Characterization of structural defects in SnSe₂ thin films grown by molecular beam epitaxy on GaAs (111)B substrates

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ABSTRACT

Tin selenide thin films have been grown by molecular beam epitaxy on GaAs (111)B substrates at a growth temperature of 150°C, and a microstructural study has been carried out, primarily using the technique of transmission electron microscopy. The Se:Sn flux ratio during growth was systematically varied and found to have a strong impact on the resultant crystal structure and quality. Low flux ratios (Se:Sn = 3:1) led to defective films consisting primarily of SnSe, whereas high flux ratios (Se:Sn $\geq$ 10:1) gave higher quality, single-phase SnSe₂. The structure of the monoselenide films was found to be consistent with the Space Group Pnma with the epitaxial growth relationship of $[011]_{\text{SnSe}} // [1\bar{1}0]_{\text{GaAs}}$, while the diselenide films were consistent with the Space Group $P\bar{3}m1$, and had the epitaxial growth relationship $[2\bar{1}\bar{1}0]_{\text{SnSe}_2} // [1\bar{1}0]_{\text{GaAs}}$.

Keywords: A1. Characterization; A1. Crystal structure; A3. Molecular beam epitaxy; B2. Semiconducting materials

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1. Introduction

Two-dimensional (2D) materials have unique electrical and optical properties that differ significantly from those of the corresponding bulk materials [1]. These properties open up many possibilities for new and exciting types of device functionalities that are just beginning to be explored [2]. Graphene is the material most studied so far, but some types of electronic devices, such as field-effect transistors, cannot be fabricated with graphene without added complexity because it is intrinsically a zero-gap material [1]. This drawback has led researchers to explore other 2D systems. Transition-metal dichalcogenides (TMDs) as well as other semiconductor chalcogenides, are among the 2D materials which have properties that are complementary yet distinct from those of graphene. The TMDs are quite diverse, with properties that vary primarily with composition and crystal structure, and include metals, semiconductors, superconductors, half-metallic magnets and super-lubricants [1,3]. Moreover, the band gap in 2D systems can be tuned using quantum confinement so that monolayer TMDs promise to be highly useful in optoelectronic and field-effect transistors [3]. Thus, TMD materials such as MoS_2 and WSe_2 which have the 2H polytype structure, are being widely studied for possible device applications. For IV-VI chalcogenides, most research has focused on PbS and PbSe nanocrystals because the band gap can be tuned across the infrared and visible spectrum by varying the nanocrystal size [5].

In comparison with many other 2D chalcogenides, the tin selenide system has so far received very little attention. The tin selenides exist primarily in two stoichiometric phases, tin monoselenide (SnSe) and tin diselenide (SnSe_2), and are known to display many polytypes that could lead to interesting devices [6-12]. SnSe , which adopts an orthorhombic layered structure (Pnma, Space Group #62 at room temperature), is reported to be a *p*-type semiconductor with a

narrow band gap (~ 0.90 eV indirect and ~ 1.30 eV direct) [6, 9, 13]. SnSe_2 has been reported to have several crystal structures, with different polytypes that are possibly linked to different types of conductivity [15]. SnSe_2 is intrinsically an *n*-type semiconductor (~ 1 eV indirect band gap) [4, 13], but it has also been found to show *p*-type conductivity [14, 15]. In general, SnSe_2 has been reported to crystallize in the CdI_2 crystal structure, with each layer of Sn atoms sandwiched between two layers of hexagonal-close-packed Se atoms, and the adjacent Se layers connected by weak van der Waals interaction [6, 13]. The interlayer stacking has several different forms which determine the specific polytype of this 2D material. SnSe_2 grown from the melt was reported to consist only of the 18R structure while SnSe_2 grown by chemical transport resulted in 2H and 18R structures [16, 17]. It was also concluded that 2H and 18R were the most common polytypes of SnSe_2 . These 2H polytypes with CdI_2 -type structure have been associated with space group $P\bar{3}m1$ [18]. However, there is some lack of consistency in the literature regarding descriptions of the SnSe_2 crystal structure since other workers have referred to this same space group in describing SnSe_2 yet described the structure as 1T [4]. Other papers have used CdI_2 -type, or 2H, or 1T, or just hexagonal when describing the crystal structure of SnSe_2 . From our understanding, these different nomenclatures all refer to the same crystal structure with space group $P\bar{3}m1$, which will be used in the remainder of this paper.

