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GROWTH AND CHARACTERIZATION OF SnSe THIN FILMS PREPARED BY SPRAY PYROLYSIS TECHNIQUE

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Tin selenide (SnSe) thin films have been deposited using chemical spray pyrolysis on non-conducting glass substrates at temperatures from 250 ºC, 300 ºC, 350 ºC, and 400 ºC. The composition, surface morphology, structural, optical and electrical properties of deposited films were studied using energy dispersive analysis by X-rays (EDAX), scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Vis spectrometry and four probe techniques. EDAX analysis yielded an atomic ratio of (50.3) Se: (49.7) Sn. SEM studies reveal that the SnSe films exhibited uniformly distributed grains over the entire surface of the substrate. The XRD studies reveal that all the films are crystalline with orthorhombic structure. Microstructural parameters such as crystallite size, micro strain, and dislocation density are calculated and found to depend upon temperatures. The optical band gap of SnSe thin films is evaluated using transmittance and absorbance data. A direct band gap of the 1.08 eV is estimated and the value is in conformity with 1.1 eV reported earlier for SnSe thin films. The electrical resistivity shows that the films are semiconducting and the resistivity is found to be minimum at optimized substrate temperature.

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Keywords: Spray pyrolysis, SnSe Thin films, SEM, XRD, EDAX, Electrical resistivity

1. Introduction

Semiconductor materials formed from elements of groups II and IV are extensively used in modern technology. Some semiconductors, such as CdS and CdSe, have been studied more extensively and their synthesis has been widely reported in the literature [1]. These materials possess the following criteria to make them potential candidates in photoelectrochemical solar cells: (i) the band gap is between 1.0 and 2.0 eV, making capable of absorbing a major portion of solar energy; (ii) they are chemically and electrochemically stable in either acid or alkaline condition; (iii) the constituent elements are abundantly available and cheap [2]. Among the uses of SnSe are, as memory switching devices, holographic recording systems, and infrared electronic devices [3]. SnSe has been studied in the form of both single crystal and thin films [2,3]. The use of SnSe for this purpose could suppress photocorrosion and enhance the fill factor in electrical switches and in junction devices [4].

For large scale production of solar cells, a thin film deposition technique that can be easily handled at low cost is needed. The SnSe thin films were prepared with different techniques such as vacuum evaporation [4], cathodic electrodepositon [5], chemical bath deposition [6], chemical vapour deposition [7-10] and spray pyrolysis. Among these methods spray pyrolysis is widely used because it is a simple, economical and viable technique, which produces films of good quality for device application [11,12].

The attempts have been made to prepare SnSe thin films by simple and low cost chemical spray pyrolysis technique. The films have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive analysis X-rays (EDAX), resistivity and optical measurement techniques and the results have been discussed.

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2. Experimental

All the chemicals used in this work were of analytical reagent grade (99% purity, E-Merck). SnSe thin films were deposited onto glass substrates from an aqueous solution bath containing 0.1 M $SnCl_2$ and 0.01 M SeO_2 were dissolved in deionized water in separate beakers. Aqueous solutions of $SnCl_2$ and SeO_2 were used as the sources of Sn and Se, respectively. The $SnCl_2$ and SeO_2 solutions were mixed for 45 min with a magnetic stirrer. The deposition of the film was carried out at various temperatures from 250 ºC, 300 ºC, 350 ºC, and 400 ºC. The colorless deposition bath turned gray in colour and then to gray-block as time progressed.

The structural characterization of the thin film was carried out by analyzing the XRD pattern obtained using a Philips Model PW 1710 diffractometer with Cu kα radiation (λ=0.1542 nm). Surface morphological and compositional analyses were carried out using a scanning electron microscope and energy dispersive analysis by X-rays setup (EDAX) attached with SEM (Philips Model XL 30). Optical measurements were carried out using a JASCO- V-570 spectrophotometer. Resistivity measurements were carried out using a four probe method.

