2088
doi:10.1017/S1431927619011176
Microsc. Microanal. 25 (Suppl 2), 2019

Atomic Resolution Analysis of Defect Structures in Multi-layer Chalcogenide Films

D.L. Medlin[1*], R. Fischer[2], R. Gannon[2], D.M. Hamann[2], and D.C. Johnson[2]

[1.] Sandia National Laboratories, 7011 East Avenue, MS 9161, Livermore, CA 94551 (USA).
[2.] Dept. of Chemistry, University of Oregon, Eugene, OR 97403 (USA).
* Corresponding author: dlmedli@sandia.gov

The layered-chalcogenides comprise a broad class of 2D materials of interest for their novel electronic and thermal properties. Particularly exciting about these materials is that the relatively weak, van der Waals-like interaction across adjacent chalcogen layers (i.e., S, Se, or Te) enables the fabrication of hierarchically layered arrangements of independent 2D layers, each with its own tailored functionality. Emergent functionalities arising in these materials include topological insulator behavior and novel thermoelectricity and could enable new approaches for manipulating charge and phonon transport relevant to many energy applications. Motivated by these possibilities, the ability to grow hierarchical chalcogenide structures with precisely tailored atomic-scale composition has advanced rapidly in recent years. For instance, the modulated elemental reactants approach [1] has enabled rigorous control of 2D layer sequencing, producing a wide variety of novel metal chalcogenide layer configurations (e.g., references [2-4]). Although the layer-sequencing can now be controlled with great precision, a key remaining challenge is to control the order and defect configurations within the layers themselves.

In this presentation, we discuss atomic-resolution, scanning transmission electron microscopy (STEM) measurements of the structure and composition of ordered metal chalcogenides in the $(SnSe)_m(TiSe_2)_n$ system, with an emphasis on establishing the nature of defects within the individual layers. Figure 1(a) shows a high angle annular dark field (HAADF) STEM image giving an overview on one such film, here a sequence of one SnSe layer (m=1) to every four $TiSe_2$ (n=4) layers. The diffractogram in Figure 1(b), obtained from the Fourier transform of the data in Figure 1(a), demonstrates the strong out-of-plane ordering of the layer sequence, showing distinct peaks corresponding to the real-space period of the superlattice. Because of in-plane rotational, or turbostratic, disorder, domain widths within the layers are of nanometer-scale. This is illustrated in Figure 5, which shows a small domain of $TiSe_2$ that is locally oriented on zone. Here, the crystalline orientation extends across the SnSe spacer layer into the next $TiSe_2$ layer. An enlargement of this domain shows a boundary separating two regions of reversed stacking arrangement. We will discuss microscopic approaches for characterizing the length-scale of the disorder and insights concerning growth and crystallization processes discerned from the atomic scale defects.

References:

[1] D.C. Johnson, Current Opinion in Solid State and Materials Science **3** (1998) 159-167.
[2] D.R. Merrill et al., Chemistry of Materials **27** (2015) 4066-4072.
[3] M.B. Alemayehu et al., Angewandte Chemie-International Edition **54** (2015) 15468-15472.
[4] D.R. Sutherland et al., Journal of the American Chemical Society **141** (2019) 922-927.
[5] DLM acknowledges support through Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE NNSA under contract DE-NA-0003525. DCJ, RF, RG, and DMH acknowledge support from the National Science Foundation under grant DMR-1710214 and acknowledge the use of instrumentation in the Center for Advanced Materials Characterization in Oregon (CAMCOR) at the University of Oregon.