Most previous studies of tin selenides have been made on bulk materials or by using nanocrystals/nanorods, with only very limited investigations of thin films. Thin films of SnSe grown on rock salt were shown to adopt the underlying NaCl structure [19]. The growth of strained-layer superlattices of PbSe/SnSe was reported, in which the PbSe material adopted the SnSe crystal structure when the PbSe layers were thinner than about 3 nm [20]. Studies of Mn-doped SnSe_2 grown by molecular beam epitaxy (MBE) showed that it was possible to produce

high quality Mn-doped SnSe₂ [21]. Another study of MBE-grown tin selenide films found that both orthorhombic SnSe and hexagonal (1T) SnSe₂ could coexist in the same MBE-grown film with transitions between the phases governed by the defect structure and the local composition [22]. The electrical and optical properties of SnSe₂ in bulk as well as layer form were recently systematically characterized [4]. Finally, exploratory studies of MBE-grown SnSe₂ have investigated the effects of using different substrates and the possibility of producing *in situ* tunnel junctions in combination with MoTe₂ [23, 24].

This present paper describes the microstructural analysis of tin selenide thin films grown by MBE on GaAs(111)B substrates, with special attention paid to the role of the Se:Sn flux ratios used during growth. The results establish a baseline for understanding and controlling the structural properties of MBE-grown SnSe₂ thin films.

2. Experimental Details

The tin selenide thin films were grown on GaAs (111)B substrates using a dual-chamber Riber 32 MBE system. The growth sequence was as follows: First, an epi-ready substrate was deoxidized by heating to 600°C in the III-V MBE chamber, and a 60-nm-thick GaAs buffer layer was then deposited. The sample was subsequently transferred via an ultrahigh-vacuum load-lock system to a second chamber for tin selenide deposition. The substrate was immediately selenated by exposure to Se₂ flux for 15 minutes at 600°C, and the RHEED pattern was observed to become streaky. The substrate was then cooled in the presence of Se flux to 150 °C, and growth of the SnSe(x) films was initiated. The tin selenide growth was then performed at the substrate temperature of ~150°C, using specific Se:Sn flux ratios. The reasons for choosing the temperature growth of 150°C were based on the following criteria. Low growth temperatures (<

~120°C) led to the formation of amorphous selenium. Conversely, a spotty RHEED pattern, indicative of 3D growth, was observed at temperatures higher than 160°C. Thus, the substrate temperature was kept as high as possible, but below the temperature where 3D growth was initiated. Finally, the samples were transferred back to the III-V chamber for deposition of a protective GaAs capping layer. The growth processes in each chamber was monitored *in situ* using reflection-high-energy electron diffraction (RHEED). Four growths were carried out using Se:Sn flux ratios of 3:1, 4.6:1, 10:1, and 40:1, and the corresponding growth rates were 115 s/ML, 36.8 s/ML, 38.4 s/ML, and 37.0 s/ML.

The materials were characterized *ex situ* by high-resolution x-ray diffraction (HR-XRD), and transmission electron microscopy (TEM). The overall crystallinity of the films was initially evaluated by HRXRD using the Cu K $_{\alpha 1}$ radiation line and a Pathfinder detector on a Bruker D8 Discover Diffractometer equipped with Ge(022) $\times$ 4 asymmetric monochromator. Cross-section samples suitable for TEM observation were made using standard mechanical polishing and argon-ion-milling techniques with the samples held at liquid-nitrogen temperature to minimize artefacts caused by ion-beam damage [25]. Samples were prepared for observation in orthogonal [110]- and [112]-type GaAs projections. The TEM observations and energy-dispersive X-ray spectroscopy (EDXS) were carried out with a Philips-FEI CM200 FEG TEM and a JEOL 2010F FEG TEM. Diffractograms (i.e., fast Fourier transforms) of high-resolution electron micrographs were used to measure lattice-fringe spacings and hence to distinguish between the monoselenide and diselenide phases.

