Effect of off-stoichiometry on properties of tin selenide crystals

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Abstract. The tin selenide crystals with different proportions of Sn and Se were grown by a direct vapour-transport technique. The layer by layer growth of crystals from the vapour phase was promoted by screw dislocation mechanism. The powder X-ray diffraction (XRD) shows good crystallinity of grown compound. The XRD patterns of grown compounds are well-indexed to orthorhombic structure. In the off-stoichiometric compound, evidence of SnSe₂ secondary phase is observed due to excess of selenium. The morphological investigations were carried out using a Carl Zeiss optical microscope. The electron diffraction was also recorded from tiny flakes using a transmission electron microscope. The electrical resistivity both parallel and perpendicular to the *c*-axis was measured in the temperature range of 303–490 K and activation energy was also calculated using Arrhenius relation. The electrical study depicts the extrinsic semiconducting nature of grown compositions.

Keywords. Crystal growth; tin selenide; secondary structure phase.

1. Introduction

In the last few decades, IV–VI semiconductors have attracted great attention due to their unique electrical and optical properties. These layered metal chalcogenides have shown great potential in the optoelectronics field [1–3]. The lamellar semiconductors, such as SnX and GeX (*X* = S, Se) are the most suitable materials for solar cell electrodes due to their appropriate band gap (1–1.4 eV) and their efficiency has been improved by multiple exciton generation i.e., on absorption of one photon, more than one electron–hole pair is generated. The multiple exciton generation improves the photo response of these compound semiconductors [4–6]. There is a growing interest in the semiconductors like SnSe and SnS [7–13], which show promise as a low cost component of photovoltaic cells. In recent years, research has been focussed on tuning of material characteristics for advanced optoelectronic devices. The properties of semiconductors can be significantly improved using conventional ways, such as doping, alloying different semiconductors or off-stoichiometry [14–17]. In the present paper, SnSe with different proportions of Sn and Se crystals have been grown by direct vapour-transport technique and their structural and electrical characterizations have been carried out.

2. Experimental

Tin selenide crystals with different proportions of Sn and Se were grown by direct vapour-transport technique using a dual

zone furnace. For the growth of stoichiometric SnSe (S-A), powder of tin (50%) (6.006 g) and selenium (50%) (3.994 g) in stoichiometric proportion and for S-B with excess Se, Sn (40%) powder (5.006 g) and Se (60%) (4.996 g) were taken in a quartz ampoule. The ampoules were sealed in a vacuum of 10^{−5}–10^{−6} Torr. The sealed ampoule was placed in a dual zone high temperature furnace. The source material placed in one end of ampoule, called the source zone was heated up to 973 K and the other end called the growth zone heated up to 923 K temperature with a heating rate of 24 K h^{−1}. The temperatures were maintained for 80 h for the growth process. During the growth period, reaction between constituents occurs in the quartz ampoule and is transported to the growth zone kept at a slightly low temperature. The temperature difference between the two zones of about 60 K provides the driving force for the transportation of materials. Then, the furnace was cooled to room temperature at the rate of 18 K h^{−1}. The grown crystals were then examined by several characterizing techniques. The elemental compositions were investigated by energy dispersive analysis of X-ray (EDAX). The lattice structure of the grown compound was studied by powder X-ray diffraction (XRD) using a Rigaku Ultima IV powder X-ray diffractometer. The diffraction was taken from powder having tiny crystals with random orientation using CuK α radiation. The crystallographic parameters such as lattice parameters and unit-cell volume were determined. By using the Debye–Scherer formula [18], the crystallite size associated with all the peaks is found and the average crystallite size is also calculated. The surface morphology of the grown crystals was examined by using a Carl Zeiss optical microscope. The grown bulk crystals were cleaved by scotch

tape and sonicated in ethanol. The nanoflakes of the grown samples were dispersed in ethanol. The electron diffraction was then taken by a 200 kV electron beam. Using the two probe method, the electrical resistivity was measured in the temperature range of 303–490 K. The resistance of grown crystals was measured by a Keithly-2700 multimeter.

3. Results and discussion

The dimensions of grown tin selenide crystals are mentioned in table 1. The chemical compositions of grown samples were studied by EDAX analysis. The measured weight (%) of constituents is also tabulated in table 1. The structural phase of grown compositions is confirmed by the powder XRD technique. As shown in figure 1a, the presence of sharp peaks in the XRD pattern is due to the larger crystallite size. The XRD patterns of S-A and S-B are indexed to the orthorhombic structure with space group $16_2 D(Pcmm)$. The results of powder XRD of stoichiometric S-A compound are well matched with standard data (JCPDS card no. 321382) of SnSe. The

peak corresponding to (004) reflection is most prominent. It shows the good stacking of Sn–Se planes along the a – b crystallographic basal plane. However, figure 1b shows that the (004) peak of S-B sample is shifted towards a lower angle side as compared to that of stoichiometric SnSe. Recently, Lim *et al* [16] have demonstrated the effect of Sn-deficiency in Sn_{1-x}Se off-stoichiometric compositions. They have reported that the most prominent (004) peak is not shifted due to Sn-deficiency because in Sn-deficient composition, the SnSe_2 secondary phase is formed and have shown the absence of Sn-vacancies in Sn_{1-x}Se polycrystalline compositions. In the present XRD pattern, shifting of SnSe-type (004) peak is observed due to the rise of strain due to compositional variation. Besides these, due to excess of selenium, peaks corresponding to the SnSe_2 -phase (secondary phase), such as (001) and (101) are also detected in the XRD pattern of the S-B sample.

