Structural and optical properties of Sb\textsubscript{x}Se\textsubscript{y} thin films obtained by chemical molecular beam deposition method from Sb and Se precursors

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\textbf{ABSTRACT}

Sb\textsubscript{x}Se\textsubscript{y} thin-films were obtained by chemical-molecular beam deposition (CMBD) on soda-lime glass from Sb and Se precursors. By the precise control of the Sb/Se ratio, Sb\textsubscript{x}Se\textsubscript{y} thin films with stoichiometric composition were successfully obtained. The elemental and phase composition, as well as the crystal structure of Sb\textsubscript{x}Se\textsubscript{y} thin-films, were studied by energy-dispersive X-ray microanalysis, X-ray diffraction, Raman spectroscopy, scanning electron microscopy and atomic force microscopy. The optical bandgap of the films was determined from the absorption spectra acquired by a spectrophotometer. The physical properties of Sb\textsubscript{x}Se\textsubscript{y} thin films with different compositions were investigated.

1. Introduction

Among binary composite semiconductors, antimony selenide Sb\textsubscript{x}Se\textsubscript{y} has been intensively studied over the last decade as an absorbing layer for thin-film solar cells since it has a strong absorption of sunlight $\alpha > 10^5$ (Zhou et al., 2014) and an optimal band gap of 1.1–1.3 eV for a single-junction solar element (Chen et al., 2017; Spalatu et al., 2021). The one-dimensional ribbon structure of (Sb\textsubscript{x}Se\textsubscript{y})\textsubscript{n} has strong anisotropic properties (Kim et al., 2017; Zhou et al., 2015) and high theoretical conversion efficiency (31% according to the Shockley–Queisser detailed balance model) (Rühle, 2016) providing excellent properties. In addition, the elements that make up these materials have a relatively low cost, with amphibiuous Sb and Se with contents of 0.2 and 0.05 ppm (parts per million), respectively, resistance to external influences and nontoxicity (Zeng et al., 2016). At present, the efficiency of thin film solar cells based on Sb\textsubscript{x}Se\textsubscript{y} in a nonplanar configuration is 9.2% (Li et al., 2019). The efficiency of an Sb\textsubscript{x}Se\textsubscript{y} solar cell is highly dependent on the physical properties of the base layer as well as the growth method. Sb\textsubscript{x}Se\textsubscript{y} films have been synthesized by various methods (rapid vacuum thermal evaporation (Wang et al., 2017), magnetron sputtering (Ma et al., 2019), chemical bath deposition (Maghraoui-Meherzi et al., 2013), pulsed laser deposition (Mavlonov et al., 2020b) etc.), but all these methods required additional processes to improve the physical properties, such as selenization and subsequent annealing (structural, morphological and optical) of the absorbing layer. In our method, we can obtain different compositions of thin films without additional procedures by changing the temperature of the precursors during growth.

Due to the ribbon-like structure and 1-D conductivity, in the literature, Sb\textsubscript{x}Se\textsubscript{y} films with crystal orientation (hk1) were more efficient for application in photovoltaics, while (hk0) was less efficient (Chen et al., 2017; Li et al., 2019; Razykov et al., 2019). Therefore, by varying the synthesis conditions and methods, it is possible to obtain highly efficient Sb\textsubscript{x}Se\textsubscript{y} thin films with the texture required for solar cells. Such a structure induces anisotropic optical and electrical properties. The film surface morphology also differs, greatly depending on the conditions (substrate and source/source temperatures) and the synthesis method (Chen et al., 2017; Mavlonov et al., 2020b).

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2. Experimental

2.1. Fabrication of thin films

Sb$_x$Se$_y$ layers were deposited by chemical molecular beam deposition (CMBD). A schematic representation of the CMBD method is shown in Fig. 1. In the presence of 99.999% high purity Sb and Se beads, Sodalime glass (SLG) was used as a substrate. The SLG substrates were cleaned with detergent, acetone, ethanol, and deionized water in an ultrasonic bath and finally dried with a stream of N$_2$ gas. The Sb and Se granules were placed separately on quartz crucibles in an evaporation chamber. Quartz crucibles were subjected to heat treatment from special molybdenum heaters, and Sb and Se granules were melted and evaporated from the crucibles at atmospheric pressure with gaseous hydrogen at a flow rate of 20 cm$^3$/min. Sb$_x$Se$_y$ thin films with a substrate temperature of 500 °C were obtained at Sb 950–1000 °C and Se 480–500 °C at an evaporation time of 30 min. The 2–3 μm thickness of the thin films was determined using a MIM-7 microscope.