3. Results and discussion

X-ray diffraction patterns recorded for the spray deposited SnSe films on glass substrates at various temperatures from 250 ºC, 300 ºC, 350 ºC, and 400 ºC are shown in Fig.1(a)-(d). The XRD studies revealed that the films of SnSe are polycrystalline in nature with orthorhombic structure. The observed diffraction peaks of orthorhombic SnSe films are found at 2θ values of 30.35, 37.49, 41.78, 49.27 and 52.84 corresponding to the hkl planes (111), (131), (002)/(200), (151), and (042)/(240) respectively. The different peaks in the diffractogram were indexed and the corresponding values of interplanar spacing '*d*' were calculated and compared with the standard values [13]. The temperature to obtained good quality films SnSe thin films deposited at temperature below 350 ºC are found to be poorly crystallized indicated by broad XRD peaks represented in Fig.1.(a). It is found that deposition temperature 350 ºC led to the formation of well – crystallized films. the height of (111) peak in X-ray diffraction pattern for SnSe thin films deposited at temperature 350 ºC has shown sharper peaks and small FWHM data resulted in the enhancement of crystallite size in the deposited films at temperature 350 ºC.

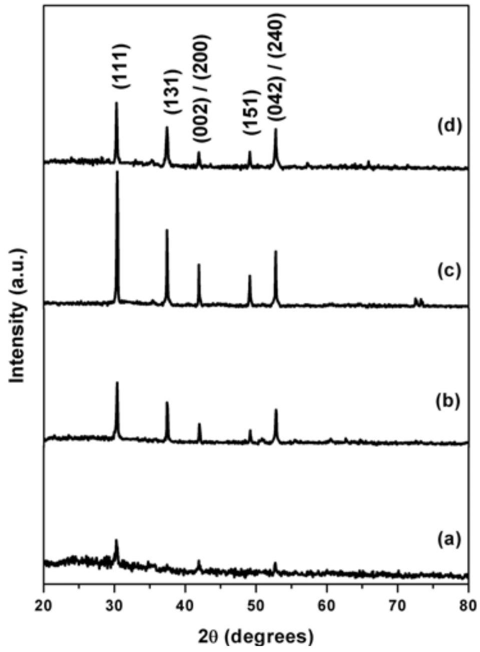

Fig.1. XRD patterns of SnSe thin films deposited at various substrate temperatures: (a) 250 ºC, (b) 300 ºC,(c) 350 ºC, and (d) 400 ºC.

X-ray diffraction patterns of SnSe thin films synthesized at substrate temperatures from 250 ºC, 300 ºC, 350 ºC and 400 ºC are recorded. Using FWHM data and Debye-Scherrer formula, the crystallite size of the films was calculated. The stain ε was calculated from the slope of $\beta\cos\theta$ versus $\sin\theta$. The variation of crystallite size and strain with bath temperature for SnSe films deposited at temperature from 250 ºC, 300 ºC, 350 ºC and 400 ºC is shown in Fig.2.(a) and (b). It is observed from Fig.2.(a), that the crystallite size increases with temperature and films deposited at 350 ºC are found to have maximum value of crystallite size. Due to the removal of defects in the lattice with increase in bath temperature, the strain in the films gets released and attained a maximum value at temperature of 350 ºC. Fig.2.(b) represents the variation of dislocation density with bath temperature for SnSe thin films. It is observed from Fig.2.(b) the dislocation density found to decrease while increasing temperature from 250 ºC and 400 ºC, thereafter it slightly increases. A sharp increase in crystallite size and decrease in strain with bath temperature are indicated in Fig.2.(a). Such a release in strain reduced the variation of interplanar spacing and thus leads to decrease in dislocation density of SnSe thin films and minimum values are obtained for films deposited at 350 ºC. SnSe thin films with lower strain, dislocation density improves the stoichiomerty of the films, witch in turn causes the volumetric expansion of thin films.