As shown in table 2, the structural parameters, such as lattice constants, unit-cell volume and crystallite size ($t = 0.9\lambda/\beta \cos \theta$, where λ = wavelength of X-ray radiation, β = full width at half maxima of XRD peaks and θ = Bragg's angle) are calculated. The larger values of crystallite size depict the good crystallinity and well-ordered structure of grown compounds. The lattice constants and unit-cell volume are found to be larger in the S-B compound due to excess of selenium.

Figure 2a shows the presence of irregular steps on the surface due to rapid growth and also confirms the layered growth of crystals. As shown in figure 2b, growth spirals are observed on the surface of the as-grown crystals. It confirms that the growth of crystal was promoted by screw-dislocation mechanism [14,15,19,20]. The rectangular spiral is observed

Table 1. Weight (%) of constituents and dimensions of tin selenide crystals.

Crystals	Weight (%) of constituents obtained from EDAX analysis		Dimensions (mm^3)
	Sn	Se	
S-A	60.06	39.94	$6 \times 5 \times 0.20$
S-B	50.06	49.96	$8 \times 5 \times 0.20$

Figure 1. (a) Powder XRD patterns and (b) magnified pattern of (004) reflection of tin selenide compounds.

Table 2. Crystallographic parameters of tin selenide compounds.

Parameters	S-A	S-B
a (Å)	4.142 ± 0.002	4.155 ± 0.002
b (Å)	4.439 ± 0.002	4.445 ± 0.002
c (Å)	11.466 ± 0.002	11.505 ± 0.002
Volume (Å) ³	210.817 ± 0.026	212.485 ± 0.026
Crystallite size (nm)	73.728 ± 0.015	73.642 ± 0.015

Figure 2. Optical microstructures of (a) layers, (b) spirals and (c) clean surface on the surface of tin selenide crystals.

on the surface of stoichiometric S-A compound and due to off-stoichiometry in S-B, the shape of the spiral is altered. The elongated circular spirals, as shown in figure 2b, depict

Figure 3. (a) TEM image of nanoflakes and (b) SAED pattern of tin selenide samples.

the presence of lattice strain that may be due to excess Se. Figure 2c illustrates the clean surface due to lateral spreading of the grown layers. Such surfaces without any dangling bond and impurity centres can be found of great importance for device fabrication. The tiny crystals of grown samples were dispersed in acetone and sonicated for 30 min. The dispersed solution was drop cast on a copper grid and used for TEM analysis. The nanoflakes are observed in TEM images as shown in figure 3a. The electron diffraction was taken from tiny flakes and representative selected area electron diffraction (SAED) patterns are shown in figure 3b. The spot pattern is observed for prepared samples.

Temperature-dependent resistivity of the grown crystals was measured in the temperature range of 307–493 K. The resistivity measurements were carried out in parallel and perpendicular to the crystallographic c -axis. The resistivity of samples decreases continuously on increasing temperature in the mentioned temperature range and it suggests the semiconducting nature of samples. Due to the presence of the SnSe_2 secondary phase, the resistivity values of off-stoichiometric sample S-B are found to be lower than that of stoichiometric SnSe [16]. The resistivity-temperature curves are seen to be exponential in nature and Arrhenius relation [21] is applied to experimental data and $\log(\text{resistivity})$ vs. $1000/T$ curves are plotted as shown in figure 4. The activation energy is also determined. The activation energy of S-B compound is 0.071 eV for perpendicular to c -axis measurements and 0.156 eV for parallel to c -axis measurements. However, for the off-stoichiometric S-A compound, activation energies are 0.108 and 0.178 eV for perpendicular and parallel measurements, respectively. Relevant to resistivity values, the activation

Figure 4. Temperature-dependent resistivity (a) perpendicular and (b) parallel to the crystallographic c -axis and (c) anisotropy variation for tin diselenide crystals.

energy of the off-stoichiometric compound is lower than the stoichiometric compound. The smaller values of activation energy show the extrinsic nature of conduction mechanism.

It is noted from figure 4 that resistivity in the parallel direction is larger than that in the perpendicular direction to the c -axis. It shows anisotropic electrical charge conduction in grown samples. The anisotropy ratio is also calculated and presented in figure 4c. The anisotropy is found to be decreased on increasing the temperature because on increasing the temperature, the flow of charge carriers starts across the layers due to the hopping process. The values of activation energy are seen to be larger for conduction of carriers parallel to the c -axis than that in perpendicular to the c -axis, which also confirms the presence of anisotropy. The anisotropy in electrical conduction is due to a unique anisotropic structure in which the atoms are bonded together by strong covalent bonds in basal planes and these planes are stacked upon one another by weak van der Waals interactions. The different interactions

lead to different inter-atom spacing along the basal plane and across the basal plane. Hence, the electrical transport also becomes anisotropic.

4. Conclusions

The crystals of tin selenide with different proportions of Sn and Se were grown by the direct vapour-transport technique and have thin plate-like appearance with micro-sized thickness. The grown samples have orthorhombic structures with the space group ($Pcmn$). The XRD pattern of S-B with excess selenium shows the presence of the $SnSe_2$ phase due to excess of selenium and strain rises in the lattice structure. Hence, growth of aimed composition i.e., Sn (40%):Se (60%) is not achieved. However, the $SnSe$ -type (004) peak is shifted on the lower angle side due to excess of selenium and it suggests changes in the $SnSe$ -lattice structure which was aimed for

the present research. The surface morphological investigation displays a layered structure, spirals and clean surface. The TEM patterns of the grown samples indicate the presence of single crystalline nature of tiny flakes. The electrical investigation confirms the semiconducting nature of the grown samples. The extrinsic charge conduction is found in tin selenide samples.

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