At the Sb (950–1000 °C) and Se (480–500 °C) evaporation temperatures, granules transfer into the vapour phase (Eq. (1)):

$$\text{Sb(s)} + 2\text{Se(s)} + \text{H}_2 = \text{Sb(g)} + \text{Se}_2\text{(g)} + \text{H}_2$$  

(1)

$$\text{Se}_2\text{(g)}$$ reacts with hydrogen, and hydrogen selenide is formed (Eq. (2)):

$$\text{Se}_2\text{(g)} + 2\text{H}_2 = 2\text{H}_2\text{Se(g)}$$  

(2)

Sb and Se atoms and H$_2$Se molecules cover the surface of the substrate, and Sb$_x$Se$_y$ films are formed as a consequence of their interaction (Eq. (3)):

$$3x\text{Sb(g)} + y\text{Se}_2\text{(g)} + \text{H}_2\text{Se(g)} = 3\text{Sb}_x\text{Se}_y\text{(s)} + \text{H}_2$$  

(3)

The composition of Sb$_x$Se$_y$ films was controlled by changing the Sb/Se ratio in the vapour phase mixture of Sb and Se (evaporated amount), which was varied by the molecular beam intensities of Sb and Se.

2.2. Measurement and characterization

We analysed Sb$_x$Se$_y$ thin films using various techniques to determine how different ratios of Sb/Se affected the crystal structure, morphology, and optical properties of the films. The crystal structure was performed by using an Ultima IV (Rigaku) X-ray diffractometer in the grazing incidence diffraction geometry (GIXD) at 1 degree of incident X-rays with CuKα radiation source (λ = 1.54178 Å). XRD analysis was carried out with the use of the database of the Joint Committee on Powder Diffraction Standard (JCPDS) and Crystallography Open Database (COD). Raman spectra were measured at room temperature, using a Nanofinder HE (LOTIS TII) confocal spectrometer. A solid-state laser, with a radiation wavelength of 532 nm, was used to excite. The power of laser radiation incident on the samples was reduced to 60 μW, to avoid thermal damage. Spectral resolution was better than 2.5 cm$^{-1}$. The size of the area, on which the laser radiation was focused on the surface of the samples, was about 0.7 μm in diameter. The surface morphology and topography were investigated by using a LEO-1455 VP (Carl Zeiss) scanning electron microscope (SEM) and a Solver Nano (NT-MDT) atomic force microscope (AFM). The AFM instrument was used in the semi-contact mode, with a scanning probe of 10 nm tip radius, at a resonance frequency of 236 kHz. The chemical composition was determined by energy dispersive X-ray (EDX) analysis using an Aztec Energy Advanced X-Max 80 (Oxford Instruments) spectrometer. The absorption spectra of the films were acquired by a spectrophotometer UV-1280 (Shimadzu).

3. Results and discussions

To determine the composition of the grown films, EDX analysis was carried out (see Fig. 2). According to the EDX analysis, the Sb/Se ratio in the films was 0.66, 0.73, and 0.85. And found a direct linear dependence between the ratio of the flow of raw materials in the vapour phase and the composition of the obtained film (solid phase). Such a linear dependence makes it quite easy to form films of a given composition.

