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INVESTIGATION ON STRUCTURAL AND OPTICAL PROPERTIES OF THERMALLY EVAPORATED SnSeTHIN FILMS

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Impact of thickness on the structural and optical properties of SnSe thin films prepared by thermal evaporation technique is reported. The thicknesses of the films were varied between 100 and 300 nm. The hexagonal crystalline structure was observed on 100 nm thickness film and it turnedto orthorhombic crystal structure with increasing thickness at 300 nm. The average crystalline sizesvaried between 6 and 18 nm. The lattice constants (a, b, c) were calculated for both the crystal structure. The optical band gap was found to be larger than the bulk value of SnSe. The room temperature photoluminescence spectra also studied and discussed.

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1. Introduction

Tin chalcogenides (SnS, SnTe and SnSe) are the great deal of attention over a last few decays due to its optical and optoelectronics applications. Among these, Tin Selenide (SnSe) is an important material which has wide range of applications such as solar cells [1] and the knowledge of its various properties has widely contributed [2-5]. In recent years, SnSe plays a vital role in phase change memory devices[2, 5] due to its low crystallization and high melting temperature in certain conditions. Recently, we reported the phase change behaviour of SnSe to $SnSe_2$ in multilayer thin films [6]. Most of the work in SnSe thin films are based on chemical route [1, 3-5], while few reports available on physical method such as PVD with high substrate temperature [7, 8]. It is worth to note that for phase changing application, the thin films prepared with room temperature substrates are preferable since the amorphous to crystallization is easily occur upon annealing in room temperature grown thin films [2]. With this consideration, the first step toward phase change memory application of SnSe thin films have been carried out as a function of films thickness. The structural and optical properties of the as grown films are carried out and the results are compared with those reported previously.

2. Experimental

SnSe thin films were prepared by thermal evaporation technique on ultrasonically cleaned glass substrates kept at room temperature. The high purity SnSe pellet (Alfa aesar, 99.999%) was placed in a Molybdenum boat (200Å) with the separation of the boat and substrates was 25 cm. The source material (SnSe) was heated with applying current at vacuum pressure of 10^{-5} torr and deposited with different thickness. The thicknesses of the films varied between 100nm to 300 nm were prepared, while the thicknesses of the films were monitored using in -situ quartz crystal thickness monitor. The structural properties of as deposited films were carried out using Shimadzu

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(XRD-6000) X-ray Diffractometer. The optical properties of the prepared films were analysed using UV-VIS-NIR spectrophotometer (Jasco-570 UV/VIS/ NIR Spectrophotometer) in the range of visible range. Room temperature Photoluminescence analysis was carried out with Xenon lamp using Fluoromax-4 spectrophotometer.

3. Results and discussion

3.1 Structural studies

The X-ray diffraction (XRD) pattern of SnSe thin films deposited on glass substrate at different thickness is shown in fig 1. It is observed that the progressive emergence of the diffraction peak for 200 and 300 nm films located at 30.7° underlining a strong preferential orientation growth along the crystallographic plans (1 1 1), which corresponds to SnSe orthorhombic structure [JCPDS card no: 32-1382]. These results are in good quantitative agreement with previous reports on chemical and physical route methods [1-5]. In general,SnSe films would crystallize in orthorhombic, cubic and hexagonal structure depending on the deposition technique and temperature treatment.

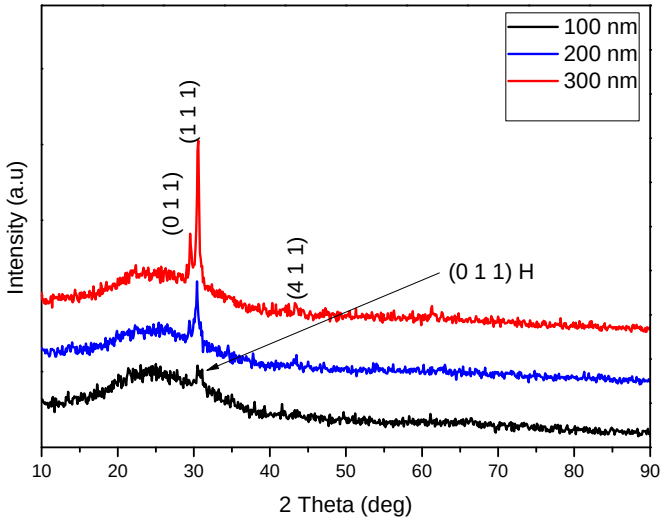

Fig.1. XRD pattern of SnSe thin films with various thicknesses.

