

## **The Effect of Selenization Temperature on Morphological and Structural Properties of Tin Diselenide Thin Films Grown by a Two-Stage Process**

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**Abstract:** Tin diselenide ( $\text{SnSe}_2$ ) thin films were prepared on soda lime glass substrates by selenization of dc magnetron sputtered Sn metallic precursors. Selenization was performed at three different temperatures 300°C, 350°C and 400°C for a fixed selenization time of 30 minutes. The effect of selenization temperature on the surface morphology of the grown films was evaluated using scanning electron microscopy (SEM). The structure of as-deposited films was investigated by X-ray diffraction and the phases present using Raman Spectroscopy. The surface morphology revealed the plate like particles grown uniformly over the substrate surface. The X-ray diffraction pattern indicated that the films formed at 350°C composed of  $\text{SnSe}_2$  with the preferred (001) orientation, exhibiting hexagonal structure while the layers formed at other temperatures had secondary phases. Raman analysis allowed the identification of phases present in the layers that showed a strong peak at  $180\text{cm}^{-1}$  due to the  $\text{SnSe}_2$  phase.

**Keywords:**  $\text{SnSe}_2$ , SnSe, Sputtering, Selenization, SEM, XRD, Raman spectra.

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### **1. INTRODUCTION**

Metal chalcogenide thin films have attracted the attention of researchers due to their interesting optical and electronic properties. These are preferred compounds for application in infrared optoelectronic devices, radiation detectors, memory devices, holographic recording systems, thermoelectric refrigerators and solar cells. In particular, IV – VI selenide compounds such as SnSe and  $\text{SnSe}_2$  are treated as potential candidates for photovoltaic applications [1,2]. Tin diselenide ( $\text{SnSe}_2$ ) is a n-type semiconductor and it has a hexagonal crystal structure of the type  $\text{CdI}_2$ . Its optical band gap is approximately 1.59eV for direct allowed transition [3] and 0.95eV for indirect allowed transition [4,9].

Many synthesis methods have been reported for the growth of tin diselenide thin films, like thermal evaporation [5,6,26], hot wall epitaxy [7,8], reactive evaporation [10,22], electro deposition [1,11,12], laser ablation [13], chemical bath deposition [14], hydro- thermal co-reduction method [24], chemical vapor deposition method [27,31], molecular beam epitaxy [28] and spray pyrolysis [6,15,23] and various physical properties were evaluated. To the best of our knowledge, very few reports were available in literature on the synthesis and characterization of  $\text{SnSe}_2$  films by selenization of metal precursors [16,17]. Therefore in the present work a two-stage method for growing  $\text{SnSe}_2$  thin films, deposition of tin metallic precursors by dc – magnetron sputtering followed by selenization of the precursors was used. A study of morphological and structural properties of tin diselenide films grown on soda lime glass substrates by using two-stage process has been studied and reported.

### **2. EXPERIMENTAL DETAILS**

Tin diselenide thin films were grown by using a two-stage process. The first stage involves the deposition of metallic precursor. DC magnetron sputtering (model no: VRSU04D) technique is used for the deposition of tin layers onto ultrasonically cleaned glass (SLG) substrates. For sputtering the metallic layer high purity (99.99%) Sn target with 2" diameter and 0.125" thickness was used. The tin layer has grown at an operating pressure of  $14 \times 10^{-3}$  mbar using Argon as sputter gas. The sputtering power was maintained at 25W and the sputtering was done for 30 minutes. The second stage involves selenization of sputtered tin layers at different temperatures by using a two zone quartz tube furnace. Here, the sputtered tin layers are placed in a graphite box with Se pellets in it and the box is loaded into the tube furnace. The quartz furnace was initially flushed with argon and selenization was

carried out at three different temperatures i.e., 300°C, 350°C and 400°C for 30 minutes. The resulting films were cooled to room temperature by natural cooling process.

