

## Stabilizing 2D SnSe Piezoelectrics

Jonathan Chin<sup>1</sup>, Marshall Frye<sup>1</sup>, Derrick Shao-Heng Liu<sup>2</sup>, Maria Hilse<sup>3</sup>, Ian Graham<sup>1</sup>, Jeffrey Shallenberger<sup>3</sup>, Ke Wang<sup>3</sup>, Mengyi Wang<sup>2</sup>, Yun Kyung Shin<sup>3</sup>, Nadire Nayir<sup>3,4</sup>, Adri C.T. van Duin<sup>2</sup>, Lauren M. Garten<sup>1\*</sup>

1. School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.
2. Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA.
3. Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA.
4. Physics Department, Karamanoglu Mehmetbey University, Karaman, 70000, Turkey.

Bulk tin selenide (SnSe) is centrosymmetric but when reduced to an odd number of layers near the monolayer limit SnSe becomes piezoelectric, and potentially ferroelectric. 2D piezoelectrics and ferroelectrics have great potential for sensing and electronics with reduced size and weight. However, unlike other 2D materials, exfoliating a monolayer of SnSe is challenging due to strong interlayer bonding. Therefore, achieving films large enough for device testing requires direct film growth with strict layer control. This work focuses on developing routes to control the layering, stability, and morphology of SnSe thin films grown by molecular beam epitaxy (MBE).

Using the MBE growth facilities at the 2DCC, the bulk *Pnma* phase of SnSe was stabilized over a broad range of Sn:Se flux ratios from 250 – 300 °C on (100) MgO and (0001) Al<sub>2</sub>O<sub>3</sub> substrates. Changing the flux ratio does not affect the film stoichiometry, but rather changes the predominant crystallographic orientation. A ReaxFF molecular dynamic simulation developed to emulate the deposition conditions for SnSe demonstrates that the limited stoichiometric change is likely due to the formation of Se clusters that weakly interact with the surface of the SnSe particles. Raman spectroscopy taken at different growth intervals supports the theory by showing that initially SnSe<sub>2</sub> occurs, as indicated by the peaks at 185 cm<sup>-1</sup>, but as the growth time increases the films transition into solely SnSe. X-ray photoelectron spectroscopy cross-sectioning shows that the film composition is SnSe with the formation of an ultra-thin, stable surface oxide layer. AFM results taken on films grown for less than a minute under different flux ratios show distinctly different nucleation rates, and grain morphologies. Overall, this study identifies the conditions for the stabilization and morphology control of SnSe thin films by MBE. These results provide insight into routes to control the layering and surface stability of 2D films that are difficult to exfoliate for the development of 2D piezoelectric devices.