For instance, our previous work on thermally evaporated SnSe multilayer films exhibits orthorhombic crystal structure while cubic crystal structure was observed upon annealing [6]. Kyung-Min Chung et al. [2] observed the mixed phases like SnSe, $SnSe_2$ and $Sn2Se_3$ due to annealing.In this present case, the films as prepared with 100 nm thickness exhibits hexagonal structure [JCPDS card no: 89-3197] with slightly amorphous in nature. The diffraction intensities gradually increased with increasing films thickness and full width half maximum of these peaks decreased. This could be attributed to the improvement of the crystallinity of SnSe thin films and removal of defects with increasing thickness. It is also noted that the secondary phase of (0 1 1) is observed with increasing film thickness. Similar,XRD pattern was observed with different annealing temperatureon SnSe films [9].The crystalline size was calculated using Debye Scherer's equation [10] and the lattice constant was determined using the equation given by[11],

Table.1. Structural parameters of SnSe thin films with different thicknesses.

Thickness (nm)	2θ (deg)	d-spacing (Å)	FWHM (Å)	Crystalline size (Å)	Lattice constant (Å)		
					A	**B**	**C**
100 (H)	30.7417	2.90607	1.3500	61	3.82	-	6.23
200 (O)	30.5154	2.92711	1.0770	76	11.43	4.21	4.51
300 (O)	30. 3555	2.94216	0.4528	181	11.42	4.18	4.47

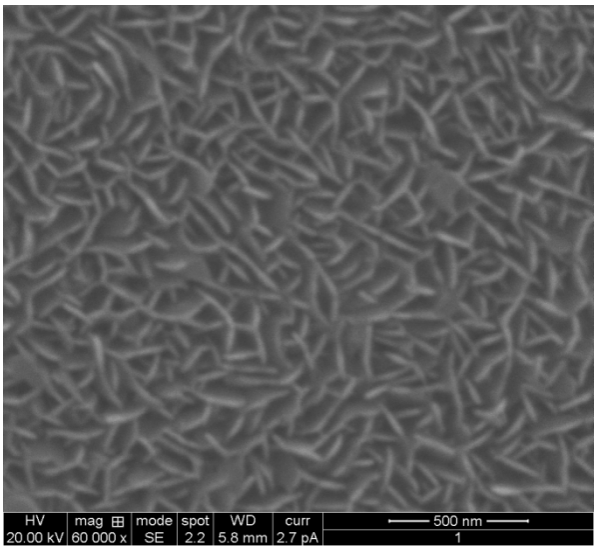

Fig.2.SEM image of SnSe thin film (300 nm thickness).

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{For orthorhombic} \quad (1)$$

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \text{For hexagonal} \quad (2)$$

The structural parameters such as grain size (D) and lattice constant were evaluated using appropriate equation and are listed in table 1. From the Table.1, it is noted that the diffraction peak (2θ) slightly shifted to lower angle side with increasing film thickness and that may be attributedthephase change from hexagonal ($SnSe_2$) to orthorhombic (SnSe) structure. The determined lattice constants also agreed with the possibilities for phase change of SnSe films at higher thickness. However for phase change recording technology, it is normally amorphous to crystalline with small applied current in the form of Joule heating. The SEM image on the morphology of the SnSe thin film with the thickness of 300 nm is shown in Fig.2. The surface shows a uniform facet like structure.

3.2 Optical studies

Optical properties of the SnSe films were examined by optical absorption, transmittance and photoluminescence measurements.The optical absorption and transmission measurements were carried out on the SnSe thin films having different thickness in the wavelength range of 200-900 nm. The absorption spectrum as a function of wavelength is shown in Fig.3 and the inset in the same figure shows the transmittance spectra of SnSe films.

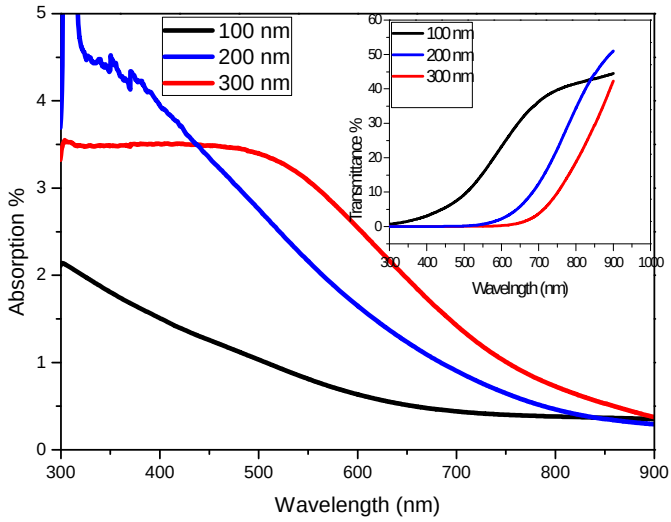

Fig.3. Optical absorption spectra of SnSe thin films with various thicknesses. Inset shows the transmittance spectra of the same thin films.