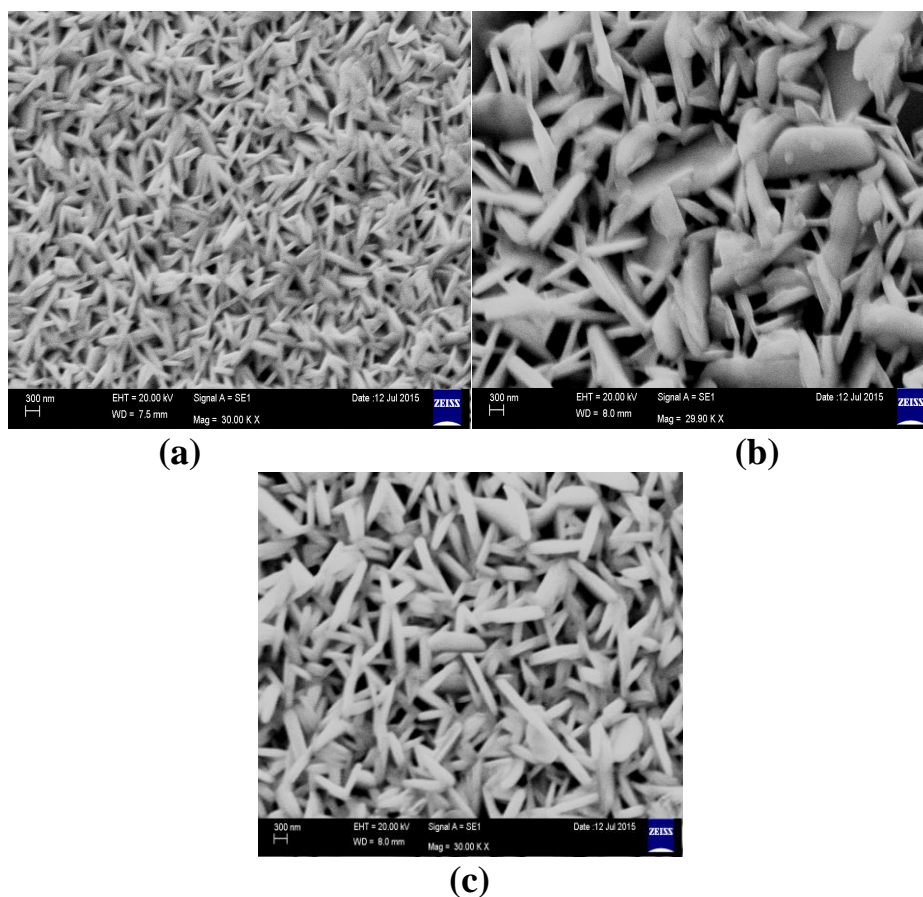
The selenized tin precursors were examined by Carl Zeiss EVO 50, Oxford instruments, U.K. to evaluate the surface morphology of the films. Seifert X-ray diffractometer (XRD) technique is used to evaluate the crystal structure and orientation of as-grown SnSe<sub>2</sub> thin films. The CuK $\alpha$  ( $\lambda=1.54056\text{\AA}$ ) radiation was used to investigate the structure and the phase identification has been carried out by comparing with powder diffraction standards. In addition to the XRD studies, Raman analysis has been made to support and confirm the phases present in selenized tin samples by using Horiba Confocal Raman Spectrometer using a laser excitation wavelength of 325 nm.

### 3. RESULTS AND DISCUSSION

All the as-grown films were uniformly grown and appeared in thick gray in colour. They were pin hole free and opaque irrespective of the selenization temperature.