The surface morphology was investigated using SEM imaging. Fig. 3 (a, b, c) shows the surface morphology of Sb$_x$Se$_y$ thin films on SLG at a substrate temperature of 500 °C. All Sb$_x$Se$_y$ thin films exhibited compact surface morphology. The grain sizes of Sb$_x$Se$_y$ thin films, which consist of a dense columnar structure at an angle from 0° to 60° to the substrate, were between 0.5 ÷ 10 μm. Average diameters and lengths of Sb$_x$Se$_y$ rods deposited at 0.66 and 0.73 Sb/Se ratios were nearly the same at 2 ÷ 5 μm and 0.5 ÷ 2 μm, respectively. At a 0.85 ratio, the length of the rods was between 4 and 10 μm. The size of Sb$_x$Se$_y$ rods is larger with the

![Fig. 1. Schematic representation of the CMBD method for obtaining Sb$_x$Se$_y$ thin films. 1, 2 – substrate and holder, 3 – substrate heater, 4 – source heaters, 5 – crucibles of evaporated components, 6 – reactor cap, 7 – flange, 8 – gas inlet, 9 – gas outlet, 10 – thermocouples.](image1)

![Fig. 2. Dependency of Sb/Se ratios in vapour and solid phases.](image2)
increase of Sb/Se ratio. This result suggested that a lower percentage of Se atoms in the Sb\textsubscript{x}Se\textsubscript{y} thin films leads to a larger grain size in the Sb/Se ratio range of 0.66–0.85.

Additionally, the distribution of Sb and Se contents among the exact lines on the film surface were determined by EDX measurements. As shown in Fig. 3 (d, e, f), Sb and Se atoms were distributed stably. As the ratio Sb/Se approaches the stoichiometric, long rods turn into shorter and smoother grains. From these EDX data, it was observed that the increase in Se content in the solid phase was directly proportional to the Se content in the vapour phase during the growth process.

Surface morphology-like average surface roughness studies carried out using atomic force microscopy (Fig. 4) showed that Sb\textsubscript{x}Se\textsubscript{y} films have a developed surface relief in the range of ~ 0.4–0.7 μm. All AFM parameters for Sb\textsubscript{x}Se\textsubscript{y} films are given in Table 1. The average and root-mean-square roughness of the surface decreases with the approach to the stoichiometric ratio. When the surface skewness increases from the characteristic values of the normal distribution (zero skewness reflects symmetrical height distribution) to a value of 0.44. This corresponds to the prevalence of surface peaks over valleys and may indicate the observation of a profile with filled valleys (Gadelmawla et al., 2002).

The values of the kurtosis for the stoichiometric ratio correspond to the normal character of sharpness of the surface height distribution (Ska ~ 3). And for selenium-depleted films, the surface has a platykurtic character (Gadelmawla et al., 2002).

GIXD measurements were taken on different samples to establish the phase composition and determine the preferred orientation of Sb\textsubscript{x}Se\textsubscript{y} layers. As shown in Fig. 5a, all diffraction lines belong to orthorhombic Sb\textsubscript{2}Se\textsubscript{3} phase (JCPDS 15–0861). The obtained diffraction patterns are in good agreement with the standard pattern, indicating good crystallinity of the films, while no other phases were detected. Virtually no noticeable change in texture is observed for the different Sb/Se ratios, consistent with the apparent stability of the synthesis process up to this point.

It is known that Sb\textsubscript{2}Se\textsubscript{3} films consist of one-dimensional (Sb\textsubscript{4}Se\textsubscript{6})\textsuperscript{n} ribbons stacked along the [001] direction due to Sb-Se covalent bonds, while (Sb\textsubscript{4}Se\textsubscript{6})\textsuperscript{n} ribbons are held together by Van der Waals forces between the ribbons (Deringer et al., 2015; Filip et al., 2013; Zhou et al.,

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**Table 1**

<table>
<thead>
<tr>
<th>Samples (Sb/Se)</th>
<th>0.85</th>
<th>0.73</th>
<th>0.66</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughness average Sa, um</td>
<td>0.72</td>
<td>0.46</td>
<td>0.43</td>
</tr>
<tr>
<td>Root Mean Square Roughness Sq, um</td>
<td>0.89</td>
<td>0.56</td>
<td>0.55</td>
</tr>
<tr>
<td>Skewness Ssk</td>
<td>0.10</td>
<td>0.13</td>
<td>0.44</td>
</tr>
<tr>
<td>Kurtosis Ska</td>
<td>2.78</td>
<td>2.77</td>
<td>3.08</td>
</tr>
</tbody>
</table>

