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Quantitative High Resolution Chemical Analysis of the $(Pb_xSn_{1-x}Se)_{1+\delta}TiSe_2$ Intergrowth System.

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Tuning the properties of materials is often achieved through chemical substitution. Chalcogenide based misfit layer compounds offer a promising class of tunable materials but have been limited by a lack of synthetic control of thermodynamic products. The modulated elemental reactant (MER) method provides a versatile diffusion limited synthesis approach for self-assembly of targeted kinetically stable products [1]. It has been shown that the nanostructure of the deposited precursor is preserved in the final products [2, 3, 4]. The added ability to form solid solutions within only the transition metal dichalcogenide constituent suggests promise for controlling the material properties on an even finer scale [5].

In this presentation, we discuss our HAADF-STEM and STEM-EDX investigations of the structure and compositional distributions in a series of $(Pb_xSn_{1-x}Se)_{1+\delta}TiSe_2$ films grown using the MER method. These films consist of alternating layers of the rocksalt-structured $(Pb_xSn_{1-x}Se)_{1+\delta}$ compound interleaved with single layers of the dichalcogenide compound $TiSe_2$. We systematically varied the Pb to Sn ratio, to investigate the effects of alloying in the rock-salt layer on electrical transport properties in the films. This analysis required detailed understanding of the macroscopic and localized alloying processes. Thus, macroscopic measurements of the structure and composition of the films, conducted through XRD and EPMA were compared against our STEM, providing further confirmation that the targeted products were synthesized. In particular, our STEM-EDX mapping provided explanations for deviations from stoichiometric composition by pointing to the formation of localized layer defects and segregation of Sn and Pb within theses defects (Figure 1).

As we will discuss, the ability to form targeted compounds using the MER technique also provides an approach for fabricating structurally controlled compositional standards for EDX quantification. We have thus employed the MER method to make binary films of SnSe and PbSe and are employing these to evaluate the level of absorption and fluorescence effect present in a series of intergrown $(Pb_xSn_{1-x}Se)_{1+\delta}TiSe_2$ films of known average composition. This data is then used to calculate the local concentration of Pb and Sn in nominally segregated films, $(PbSe)_{1+\delta}TiSe_2(SnSe)_{1+\gamma}TiSe_2$. These results are compared to calculated average concentrations obtained from x-ray diffraction methods.

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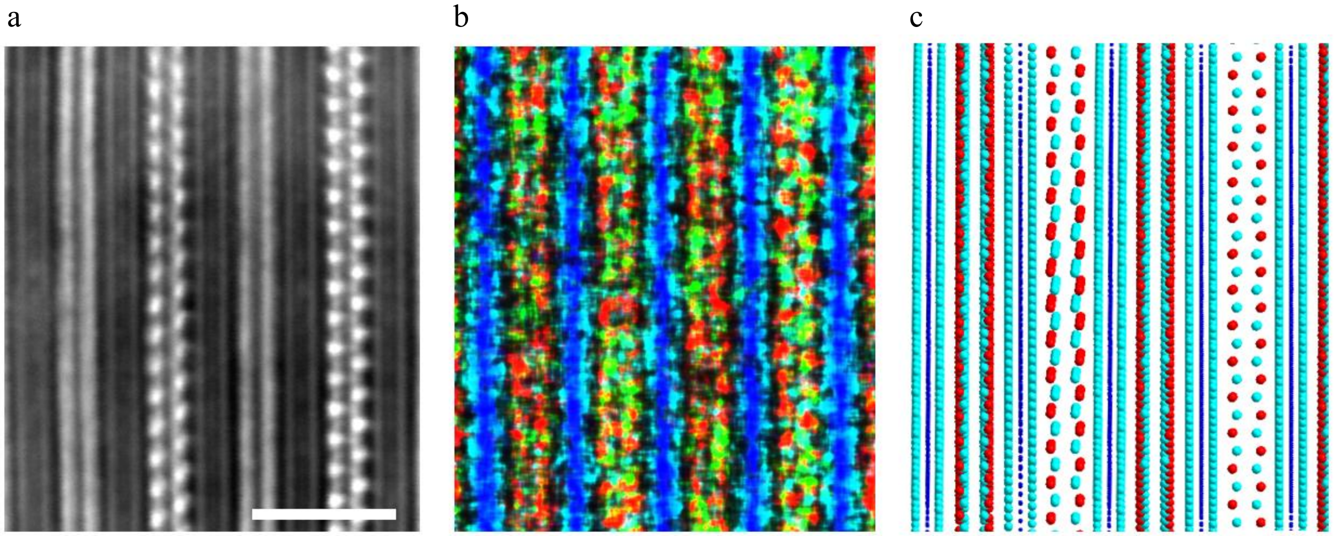

Figure 1. (a) A HAADF-STEM image showing resolved atomic planes of a $(Pb_xSn_{1-x}Se)_{1+\delta}TiSe_2$ intergrowth and a 2 nm scale bar, (b) the corresponding composite EDX map showing distributions of Ti (blue), Pb (red), Sn (green), and Se (cyan), and (c) a cartoon model of the image demonstrating turbostratic disorder. Sn and Pb are both represented by the red positions while Se (cyan) and Ti (blue) correspond to the colors in (b). The [110] orientation of $(Pb_xSn_{1-x}Se)$ is seen in the HAADF while the rest of the layers exhibit off of zone axis rotation.