3. Results and Discussion

Figure 1 compares RHEED patterns taken in orthogonal [110] and [112] directions of the GaAs (111) buffer layer, and for samples grown with Se:Sn flux ratios of 3:1 and 40:1. After deposition of tin and selenium for 2 minutes, a streaky RHEED pattern became visible for all samples, as shown in Fig. 1, indicating formation of a reasonably flat surface. Two types of RHEED pattern are observed, depending on the Se:Sn flux ratio. As shown in Fig. 1, the sample with the higher Se:Sn flux ratio yields an unreconstructed pattern with distinctly different features observed for the GaAs [110] and [112] directions. This feature is attributed to the hexagonal symmetry of the surface. On the other hand, a low Se:Sn flux ratio (< 4.6) yields a complex RHEED pattern that is the same for both GaAs [110] and [112] directions. We attribute this to the coexistence of two RHEED patterns, indicating the formation of multigrain structures.

At the beginning of growth, clear RHEED oscillations of the specular spot are observed, with each oscillation corresponding to the growth of one monolayer of the compound being deposited, indicating that the growth of the selenide films is initiated as a layer-by-layer mode. Figure 2 compares RHEED oscillations observed with different Se:Sn flux ratios. We observe for Se:Sn ratios larger than 4.6:1 the period of the oscillations is essentially the same, indicating that the growth rate in this case is directly controlled by the Sn flux. On the other hand, the period of the oscillations for low Se:Sn flux ratios becomes considerably longer (e.g., for Se:Sn = 3:1, the period is 115 sec), indicating that the growth rate in that range is limited by the Se flux.

Figure 3 shows HR-XRD patterns obtained from films grown with two different Se:Sn flux ratios. For the film grown with a Se:Sn ratio of 3:1, only reflections from {200}-type lattice planes of SnSe are visible. For the film grown with Se:Sn ratio of 40:1, only reflections from {001}-type lattice planes of SnSe₂ are observed, which also indicates highly pronounced *c*-axis

growth of the film. Layer thicknesses calculated from the XRD data give the lattice parameter values $d = 11.72 \pm 0.13 \text{ \AA}$ for SnSe and $d = 6.16 \pm 0.01 \text{ \AA}$ for SnSe₂, respectively. These numbers are close to the published values of $a = 11.49 \text{ \AA}$ for bulk SnSe [9], and $c = 6.14 \text{ \AA}$ for bulk SnSe₂ [26,27].

Cross-section electron micrographs of the ~30-nm-thick tin selenide films generally showed flat selenide/GaAs interfaces and relatively flat top surfaces, while improved crystallinity was apparent for the samples grown with higher Se:Sn flux ratios. Observations at higher magnification provided more detailed information about the crystal structure, as well as indicating the presence of structural defects. As an example, Fig. 4 shows two different areas of the tin selenide thin film for the sample grown with the flux ratio Se:Sn = 3:1, which was the lowest flux ratio used in this study. Both images were recorded with the GaAs substrate oriented in the $[1\bar{1}0]$ projection. Overall, the film showed reasonable crystallinity and the structure was consistent with layer-by-layer growth. However, a high density of horizontal stacking faults and dislocations was visible, and the film appeared to have several layers of differing thickness. Figure 4 (a) shows two distinctive layers. The bottom part of the film has a layer that can be identified by digital diffractograms (described later) as SnSe oriented along the $[011]$ direction, while the upper layer is identified as SnSe₂ oriented in the $[0\bar{1}10]$ direction. Figure 4 (b) shows an area that consists primarily of SnSe with many stacking defects. Regions of SnSe₂ were also identified in this sample, although SnSe was the predominant selenide phase that was present.