#### 3.1. Surface Morphological Studies

Figure 1 portrays the surface morphology of as-deposited films grown at  $T_s=300^\circ\text{C}$ ,  $350^\circ\text{C}$  and  $400^\circ\text{C}$ . The images were taken at a magnification of 30000x and at a range of 300 nm. The SEM micrographs revealed that the grown films were free from micro cracks. The images clearly displayed that a large number of plate like particles or flakes were uniformly distributed throughout the surface of the substrate. These particles were regular in shape and were grown parallel to the substrate surface. The observed SEM characteristics of SnSe<sub>2</sub> are in good agreement with the reported data [24,27,31]. It was noticed that the grain size of the grown layers varied with the increase of selenization temperature. Among the three selenization temperatures used in this work,  $T_s=350^\circ\text{C}$  showed large particle size. The reduction of particle size at  $T_s=400^\circ\text{C}$  might be due to the re-evaporation of some of selenium from the film.



*Fig1: SEM images of SnSe<sub>2</sub> films selenized at (a) 300°C (b) 350°C (c) 400°C*

#### 3.2. X-ray diffraction studies

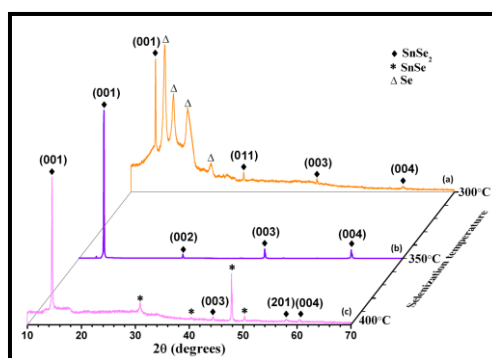
Figure 2(a,b,c) depicts the X-ray diffraction studies of as-deposited films grown at three different selenization temperatures such as 300°C, 350°C and 400°C respectively. The XRD analysis is carried

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out for  $2\theta$  values varying from  $10^\circ$  to  $70^\circ$ . All the films showed an intense peak at  $2\theta \approx 14.57^\circ$  which corresponds to the (001) plane [22-29]. Films also showed small peaks corresponding to (002), (003) and (004) planes which relates to the  $\text{SnSe}_2$  phase. The evaluated crystal structure was hexagonal and the corresponding lattice parameters are calculated and given in Table 1. The calculated axial ratio  $c/a$  value specifies that the tin atoms occupy the interstices of close packed selenium planes, such that they are surrounded by 6 Se atoms in an octahedral configuration and thus indicates  $C_6$  structure to  $\text{SnSe}_2$  [32]. All the structural data observed in this work closely matched with the Joint Committee on Powder Diffraction Standard (JCPDS) card no.: 89-3197.

**Table1.** Structural parameters of  $\text{SnSe}_2$  thin films

S. No.	Structural parameter	Standard JCPDS value	Calculated value
1	Inter planar spacing 'd'	6.14 Å	6.074 Å
2	Lattice constant 'a'	3.81 Å	3.72 Å
3	Lattice constant 'c'	6.14 Å	6.074 Å
4	c/a ratio	1.61	1.63



**Fig2.** XRD pattern of tin diselenide films selenized at (a)  $300^\circ\text{C}$  (b)  $350^\circ\text{C}$  and (c)  $400^\circ\text{C}$

Figure 2(a) indicates that the  $\text{SnSe}_2$  thin films grown at  $300^\circ\text{C}$  were rich in selenium content. The peaks present at  $2\theta = 16.33^\circ$ ,  $17.91^\circ$ ,  $20.54^\circ$  and  $27.78^\circ$  indicates the presence of Se. However in the layers selenized at  $350^\circ\text{C}$ , all the Se peaks disappeared, but the intensity of (001) peak was enhanced and the diffraction peaks in figure 2(b) clearly showed the formation of  $\text{SnSe}_2$  phase and no other secondary phase exist. The layers had very good crystallinity and showed hexagonal structure. But the films selenized at  $400^\circ\text{C}$ , as shown in figure 2(c), exhibited the existence of slightly selenium deficient  $\text{SnSe}_2$  phase. The XRD spectra revealed the presence of (111), (102), (600) and (221) planes at  $2\theta = 30.89^\circ$ ,  $40.33^\circ$ ,  $47.83^\circ$  and  $50.23^\circ$  respectively that correspond to  $\text{SnSe}$  phase with orthorhombic crystal structure. In addition, planes related to  $\text{SnSe}_2$  phase were noticed from the X-ray diffraction data with the appearance of (003), (201) and (004) planes, which are also matched with the reported planes for  $\text{SnSe}_2$ .