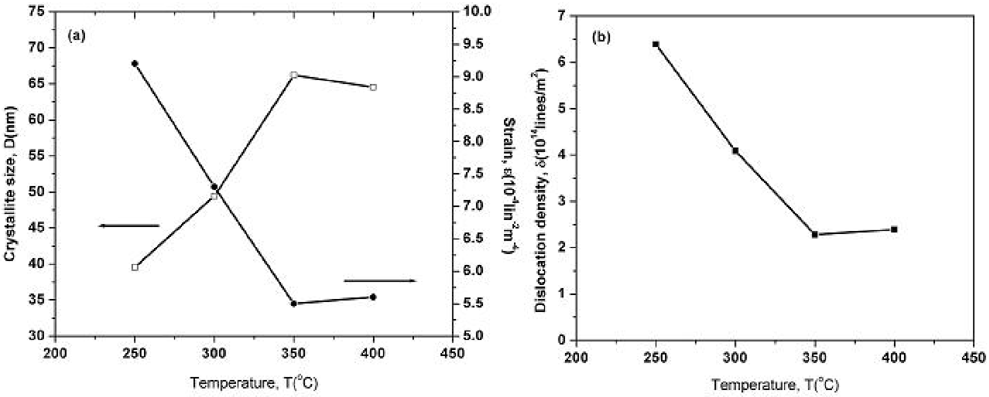

Fig.2(a) Variation of crystallite size and strain with temperature of SnSe thin films. (b).Variation of dislocation density with bath temperature for SnSe thin films.

Scanning electron microscope (SEM) studies were carried out to assess the quality of the SnSe films spray deposited at temperature 350 ºC for deposition time 10 min is shown in Fig.3. From the micrographs one can see the uniform distribution of grain size over total coverage of the substrate with a compact and fine grained morphology. At temperature 350 ºC there is an increase in nucleation over growth and the film surface is covered with uniform grain without pinholes as seen in Fig.3.

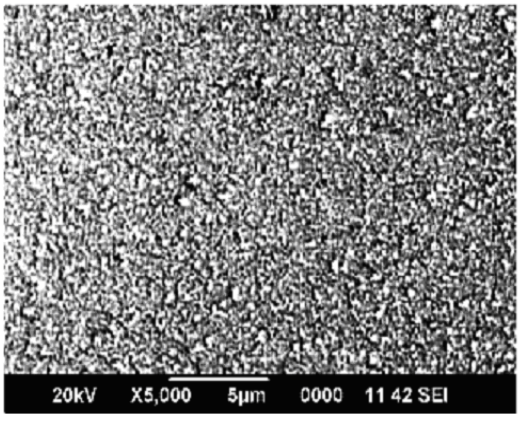

Fig.3. SEM image of the spray deposited SnSe thin film at temperature 350 ºC.

The composition of the films was investigated using an energy dispersive analysis by X-rays (EDAX) setup attached for the spray deposited SnSe thin films spray deposited onto glass substrate to study the stoichiometry of the film. Fig.4 shows a typical EDAX pattern and the elemental analysis was carried out only for Sn and Se. the average atomic percentage of Sn: Se was 49.7:50.3 showing that the sample was slightly selenium rich, which is in good agreement with the reports of Tomkiewicz et al [14] and Skyllas Kazcos and Miller [15].

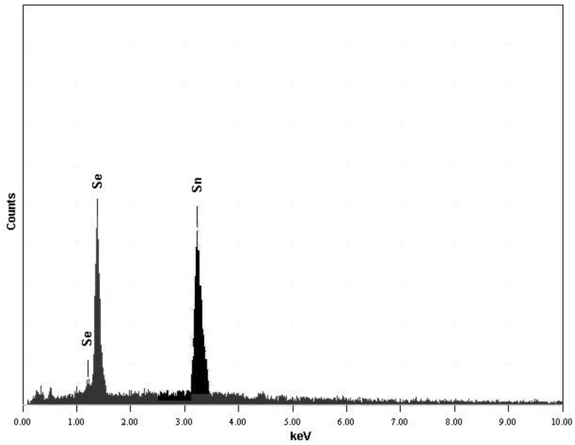

Fig.4. EDAX analysis of the spray deposited SnSe thin film at temperature 350 ºC.