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**Fig. 4.** AFM images of Sb\textsubscript{x}Se\textsubscript{y} thin films with different compositions.
To analyze the change in texture, 11 lines were selected that have the highest intensity: (0 2 0), (1 2 0), (1 3 0), (2 3 0), (2 1 1), (2 2 1), (3 0 1), (3 2 1), (4 3 1), (6 0 1). To determine the difference in orientations of thin films deposited at different Sb/Se ratios, the texture coefficient (TC) of different oriented peaks of samples was calculated by the following Eq. (4) (Li et al., 2017):

$$\text{TC}_{\text{(hk)l}} = \frac{I(hkl)}{\sum_{l=1}^{N} I(hkl)}$$

where $I(hkl)$ and $I_0(hkl)$ are the diffraction peak intensities of the $(hkl)$ planes in the measured and standard XRD patterns of Sb$_2$Se$_3$ (JCPDS 15–0861), respectively; $N$ is the total number of orientations considered for the calculation. A larger TC value indicated a preferred orientation of the grain along this direction (Fig. 5b).

For the Sb$_2$Se$_3$ thin films prepared at a stoichiometric Sb/Se ratio of 0.66, the intensity of the peaks (hk1) is stronger than that of the peaks (hk0) — for samples with the Sb/Se ratios of 0.73 and 0.85. The ratio of the sum of TC lines (hk1) such as (2 1 1), (2 2 1), (3 0 1), (3 2 1) and (0 6 1) to the sum of TC lines (hk0) such as (0 2 0), (1 2 0), (1 3 0), (2 3 0) and (2 4 0), is equal to 1.2. Accordingly, peaks with the preferred orientation (hk1) are dominant, which are attributed to vertically oriented ribbons. Among the orientations (hk1), the preferred orientations (2 1 1) and (2 2 1) became more intense. (hk1)-Oriented grains, consisting of (Sb$_2$Se$_3$)$_n$ ribbons, have a certain angle of inclination with the substrate, which has the best carrier transport ability (Guo et al., 2019). It can be imagined that the transfer of carriers in the direction of the preferred (hk1) orientation will be easier than in the direction of the (hk0) orientation, which prevents the movement of carriers through the volume.

In addition, theoretical calculations have shown that the formation energy varies depending on the crystal orientations. For example, the (hk0) orientations, i.e. corresponding to the (1 1 0) and (1 2 0) planes, have lower formation energies compared to other crystal orientations because of the absence of dangling bonds in the (hk0) orientations (Mavlonov et al., 2020a; Zhang et al., 2021). As a result, these preferred orientations have been found to be useful for designing high-performance Sb$_2$Se$_3$-based solar cells (Choi et al., 2014; Wen et al., 2018) due to less recombination and improved carrier transport due to its soft grain boundaries and better carrier transport capability. Thus, the Sb$_2$Se$_3$ films exhibited strong anisotropy. This unique trend appears to be related to the anisotropic properties of the one-dimensional crystal structure of Sb$_2$Se$_3$ (Lei et al., 2019).

Raman scattering measurements were performed for more details about the structure of Sb$_2$Se$_3$ thin films deposited at different Sb/Se ratios, as indicated in Fig. 6. As seen from the figure, the Raman spectra display peaks at approximately 80, 100, 126, 145, 153, 190, 211, 237 and 441 cm$^{-1}$. The peaks at approximately 80, 100, 126, 153, 190, and 211 cm$^{-1}$ are commonly reported and assigned to the Sb$_2$Se$_3$ phase (Kumar et al., 2021; Lei et al., 2019; Shongalova et al., 2018a). The peak at about 153 cm$^{-1}$ has been attributed to the $A_g$ mode of the Sb–Sb bond (Lei et al., 2019), while the peaks at about 190 and 211 cm$^{-1}$ are commonly assigned to the $A_g$ mode of the Sb–Se–Sb bending vibrations of Sb$_2$Se$_3$ (Kumar et al., 2021; Shongalova et al., 2018a). In (Vidal-Fuentes et al., 2019), the peaks at 80 and 100 cm$^{-1}$ are also designated as $A_g$ vibrations. The sample with an Sb/Se = 0.66 ratio exhibits peaks at 80, 145, 237 cm$^{-1}$ (441 cm$^{-1}$ is second order of 237 cm$^{-1}$), which are attributed to the trigonal Se stretching vibration mode in Sb$_2$Se$_3$ (Nagata et al., 1981; Shongalova et al., 2018b; Vidal-Fuentes et al., 2019), which agrees with elemental analysis of this samples.