The average crystallite size (D) of the  $\text{SnSe}_2$  layers was evaluated by using the Debye-Scherrer formula (1) using the intense peak obtained in the XRD spectrum [18,19]. It was observed that the crystallite size varied with the change of  $T_s$  as observed in SEM images. The crystallite size increased initially from 25 nm with the increase of selenization temperature and reached a maximum value of 106 nm at a temperature of  $350^\circ\text{C}$ . With further increase of selenization temperature the crystallite size again decreased and reached a value of 85 nm at a temperature of  $400^\circ\text{C}$ . The dislocation density ( $\delta$ ) in the grown  $\text{SnSe}_2$  layers was also calculated from Williamson and Smallman's formula (2) [20]. The  $\delta$  value reached a minimum at  $T_s=350^\circ\text{C}$ , which conveys that the film has less defects at this temperature. The lattice strain ( $\epsilon$ ) in the films was determined using the formula (3) [21]. These two parameters also varied with  $T_s$  similarly but in a reverse manner of crystallite size. The changes in FWHM and corresponding estimated values of crystallite size, dislocation density and lattice strain with respect to selenization temperature ( $T_s$ ) were tabulated in Table 2.

**Table2.** The structural parameters of  $\text{SnSe}_2$  films grown at different selenization temperatures.

S. No.	Selenization temperature $T_s$ ( $^\circ\text{C}$ )	FWHM	Crystallite size D (nm)	Dislocation density $\delta$ (lines/ $\text{m}^2$ )	Lattice strain $\epsilon$
1	300	0.334	25	$1.59 \times 10^{15}$	$1.44 \times 10^{-3}$
2	350	0.078	106	$8.85 \times 10^{13}$	$3.40 \times 10^{-4}$
3	400	0.098	84	$1.38 \times 10^{14}$	$4.25 \times 10^{-4}$

➤ Debye-Scherrer's equation for Crystallite size (D)

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (\text{nm}) \quad (1)$$

where  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half maximum (FWHM) intensity of the peak in radians and  $\theta$  is the diffraction angle.

➤ Dislocation density ( $\delta$ )

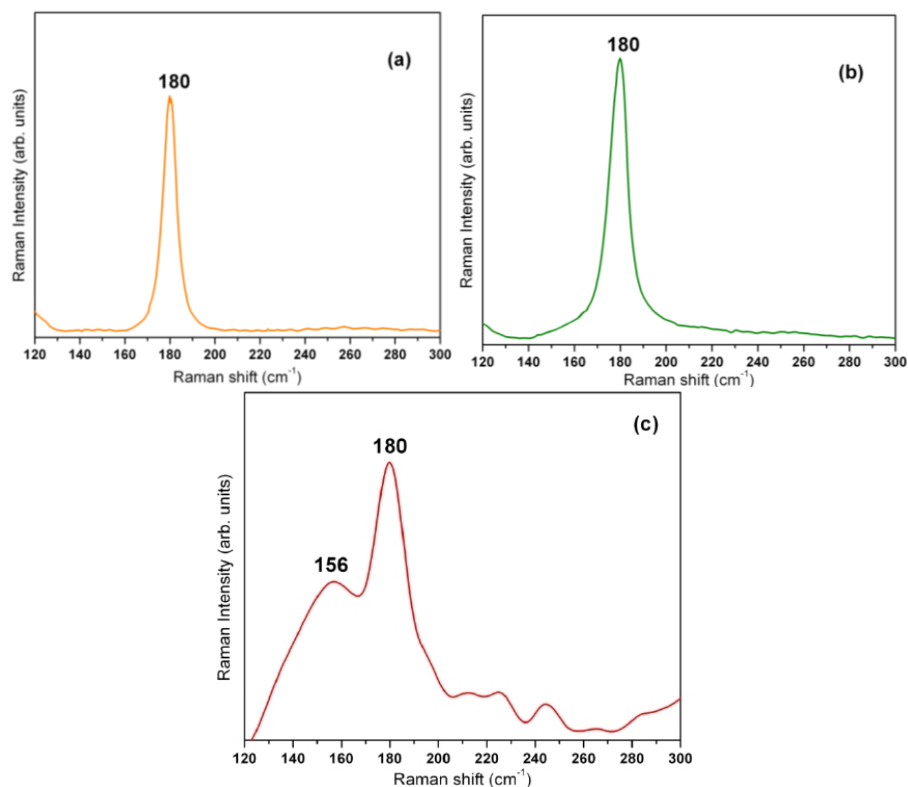
$$\delta = \frac{1}{D^2} \quad (\text{lines/m}^2) \quad (2)$$

