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Thin Films of $SnSe_2$ Grown by Molecular Beam Epitaxy on GaAs (111)B Substrates

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Transition metal dichalcogenides (TMDCs) and semiconductor chalcogenides (IV-VI) have layered structures and diverse properties that are determined by the crystal structure and composition, and the number and stacking sequence of layers [1]. MoS_2 and WSe_2 are the most studied TMDCs due to their stable phase, and PbS and PbSe are the most studied IV-VI due to the ability to tune the band gap across the infrared and visible spectrum by adjusting the nanocrystal size. Recently, there has been renewed interest in the tin selenide system due to excellent thermal and promising optical properties. The tin selenide system is comprised of two stoichiometric phases, orthorhombic SnSe and hexagonal $SnSe_2$, and has many possible applications [2]. SnSe is an intrinsic *p*-type semiconductor with ~0.9eV indirect band gap, and $SnSe_2$ is an intrinsic *n*-type semiconductor with ~1eV indirect band gap. Many studies have explored the crystal structure, electronic, and optical properties of $SnSe_2$ but few have investigated the associated defects. This study presents transmission electron microscopy (TEM) characterization of tin selenide thin films grown by MBE on GaAs (111)B substrates at four different selenium to tin flux ratios. Cross-section samples suitable for TEM observation were prepared using standard mechanical polishing and argon-ion milling techniques with the samples held at liquid-nitrogen temperature to minimize artefacts. The TEM images and EDX spectra were recorded with a Philips-FEI CM200 FEG TEM and a JEOL 2010F FEG TEM.

Figure 1 shows that the quality of the films increases with increasing Se_2:Sn flux ratio. The films with the lowest ratio of 3:1 show three layers with extensive stacking faults and areas of both SnSe and $SnSe_2$. Hexagonal $SnSe_2$, with varying degrees of defects, is observed for the higher ratios (4.6:1, 10:1, and 40:1): two examples are shown in fig. 2. Grain boundaries are visible and columnar growth is evident. Lattice parameters are calculated using diffractograms and comparison to bulk crystals show that the films are unstrained. Overall, excellent crystal quality was obtained for growth with high enough flux ratios [3]. The introduction of magnetic dopants into a 2D lattice could potentially bring out new functionalities, including new opportunities for spintronic applications. Thus, Mn ions were introduced into the $SnSe_2$ lattice during growth via an extra molecular beam and three different Mn temperatures. The resultant films were analyzed and it was found that Mn addition resulted in a crystal structure that was different than bulk $SnSe_2$, as shown by the example shown in fig. 3. The spatial distribution of the Mn across the film was also found to be affected by the source temperature: Samples grown at 710°C displayed the best uniformity in composition.

References

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[3] The authors acknowledge partial support from AFOSR and the use of facilities within the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University and to NSF Grant DMR14-00432 at Notre Dame.