Optical transmittance measurements of the films were used to estimate the band energy from the position of the absorption coefficient edge. The absorption coefficient can be calculated using the relation.

$$\alpha = A/h\nu\ (h\nu - Eg)^{-1/2}$$

Where, A is a constant (slope) and Eg is the energy gap. From the calculated values of the absorption coefficients a plot of $(\alpha h\nu)^2$ versus $h\nu$ (Tauc's plot), where α is the optical absorption coefficient of the material and $h\nu$ is the photon energy. Extrapolation of the plots to the x-axis gives the band gap energy of the SnSe films deposited at 350 ºC and 400 ºC shown in Fig.5(a) and (b). The band gap of energy of the SnSe films deposited at 350 ºC with optimized condition is 1.08 eV. This value is in good agreement with the value reported earlier [2].

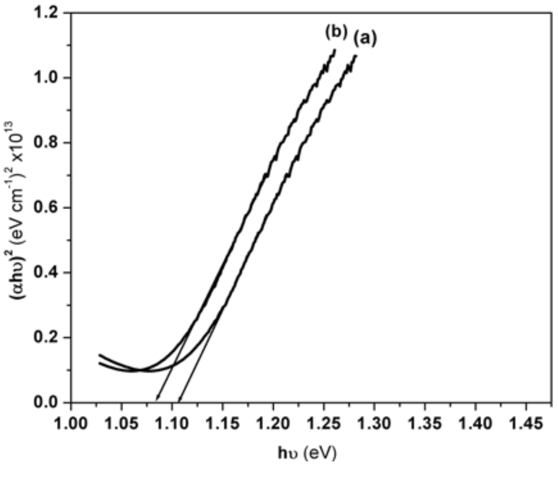

Fig.5 $(\alpha h\nu)^2$ versus hν plot of SnSe thin films spray deposited at various temperature: (a) 400 ºC and (b) 350 ºC.

The variation of *log ρ* versus inverse of temperature (1000/T) for the films spray deposited at optimized substrate temperature is shown in Fig.6, which reveals that the resistivity obeys the relation

$$\rho=\rho_o\, e^{Eg/kT}$$

Where, Eg is the activation energy and k is the Boltzmann constant. It is well known that resistivity depends on the temperature, carrier concentration and mobility. In a semiconductor, carrier concentration is a rapidly increasing function of temperature in the 'intrinsic' region. This increase is due to thermal excitation of electrons, either from imperfections or across the band gap. It is clear from Fig.6 that the resistivity decreases as the temperature increases, showing semiconducting behaviour of the SnSe thin films.

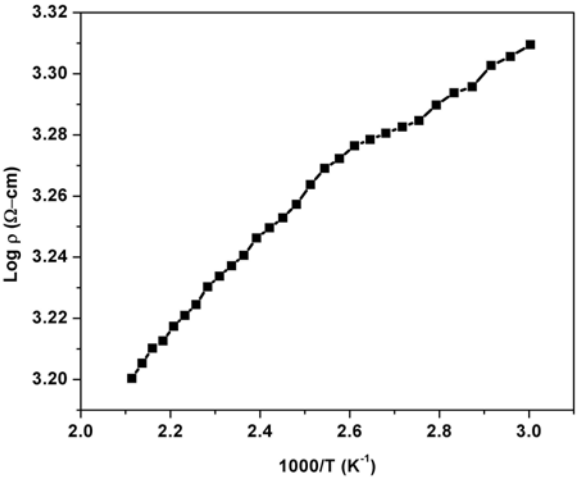

Fig.6. Plot of log ρ versus 1000/T for SnSe thin film deposited at temperature 350 ºC.

4. Conclusion

The SnSe thin films were successfully deposited on glass substrates at temperatures 250 ºC, 300 ºC, 350 ºC and 400 ºC using an spray pyrolysis technique. X-ray diffraction analysis confirmed that the deposition SnSe films with an orthorhombic structure. Various structural parameters such as crystallite size, strain, dislocation density are calculated and are found to depend upon various temperatures. The crystallinity of the films increased with increasing temperature from 250 ºC to 350 ºC. SEM studies reveal that the SnSe films exhibited uniformly distributed grains over the entire surface of the substrate. The average sizes of the grains are found to be 478 nm. The presence of elemental constituents was confirmed from EDX analysis. Optical transmittance measurements indicate that the deposited films have a direct band gap of 1.08 eV which confirm the formation of well-crystallized SnSe films. The optimized SnSe thin film has higher crystallinity, lower resistivity.

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