct colors for certain optical polarization angles and the color depends on domain orientation. We use our method to confirm a high density of twin boundaries in SnSe epitaxial films on MgO substrates, with square symmetry that results in degeneracy between SnSe 90° domain orientations. We then demonstrate that growing instead on a-plane sapphire, with rectangular lattice-matched symmetry that breaks the SnSe domain degeneracy, results in single-crystalline films with preferred orientation, with twin domains all-but-eliminated. Our SnSe bottom-up film synthesis by MBE is enabling for future applications of this vdW material that is particularly difficult to process by top-down methods. Our optical metrology is fast and easy and can apply to all triaxial vdW materials.

# Author Index

## Bold page numbers indicate presenter