The corresponding Tauc plots for the Sb$_2$Se$_3$ thin films are shown in Fig. 7a. The optical band gap ($E_g$) of samples can be calculated according to the Tauc formula (Eq. (5)) (Yang et al., 2020):

$$\alpha(hv) = A(hv - E_g)^n$$

where $\alpha$ is the absorption coefficient, $hv$ is the photon energy, $A$ is a constant, and $n$ is a dimensionality factor (Fig. 7b). The values of $E_g$ for the different Sb/Se ratios are shown in Fig. 7b. The results show that the optical band gap decreases as the Sb/Se ratio increases.
constant related to effective mass, and $n$ is equal to 2 and 1/2 for direct and indirect bandgap semiconductors, respectively. Here, $n$ equals 2 because Sb$_{x}$Se$_{y}$ has a direct bandgap, and $E_g$ for various compositional thin films is determined to be 1.09, 1.14 and 1.17 eV for 0.85, 0.73 and 0.66 Sb/Se ratio samples. A slight change in the band gap width compared with pure Sb$_{x}$Se$_{y}$ thin film (1.15 eV) (Chen et al., 2015) was observed due to the change in atomic arrangement from disorder to order. These results indicate that the structural and optical properties of Sb$_{x}$Se$_{y}$ thin films are closely related to the Sb/Se ratio, which is consistent with previous reports (Jiang et al., 2020).

To study the structural disorder of Sb$_{x}$Se$_{y}$ films, the Urbach energy ($E_U$) was also calculated. The existence of an exponential increase in the absorption coefficient near the band edge (Urbach tail) indicates the presence of localized states or impurity states in the band gap region that causes disturbance in the band structure of the polycrystalline films. The value of $E_U$ indicates the level of crystallinity and structural defects present in the films. In the low photon energy range, an exponential variation in the absorption edge followed the Urbach empirical equation (Eq. (6)):

$$
\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_U} \right) \tag{6}
$$

where $\alpha_0$ is a constant. The value of $E_U$ can be obtained from the inverse slope of the linear plot of $\ln(\alpha)$ vs $h\nu$ (Fig. 7b). The lower value of $E_U$ at elemental composition approaching the stoichiometric ratio indicates the decrease in structural defects and localized states density in the band gap region of the films.

4. Conclusions

In conclusion, we systematically studied the morphological, structural, and optical properties of Sb$_{x}$Se$_{y}$ films with different compositions produced from separate sources of Sb and Se by the CMBD method. Our CMBD method performs an excellent control to tune the band gap of Sb$_{x}$Se$_{y}$ films by changing the Sb/Se ratio during the growth process and the evaporation temperature. SEM imaging shows the surface morphology of Sb$_{x}$Se$_{y}$ thin films deposited on SLG at a substrate temperature of 500 °C. All Sb$_{x}$Se$_{y}$ thin films showed compact surface morphology. The average diameters and lengths of Sb$_{x}$Se$_{y}$ thin film rods, which consist of a dense columnar structure grown with an angle from 0° to 60° respect the substrate, ranged between 0.5 - 2 µm and 2 - 10 µm, respectively. From EDX data, it was observed that the increase in Se content in the solid phase was directly proportional to the Se content in the vapour phase during the growth process. The grazing incidence X-ray diffraction study describes that Sb$_{x}$Se$_{y}$ thin films with micro-sized crystal grains exhibit (hk1) preferential orientation at the stoichiometric composition. The Raman spectroscopy measurement shows that there is a blueshift of most of the Raman peaks of Sb$_{x}$Se$_{y}$ samples; as a result, we can conclude that there might be a slight amount of compressive strain present in the film structure. The direct band gap obtained from Tauc’s plot indicate that deposited Sb$_{x}$Se$_{y}$ films are suitable for thin-film photovoltaics. Calculated value of the Urbach energy indicates low density of localized states in the band gap region for Sb$_{x}$Se$_{y}$ films, synthesized with an elemental ratio close to stoichiometry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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