Spontaneous nanostructuring of TiNiSn half-Heusler films for thermoelectric applications: a refined STEM-EELS study

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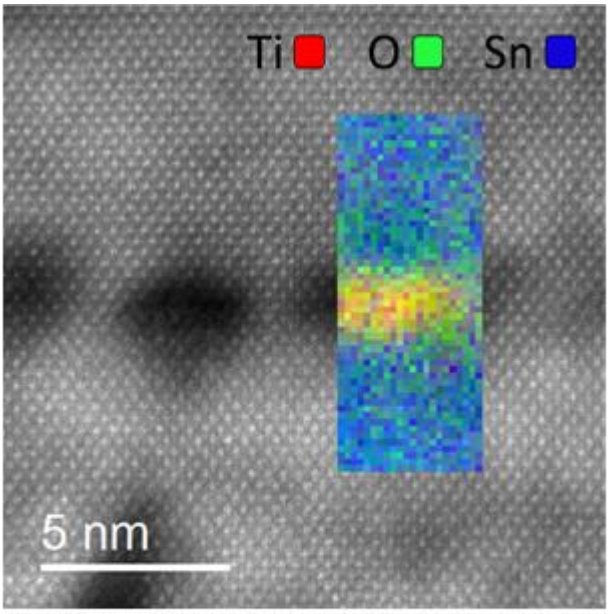
Thermoelectric power generation presents an opportunity to 'scavenge' energy which would otherwise be wasted as heat, if appropriate materials can be engineered. Heusler alloys are a promising solution as they employ inexpensive, non-toxic materials. Recently, more efficient thermoelectric Heusler alloys have overcome a performance-limiting thermal conductivity by introducing nanostructures that scatter phonons and impede thermal transport. However, the nature and stability of the nanostructures can be difficult to discern. A particular problem is distinquishing minor compositional variation, including the formation of full-Heusler inclusions. Here, we perform absolute quantification via STEM-EELS and revealed interesting instabilities in the alloy system.

We present a transmission electron microscopy (TEM) investigation of thin films of the half-Heusler TiNiSn, which is a particularly promising and economic material for thermoelectric power generation. We first describe the pulsed laser deposition (PLD) of TiNiSn for controlled epitaxial growth of model thin films on MgO(001) substrates, focussing on optimising the deposition conditions. Structural assessments made using in-situ RHEED are supplemented by TEM diffraction and dark field imaging of FIB-prepared cross sections. A combination of nanoprobe convergent beam diffraction (CBED) and aberration-corrected STEM-EELS spectrum imaging highlight unexpected phase segregation, oxide inclusions and a detrimental interfacial reaction that forms a titanium oxide layer at the substrate/film interface. The propensity of titanium to oxidise results in the formation of an unusual TiO nano-layer at the substrate interface which can maintain epitaxy but perturbs the subsequent film composition.

Quantification of the compositions of alloys formed by phase segregation is facilitated by accurate calibration of the elemental cross-sections measured in electron energy-loss spectroscopy. We outline a refined methodology for processing STEM-EELS data, measuring and accounting for the non-linearity and fixed pattern noise in the dispersion, and using experimentally determined cross-sections to provide absolute quantification of elements present. The latter is essential in overcoming the large uncertainty associated with fitting to the theoretical tin M-edge Hartree-Slater cross-sections, and facilitates a study of phase segregation with accuracies of a few percent. Our absolute quantification of EEL spectra has also revealed coherent TiO nano-inclusions that can form throughout the film in the presence of trace amounts of oxygen and drive further decomposition of the Heusler material. These observations are essential to the design of optimised Heusler alloy thermoelectric generators.



Column Resolved STEM-HAADF image of TiO nano-inclusions in TiNiSn thin film. Overlay is false colour elemental map from STEM-EELS spectrum image analysis.

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