Figure 5 shows electron micrographs taken from different areas of the film grown with Se:Sn = 4.6:1 flux ratio, where the electron beam is oriented along the $[1\bar{1}0]$ crystal direction of the GaAs substrate in both cases. The film here consists entirely of hexagonal SnSe₂, and it has the epitaxial relationship of $[2\bar{1}\bar{1}0]_{\text{SnSe}_2} // [1\bar{1}0]_{\text{GaAs}}$. The material also displays a considerable

density of horizontal stacking faults and has a thin layer of interfacial defects. The partially crystalline layer visible at the top of the selenide film is the GaAs capping layer.

Figure 6 shows electron micrographs of the tin selenide film grown with the flux ratio of Se:Sn = 10:1, as viewed in the two orthogonal directions identified as $[0\bar{1}10]$ and $[2\bar{1}\bar{1}0]$ for hexagonal SnSe₂. The overall high quality of the SnSe₂ crystal lattice is readily apparent. It is interesting that the SnSe₂ lattice is observed to be tilted by $\sim 0.5^\circ$ with respect to the substrate, as found by comparing the angular alignment of spots in the diffractogram corresponding to the substrate and the film. Fewer defects are present in this sample compared with the samples grown with lower flux ratios, indicating that the crystal quality of SnSe₂ grown on the GaAs (111)B substrate had improved when the Se₂ flux during growth was increased to Sn:Se = 10:1. However, as shown and discussed further below, the density of structural defects was variable from place to place across the film.

Figure 7 shows further electron micrographs of the tin selenide film grown with Se:Sn = 10:1 flux ratio: these correspond to the $[1\bar{1}0]$ GaAs and $[2\bar{1}\bar{1}0]$ SnSe₂ crystal projections. Misfit dislocations, stacking faults, and grain boundaries are visible at different locations. Figure 7 (a) shows a large single crystal grain with relatively few dislocations or stacking faults. Similar to the previous examples, a thin layer is visible near the interface where most of the misfit dislocations are confined. Figure 7 (b) clearly shows a stacking fault and a grain boundary, and there is a small area in the image where two grains seem to overlap along the viewing direction. The left side of the image shows an area of SnSe₂ oriented in the $[0\bar{1}10]$ projection, while the right side of the image shows an area identified as SnSe₂ oriented in the $[2\bar{1}\bar{1}0]$ projection. Figure 7 (c) shows a complete grain of SnSe₂, which is considerably smaller than most that are

visible in the film. The top surface also has noticeable grooves at the grain boundaries. The topography of this grain suggests columnar growth.

Figure 8 shows electron micrographs taken in two orthogonal directions, namely $[0\bar{1}10]$ and $[2\bar{1}\bar{1}0]$, for the tin selenide film grown with the highest selenium to tin flux ratio used in this study (Se:Sn = 40:1). A high quality SnSe_2 crystal with minimal defects is observed with lattice planes that are again found to be tilted by $\sim 0.5^\circ$ with respect to the substrate surface. The growth defects here are mainly confined to a region within a few nanometers of the GaAs substrate surface, most likely due to the lattice mismatch between GaAs and SnSe_2 . The threading defect visible within the bulk of the film (arrowed) can be traced back down to the termination of an extra GaAs monolayer step at the interface, suggesting the possibility of columnar growth.

Figure 9 presents two EDXS spectra from the two tin selenide phases observed in this study. Figure 9 (a) shows the spectrum from the orthorhombic phase of SnSe observed in the selenide film grown with Se:Sn = 3:1. The relative heights of the Sn-L and the Se-K peaks (arrowed) should be noted. For comparison, Fig. 9 (b) shows the spectrum from the hexagonal selenide film grown with Se:Sn = 40:1, and the relative peak heights have changed, reflecting the difference in composition. The relative intensities of the Sn-L and Sn-K peaks arrowed in the two spectra reinforce that the orthorhombic film grown under Se:Sn = 3:1 is SnSe while the selenide film grown under Se:Sn = 40:1 is SnSe_2 .