➤ Strain ( $\varepsilon$ )

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

### 3.3. Raman scattering studies

Raman analysis can provide information about the phase identification and spatial location of the phases too. The earlier literature predicts one  $A_{1g}$  and  $E_g$  mode and 3 infrared active  $A_{2u}$  and  $E_u$  modes for  $\text{SnSe}_2$  [33, 34]. The figure 4 (a,b,c) shows the Raman scattering results of the samples prepared at selenization temperatures  $300^\circ\text{C}$ ,  $350^\circ\text{C}$  and  $400^\circ\text{C}$  respectively by using a laser excitation wavelength of 325 nm. The Raman spectra showed only a sharp intense peak at  $180\text{ cm}^{-1}$  for all the samples irrespective of the selenization temperatures. This is the characteristic of hexagonal  $\text{SnSe}_2$  phase and is related to the  $A_{1g}$  vibration mode. A similar result was reported in literature by other researchers for  $\text{SnSe}_2$  layers grown using variety of methods [16, 27, 30, 31]. It was noticed that the intensity of this peak was reduced at  $T_s=400^\circ\text{C}$ . This might be due to the deprivation of Se at this temperature. In addition to  $180\text{ cm}^{-1}$  peak a small shoulder was also observed at  $156\text{ cm}^{-1}$  for the films grown at  $400^\circ\text{C}$ , which indicates the presence of SnSe as secondary phase. This peak is related to  $A_g$  vibration mode of SnSe phase as reported in literature. This indicates that as the selenization temperature increases to  $400^\circ\text{C}$ , some of the selenium gets re-evaporated from the film surface because of its higher vapor pressure at such temperatures. This results in a change from hexagonal  $\text{SnSe}_2$  phase to orthorhombic SnSe phase which was also supported by the XRD pattern.



**Fig4.** Raman spectra of tin diselenide films selenized at (a)  $300^\circ\text{C}$  (b)  $350^\circ\text{C}$  and (c)  $400^\circ\text{C}$ .

#### **4. CONCLUSION**

Tin diselenide thin films were successfully grown by using a two stage process. This process involves the selenization of tin precursors at three different temperatures such as 300°C, 350°C and 400°C using argon as carrier gas. The SEM micrographs revealed that the as-grown films are pin-hole and crack free and the grain sizes are varied with selenization temperature. The XRD spectrum of sample synthesized at a temperature of 350°C showed the characteristic peaks of SnSe<sub>2</sub> phase with hexagonal structure. Layers synthesized at temperatures of 300°C had peaks corresponding to Se in addition to SnSe<sub>2</sub> phase, as this temperature is not sufficient to convert Sn completely into SnSe<sub>2</sub>. However when the selenization temperature was increased to 400°C SnSe phase was also developed along with SnSe<sub>2</sub>. Other structural parameters such as crystallite size, dislocation density and lattice strain were also evaluated. The Raman scattering studies confirmed these observations made from the XRD analysis.

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