Structural distortions and surface/bulk competition in quasi-2D SnSe-$TiSe_2$ nanolayered heterostructures

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Low dimensional materials and their heterostructures are becoming increasingly important due to their emergent properties not observed in bulk analogues. As the fraction of surface or interface atoms become comparable to the bulk, so too do their contributions to the free energy. Since the most stable interface structure does not necessarily agree with the most stable bulk structure, competition between structures can cause size-dependent distortions or phase transitions. These structural behaviors can fundamentally alter the electronic environment, significantly affecting the material properties.

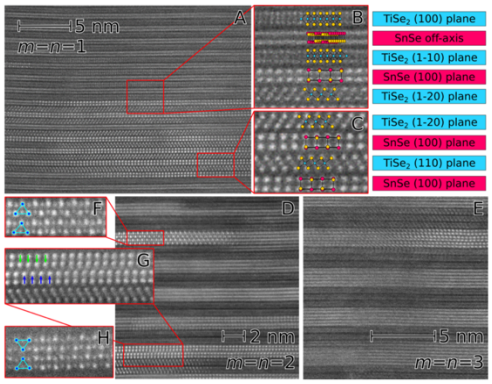

Figure 1: *STEM micrographs of SnSe-$TiSe_2$ heterostructures show templated interfaces in thin layers, and several structures in thicker SnSe.*

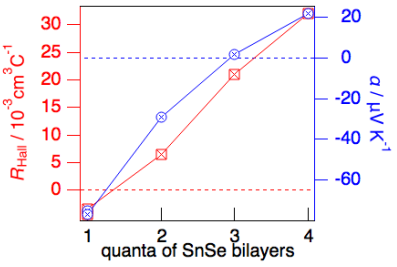

Figure 2: *Hall and Seebeck measurements show change in carrier type with SnSe thickness.*

I will present on multilayer heterostructures formed by self-assembly of designed precursors. This will focus on a system containing quasi-2D layers of SnSe interleaved with $TiSe_2$, which exhibits size-dependent structures and transport properties. When a single bilayer of SnSe is present all atoms reside at a $TiSe_2$ interface, templating is observed and long-range 3-dimensional order is established in the heterostructure.[1] However, as the number of SnSe layers increases and "bulk" atoms are introduced, distortions, additional structures, and new stacking sequences are observed.[2] These findings are corroborated by DFT calculations. The changing SnSe structure has profound effects on the composite transport properties with a shift in carrier type, as shown by Seebeck coefficient and Hall measurements.

This designed precursor approach has also been used to study thermoelectric enhancement[3] and quantum phase transitions[4] as a function of layer thickness in other selenides. Work extending this approach to sulfides is currently underway at NREL, and I will briefly present our initial results synthesizing similar heterostructures via combinatorial sputter deposition.

[1] D. M. Hamann, *et al*, *Inorg. Chem.* **2017**, *56*, DOI 10.1021/acs.inorgchem.6b03063.
[2] D. M. Hamann, *et al*, *ACS Nano* **2018**, *12*, DOI 10.1021/acsnano.7b07506.
[3] S. R. Bauers, *et al*, *J. Mater. Chem. C* **2015**, *3*, 10451.
[4] M. Falmbigl, *et al*, *Nano Lett.* **2015**, *15*, 943.

Supplementary information:

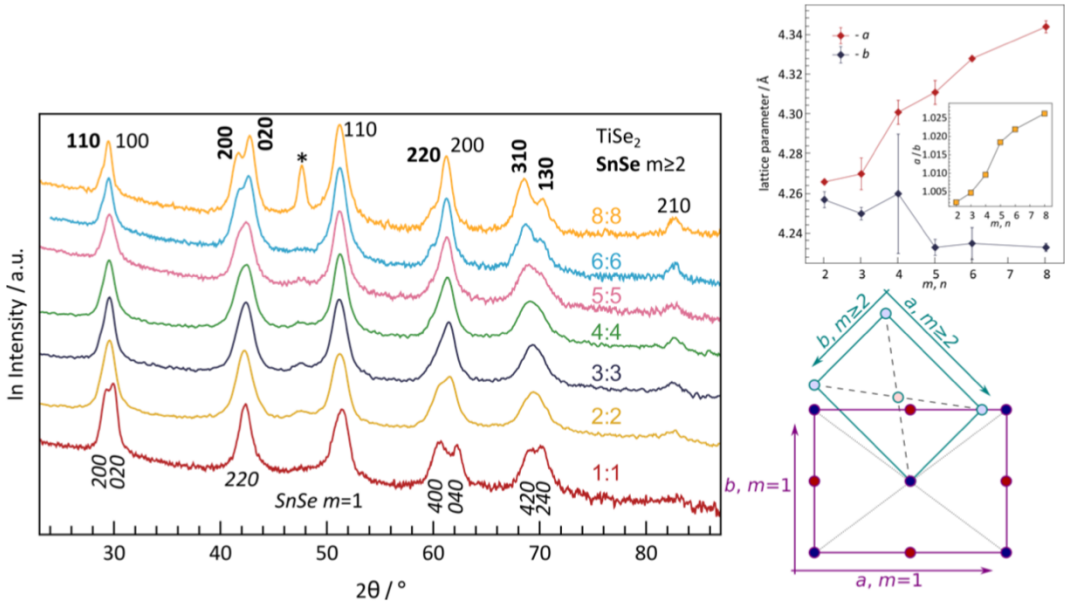

Figure 3: *In-plane x-ray diffraction of SnSe-$TiSe_2$ heterostructures. A symmetry shift in SnSe is observed as a function of layer thickness, which is correlated with formation of coherent interfaces in $TiSe_2$. Unpublished data.*

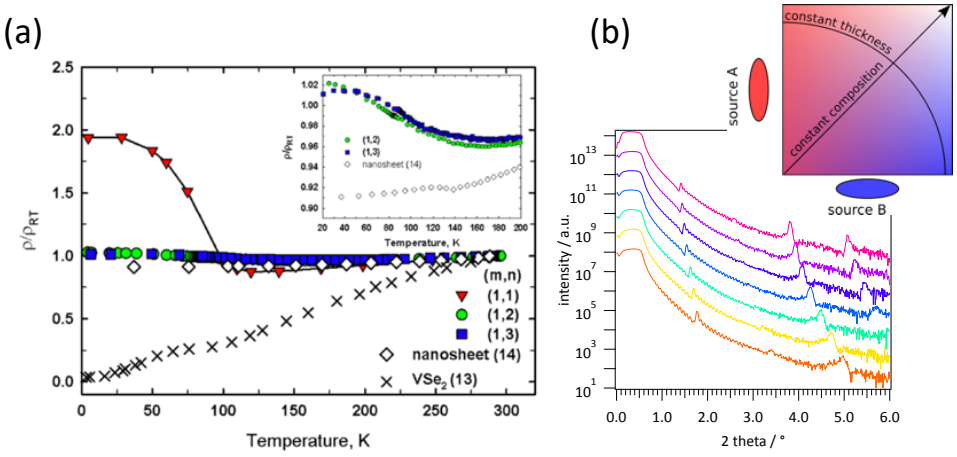

Figure 4: *(a) charge density wave amplitude as a function of VSe_2 dimensionality in SnSe-VSe_2 heterostructures. Image from ref.[4] (b) combinatorial sputter deposition of sulfide heterostructure precursors allows for precludes precise calibration, since conditions with correct relative composition integer layer thickness exists in the combinatorial gradient.*