The crystal structure of the two different films was confirmed by measuring spots that are visible in diffractograms (FFT) of the high-resolution electron micrographs, using the lattice spacings of the GaAs substrate for internal calibration purposes. Examples of diffractograms for the two tin selenide phases in this study are shown in Fig. 10 and the lattice parameters

calculated from these diffractograms are summarized in Table 1. The diffraction spots in Figs. 10 (a) and (b) are consistent with [011] and [012] diffraction patterns, respectively, for the Pnma Space Group using the published SnSe lattice parameters [9]. The diffraction spots in Figs. 10 (c) and (d) are consistent with $[2\bar{1}\bar{1}0]$ and $[0\bar{1}10]$ diffraction patterns, respectively, for the $P\bar{3}m1$ Space Group when the published lattice parameters for SnSe₂ are used [26, 27]. Based on the diffractograms in Figs. 10 (a) and (b), the lattice parameters for the SnSe region of the film grown with Se:Sn = 3:1 were calculated to be $a = 11.7 \text{ \AA}$, $b = 4.61 \text{ \AA}$, and $c = 3.80 \text{ \AA}$, which compare quite closely with the published values of $a = 11.49 \text{ \AA}$, $b = 4.44 \text{ \AA}$, and $c = 4.135 \text{ \AA}$ [9]. The discrepancy on the b and c lattice parameters is possibly due to the limited region of the sample present in the electron micrograph. The lattice parameters for the tin selenide film grown with Se:Sn = 40:1 were calculated to be $a = 3.84 \text{ \AA}$ and $c = 6.14 \text{ \AA}$, which compare closely with the published values of $a = 3.810 \text{ \AA}$ and $c = 6.140 \text{ \AA}$ [26, 27].

The agreement of the measured lattice parameters with those published elsewhere suggests that the tin selenide films grow unstrained despite having large lattice mismatch with the substrate. The GaAs (111) surface shares the six-fold symmetry of the [0001] planes of the $P\bar{3}m1$ structure, which results in the hexagonal selenide film growth direction also being [0001]. Moreover, the tin selenide films display the common epitaxy relationships orthorhombic//GaAs = [011]//[1 $\bar{1}$ 0] and hexagonal//GaAs = $[2\bar{1}\bar{1}0]$ //[1 $\bar{1}$ 0]. However, it was also found that there were some areas of the hexagonal selenide film with $[0\bar{1}10]$ //[1 $\bar{1}$ 0], and the orthorhombic selenide film was ordered in the growth direction but not aligned to a (low-order) zone axis in the other directions.

4. Conclusions

This study has determined that high quality SnSe₂ films can be grown on GaAs (111)B substrates when high Se:Sn ratios ($\geq 10:1$) are used during MBE growth. For the lowest selenium to tin flux ratio of Se:Sn=3:1, defective layers of orthorhombic SnSe of varying thickness were visible, and both SnSe and hexagonal SnSe₂ were observed to coexist. As the flux ratio was increased, the presence of SnSe rapidly diminished. Furthermore, the crystal quality of the 2D SnSe₂ continued to improve with increasing Se₂ flux intensity, with decreasing concentrations of misfit dislocations. As a byproduct of this investigation, it was also observed that the GaAs capping layer deposited on the SnSe₂ retained its crystalline character: this may prove to be important in future attempts at integration of SnSe₂ with GaAs and other semiconductor systems.

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Table 1

Lattice parameters for tin selenide phases as calculated from digital diffractograms of HREM images, and corresponding values for bulk samples published in the literature.