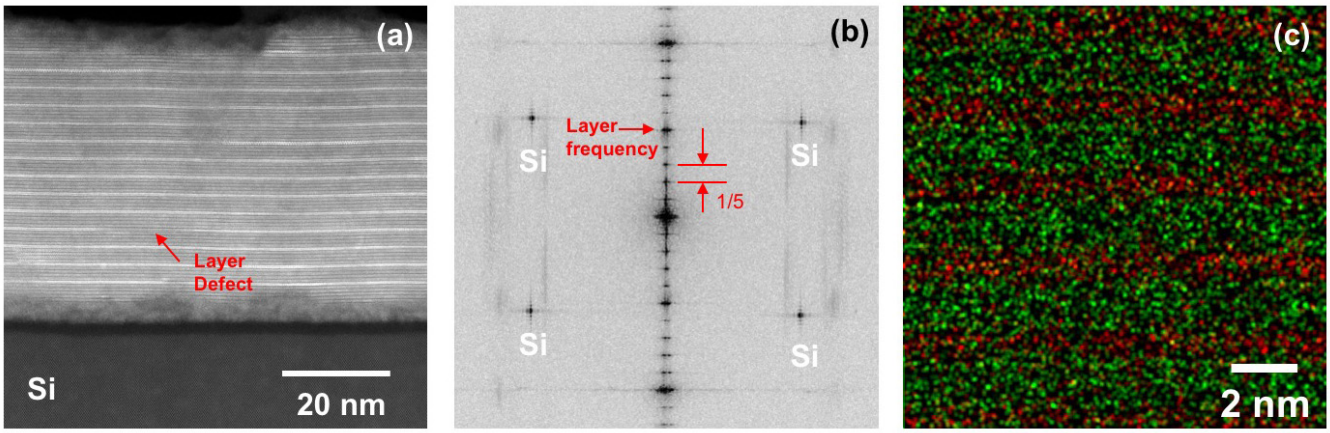

Figure 1. (a) HAADF-STEM image of a 1:4 $(SnSe)_m(TiSe_2)_n$ film. Note the layer defect corresponding an incomplete SnSe layer (which show bright contrast in HAADF-STEM). (b) Diffractogram from data in (a). The strong out-of-plane layer ordering produces superlattice spots. Because the SnSe and $TiSe_2$ layers have comparable spacings, the superlattice peaks arise at 1/5 of this fundamental frequency. Additional features in the pattern arise from thin domains within the layers, which exhibit a distribution of rotational configuration as well as spots from the Si substrate. (c) A composite EDS spectrum image from a 1:3 specimen showing the distribution of Sn (red) and Ti (green).

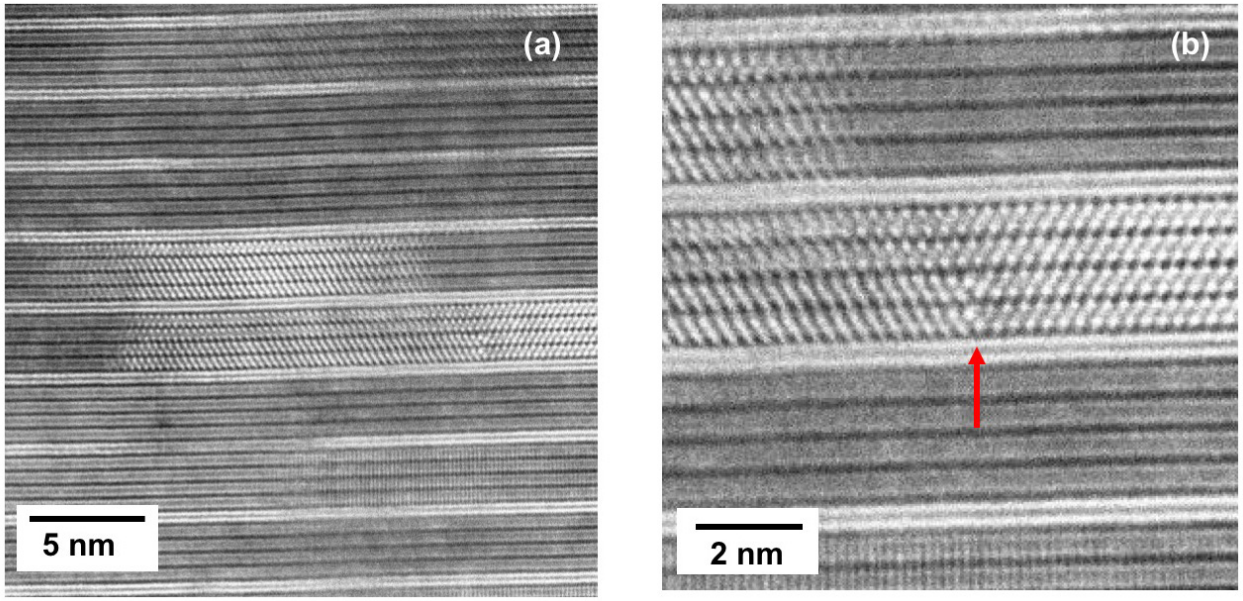

Figure 2. (a) HAADF-STEM image of a 1:4 $(SnSe)_m(TiSe_2)_n$ film. Because of in-plane rotational disorder, domain widths within the layers are of nanometer-scale. Here, one such domain in the $TiSe_2$ phase is oriented locally on zone. Interestingly, the orientation extends across the SnSe layer. The domains themselves can exhibit defects. For instance, (b) shows an enlargement of the $TiSe_2$ domain in (a). The arrow points to a boundary separating a reversal of the $TiSe_2$ stacking.

https://doi.org/10.1017/S1431927619011176