The fundamental absorption edge is one of the most important features of the absorption spectrum of a semiconductor. The increased absorption near the edge is caused by the transition of electron from the valance band to conduction band [12]. From Fig.3, we can obviously see that the absorption edge is shifted to longer wavelength with increasing thickness and this is due to the presence of more atoms in the thicker films. Here we are not disusing about the hexagonal to orthorhombic formation but it is rather good to discuss with amorphous to crystalline formation in this work. The optical band gap (E_g) values are calculated from absorption spectra using absorption coefficient (α) in the strong absorption region by Tauce relation [13],

$$\alpha = \frac{A}{h\gamma}(h\gamma - E_g)^n \tag{3}$$

The absorption coefficient (α) in strong absorption region can be estimated from Lambert's law [14]

$$\alpha = 2.303 \times \frac{Absorption}{t} \tag{4}$$

Where A is a constant and E_g is the band gap of the material and exponent n depends on the type of transition. For direct allowed n = 1/2, indirect allowed transition, n = 2, and for direct forbidden, n = 3/2 and t is the thickness of the film. The variation of $(\alpha h\gamma)^2$ versus photon energy (hγ) is shown in Fig. 4 andis linear at the absorption edge confirmed that direct band gap transition in SnSe films. Extrapolating the straight-line portion of the plot $(\alpha h\gamma)^2$ versus hγ gives the values of optical band gap.

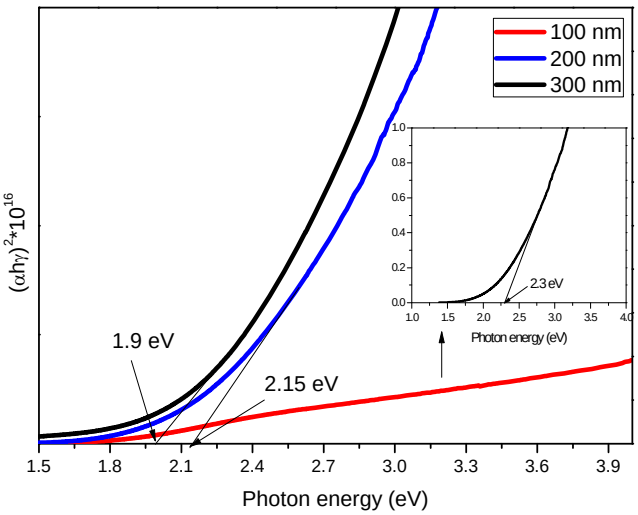

Fig.4. Optical band gap of SnSe thin films with different thicknesses.

The evaluated E_g values are varied from 1.9 to 2.3 eV for different thickness. It is significantly higher than the band gap value of bulk SnSe (1.3 eV). The band gap value at low thickness (100 nm) found to be wide band gap (2.3 eV) than other thickness; it may be due to the amorphous nature of the films. Hence, it can be related with the XRD pattern for the 100 nm thickness film. This comparable feature in optical band gap was obtained by many authors [8-11]. This size effect is beneficial for several optical applications like the photovoltaic devices, blue light emitting diodes, solar cells and laser diodes.

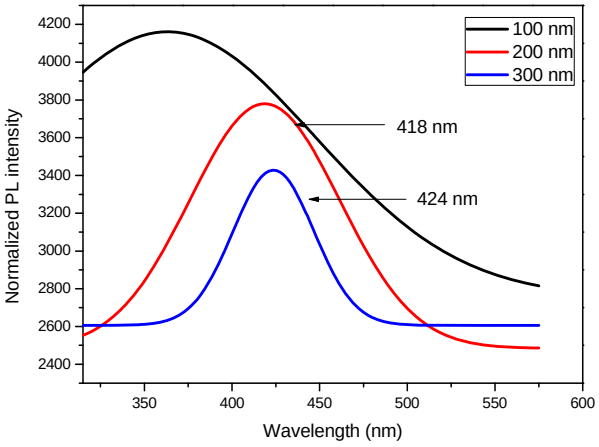

Fig.5. Room temperature PL spectra of SnSe thin films.

The photoluminescence (PL) spectral distribution of SnSe thin films deposited with the thickness of 100 to 300 nm under the excitation with a wavelength of 350 nm is shown in Fig.5. The well resolved peak centred at 418 and 424 was observed on the films with the thickness of 200 and 300 nm respectively, which is associated with band to band transition of SnSe thin film. The comparable feature was observed on colloidal SnSe quantum dots [15].The film with amorphous nature (100 nm) not showing any well resolved features.The position of the peak slightly changes with thickness could be attributed to the change in grain size. The absorption edge of the transmittance and absorption spectra also start at around 400 nm, which sustain the PL result shown in Fig.5. The intensity of the peak decreases with thickness can be explained in terms of surface defects as seen by the XRD.

4. Conclusion

Tin Selenide thin films were prepared by thermal evaporation technique onto room temperature glass substrates. Phase change formation from hexagonal to orthorhombic crystal structure was observed with increasing film thickness. The calculated lattice constants also agreed with the phase change upon increasing film thickness. The calculated crystalline size varied between 6 and 18 nm and the optical band gap varied between 1.9 and 2.3 eV. The room temperature photoluminescence emission centred at around 420 nm indicates the band to band transition of the prepared material. Further, the indication of the phase change even upon increasing film thickness may lead to phase change application with controlled crystallization and melting temperature.

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