	SnSe Lattice Parameter (Å)		
Se:Sn Flux Ratio	<i>a</i>	<i>b</i>	<i>c</i>
3:1	11.7	4.61	3.80
From Ref. [9]	11.49	4.44	4.135
	SnSe₂ Lattice Parameter (Å)		
Se:Sn Flux Ratio	<i>a</i>		<i>c</i>
3:1	3.80		6.16
4.6:1	3.84		6.14
10:1	3.83		6.07
40:1	3.84		6.14
From Refs. [26,27]	3.810		6.140

Figure Captions

Fig. 1. RHEED patterns for two orthogonal orientations of GaAs (111) substrate during MBE growth of tin selenide compounds. Left panels: GaAs (111) surface; center panels: multigrain growth mode (which is assumed to be dominated by SnSe, based on XRD measurements); right panels: single phase growth mode (ascribed to SnSe₂). Se:Sn ratios indicated at upper right of panels).

Fig. 2. RHEED intensity of the specular point vs. growth time observed for different Se:Sn flux ratios.

Fig. 3. HR-XRD patterns for tin selenide films grown on GaAs (111)B substrates. SnSe forms when the Se flux is weak (Se:Sn = 3), while conditions for formation of SnSe₂ are favorable in the presence of strong Se flux (Se:Sn = 40).

Fig. 4. High-resolution electron micrographs of tin selenide thin film grown with flux ratio of Se:Sn=3:1: (a) region of sample with both SnSe and SnSe₂ phases present; (b) highly defective crystal with many stacking faults resulting in what almost appears to be three ill-defined layers. The substrate projection is GaAs $[1\bar{1}0]$ for both images.

Fig. 5. High-resolution electron micrographs of SnSe₂ thin film grown with flux ratio of Se:Sn = 4.6:1: (a) partially defective single crystal; (b) grain boundary between two crystals. The crystal projections are SnSe₂ $[2\bar{1}\bar{1}0]$ and GaAs $[1\bar{1}0]$ for both images.

Fig. 6. High-resolution electron micrographs of SnSe₂ thin film grown with flux ratio of Se:Sn = 10:1, shown in two orthogonal directions: (a) SnSe₂ $[2\bar{1}\bar{1}0]$ and GaAs $[1\bar{1}0]$; (b) SnSe₂ $[0\bar{1}10]$ and GaAs $[\bar{1}\bar{1}2]$.

Fig. 7. High-resolution electron micrographs of SnSe₂ thin film grown with flux ratio of Se:Sn = 10:1 displaying regions of different crystal quality: (a) single phase crystal, (b) partially defective single crystal with grain boundary on the left; (c) unusual narrow grain. The crystal projections are primarily SnSe₂ [2 $\bar{1}$ $\bar{1}$ 0] and GaAs [1 $\bar{1}$ 0] for all images.

Fig. 8. High-resolution electron micrographs of SnSe₂ thin film grown with flux ratio of Se:Sn=40:1, shown in two orthogonal directions: (a) SnSe₂ [2 $\bar{1}$ $\bar{1}$ 0] and GaAs [1 $\bar{1}$ 0]; (b) SnSe₂ [0 $\bar{1}$ 10] and GaAs [$\bar{1}$ $\bar{1}$ 2].

Fig. 9. Energy-dispersive x-ray spectra recorded for: (a) orthorhombic tin selenide film grown with Se:Sn = 3:1 and (b) hexagonal tin selenide film grown with Se:Sn = 40:1. Arrows indicate peaks for Sn-L (left) and Se-K (right), respectively.

Fig. 10. Diffractograms (fast Fourier transforms) of high-resolution electron micrographs of tin selenide films. (a) and (b) correspond to [011] and [012] projections, respectively, of Space Group Pnma, as measured for the SnSe film grown with Se:Sn = 3:1. (c) and (d) correspond to P $\bar{3}$ m1 along orthogonal orthogonal, [2 $\bar{1}$ $\bar{1}$ 0] and [0 $\bar{1}$ 10] projections, respectively, as measured for SnSe₂ film grown with Se:Sn = 40:1.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10