Controlling nucleation and growth of IV-VI rocksalt PbSe and PbSnSe on III-V zincblende substrates

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Pb-rich PbSnSe is a rocksalt semiconductor with a conventional direct bandgap ranging from 0.3 eV to 0 eV, after which for alloy compositions >30% Sn, PbSnSe becomes a topological crystalline insulator with an inverted gap[1]. Recognizing that both infrared and potential quantum technologies require very high material quality, to us this system provides a fantastic opportunity to study heavily mismatched cross-materials-system heteroepitaxy. Previously, IV-VI growth has been dependent on fluorite substrates and buffer layers[1,2], but in this work, we explore PbSe growth on more conventional III-V substrates. This IV-VI/III-V interface incorporates a change in valency, surface charge, and crystal structure. GaSb and InAs are both nearly-lattice-matched to PbSe, but present chemically different surfaces, making this a model system for investigation.

We demonstrate that the nucleation behavior of PbSe can be controlled by modifying the III-V surface reconstruction and chemistry prior to growth. Specifically, by exposing arsenide surfaces to PbSe flux at high temperature, we can convert the surface into a suitable template for single-orientation nucleation of PbSe, resulting in a cube-on-cube epitaxial arrangement for both (001)- and (111)-oriented substrates. Interestingly, this result does not extend to antimonide surfaces or untreated arsenide surfaces, where the interfacial energy between substrate and film is so high as to make PbSe nucleation orientationally ambivalent. Uncontrolled nucleation results in a mixture of (001), (110), and {221}-type grains on (001) substrates, and rotations of (111) grains on (111) substrates. This behavior highlights the importance of surface chemistry in this heteroepitaxial system.

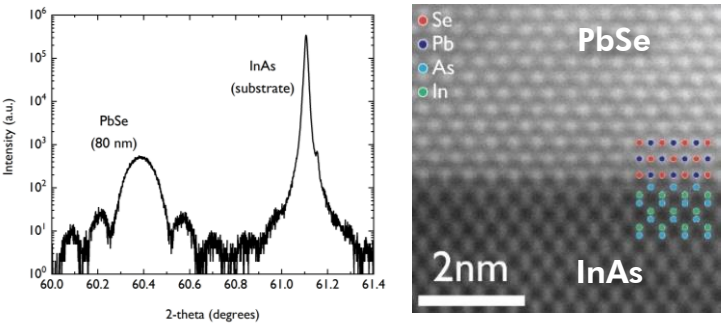

Figure 1: (left) Symmetric XRD scan of the PbSe and InAs (004) peaks. (right) HAADF STEM shows an atomically sharp (001)PbSe/(001)InAs interface.

With this method, we have produced (001)-oriented PbSe films with 369 and 185 arcseconds of tilt about the $[1\bar{1}0]$ and [110] directions, respectively, in films only 80 nm thick. This result is on par with multi-micron-thick films from other studies[3]. The ability to recover higher-quality material in thinner layers has great implications for devices, especially those with electrically active heterojunctions. On (111)-oriented substrates, we further demonstrate for the first time growth of rocksalt compositionally (metamorphic) graded buffers in the PbSnSe alloy system, opening new avenues for fabrication of IV-VI devices.

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[3] X.J. Wang, Y.B. Hou, Y. Chang, C.R. Becker, R.F. Klie, T.W. Kang, R. Sporken, and S. Sivananthan. *J. Cryst. Growth* 311 (2009)
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Supplementary Figures:

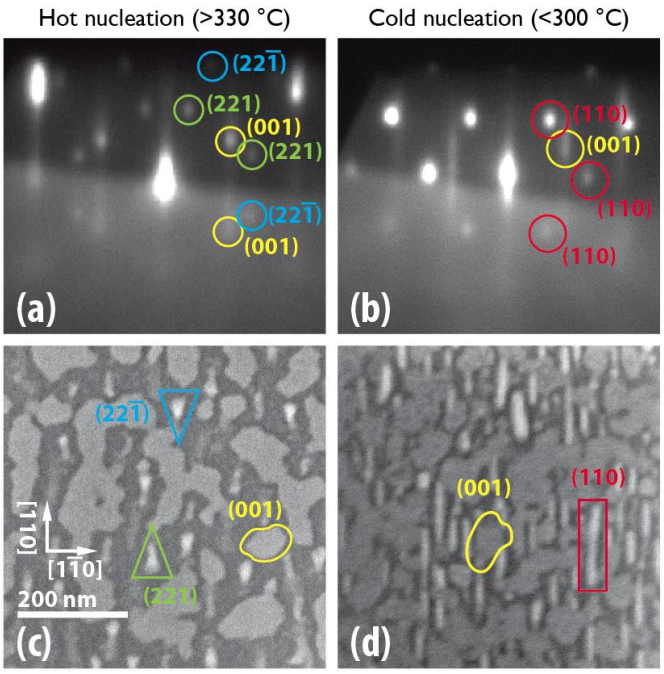

Figure S1 – PbSe nucleation on (001) GaSb varies based on substrate temperature: (a,b), [1$\bar{1}$0] RHEED patterns of PbSe nucleated above 330 °C, and PbSe nucleated below 300 °C. As multiple orientations of PbSe can nucleate simultaneously, these RHEED diffractograms are superpositions of multiple patterns. The labels on specific diffraction spots denotate which pattern (nuclei orientation) those spots correspond to. (c,d) SEM micrographs of 90-second (nominally ~15 ML) growths of PbSe on GaSb, showing (c), a mix of (001), (221), and (22$\bar{1}$) nuclei, and (d), a mix of (001) and (110) nuclei. The flat tops of the (001) nuclei and the 3D nature of the misoriented nuclei is also reflected in the shape of the observed diffraction spots – the (001) spots appear vertically stretched.

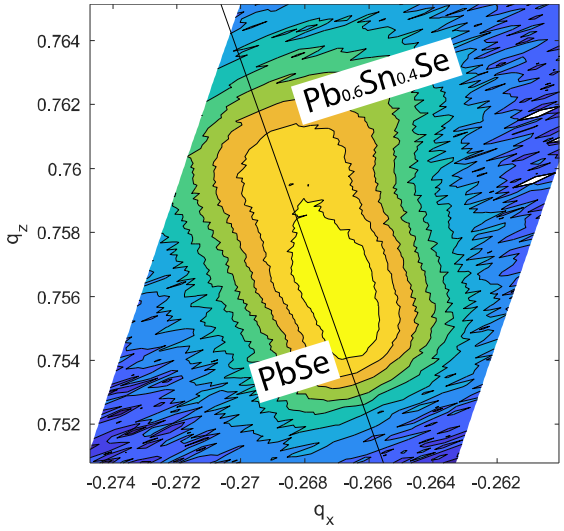

Figure S2: (224) RSM of a PbSe→PbSnSe graded layer grown on a PbSe-treated (111) GaAs substrate. The black diagonal line represents full relaxation to the GaAs substrate. As the Sn content increases from PbSe the rocking curve peak width increases slightly.