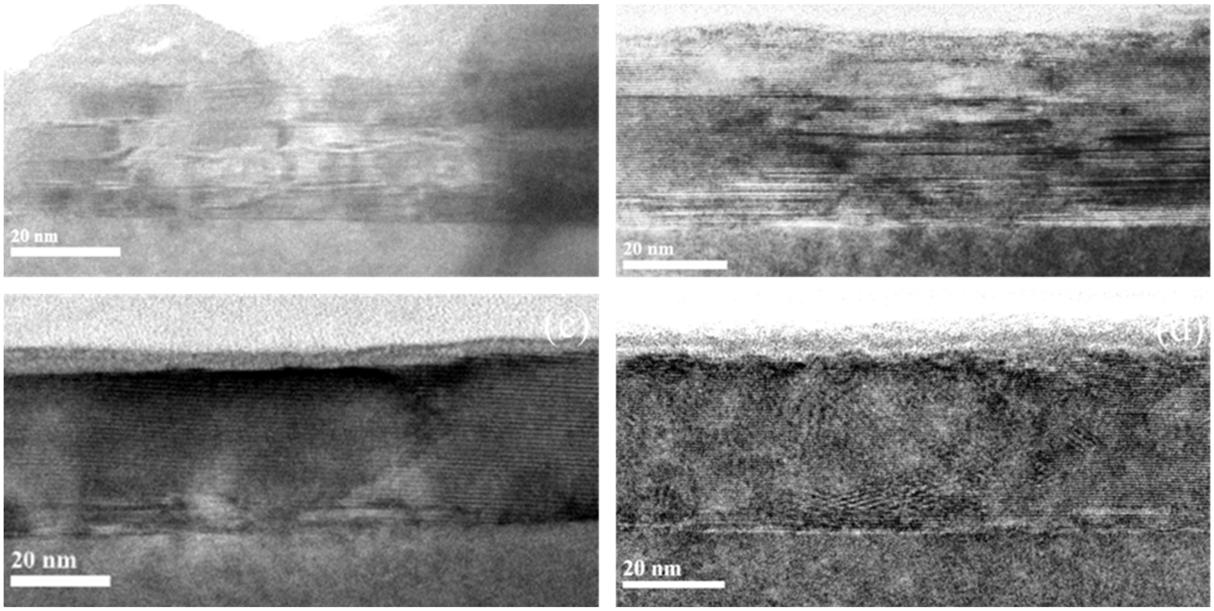

Figure 1. Cross-section electron micrographs showing MBE-grown $SnSe_2$ films on GaAs (111)B substrates with four different selenium to tin flux ratios (a) Se_2:Sn=3:1, (b) Se_2:Sn=4.6:1, (c) Se_2:Sn=10:1, (d) Se_2:Sn=40:1.

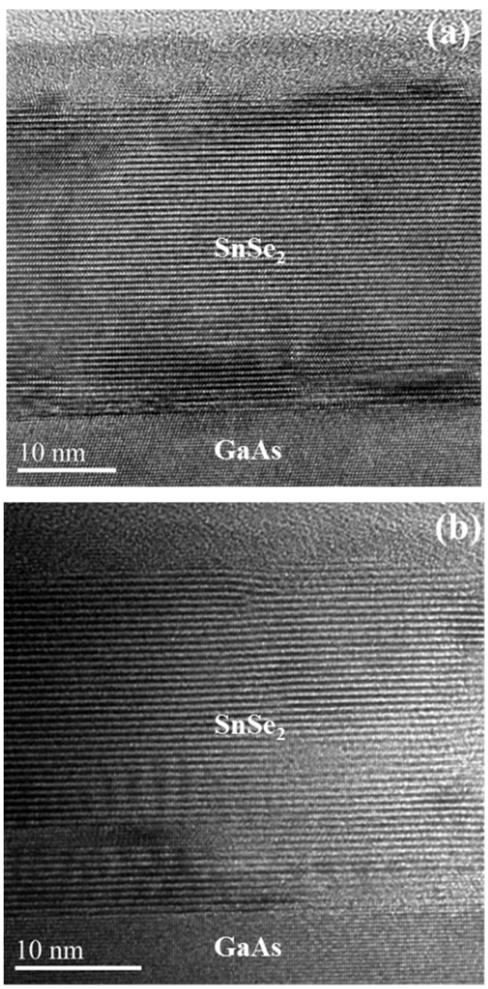

Figure 2. (Left) High-resolution electron micrographs of the $SnSe_2$ thin film grown with flux ratio of Se_2:Sn=10:1, shown in two orthogonal directions: (a) GaAs [110] and $SnSe_2$ [2-1-10]; (b)

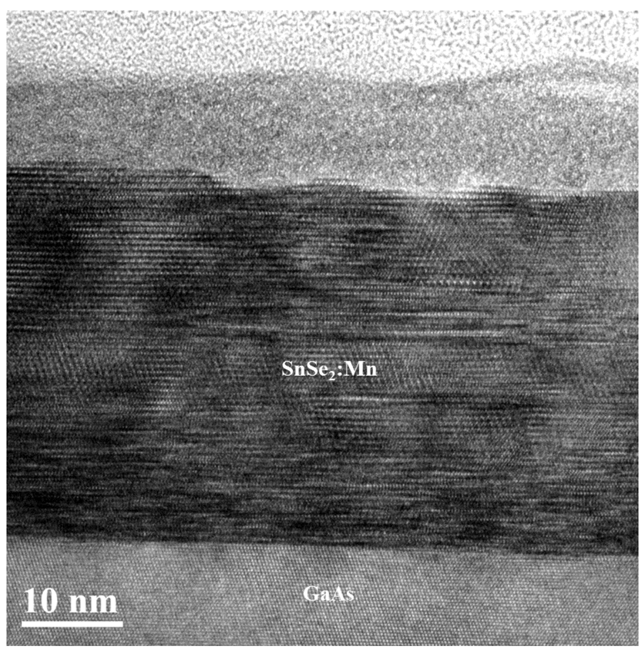

Figure 3. High-resolution electron micrograph of the $SnSe_2$:Mn thin film grown with T_{Mn}=690°C. The GaAs is oriented in the [110] zone axis.

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