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Electrical and Photoelectrical Properties of Vacuum Deposited SnSe Thin Films

Polycrystalline thin films of tin selenide have been prepared by vacuum deposition at a substrate temperature of 150ºC and reported. X-ray diffraction, optical transmission, electrical conductivity and photoconductivity studies have been carried out on these films. Annealing the films at 300ºC for 2 hours improves the crystallinity and a preferred orientation along the (111) plane develops. The optical transmission measurement reveals that the SnSe thin films have a direct allowed band gap of 1.26 eV. Electrical conductivity study shows that the conductivity increases with increasing temperature. The observed electrical conductivity at low temperature is explained based on hopping conduction mechanism. The photoconductivity measurement indicates the presence of continuously distributed deep localised gap states in this material.

1. Introduction

Metal chalcogenides offer a range of optical band gaps suitable for various optical and optoelectronic applications. Among the IV-VI compounds, tin selenide has potential applications in memory switching devices, as efficient solar material and in holographic recording systems [BAXTER, MCLENNAN; BENNOUNA et al]. SnSe has been studied in the form of both single crystals and thin films [YU et al; AGNIHOTRI et al; TERADA]. It has an orthorhombic crystal structure with layers stacked along the c axis with a=4.30 Å, b=4.05 Å and c=11.62 Å. Considerable efforts have been made by the researchers for the preparation of SnSe thin films by various techniques and their characterisation [SUBBA RAO, CHAUDHURI; BHATT et al, ENGELKEN et al]. In the present work, SnSe semiconducting thin films are prepared by vacuum deposition. The structure of the thin films strongly influences the electronic properties and is highly dependent upon the preparation technique and deposition conditions. In view of this, the study of the structural, optical, electrical and photoelectrical properties of the SnSe thin films are carried out and the results are reported.

2. Experiment

The bulk tin selenide material was synthesised by mixing tin and selenium (both Aldrich, 99.99%) powders in the stoichiometric ratio. The mixture was sealed in a quartz ampoule at a pressure of 10^{-4} Pa and melted at 900°C. The melt was homogenised for 10 hours and the ampoule was rotated slowly for homogeneous mixing and then cooled to room temperature.

The d values obtained by X-ray powder diffraction pattern for the synthesised compound coincides with the SnSe orthorhombic structure reported in the literature. The lattice constants are calculated from the measured d spacings and found to be a = 4.36 Å, b = 4.05 Å and c =11.59 Å.

Thin films of SnSe were deposited using the synthesised powders in a Hind Hivac Vacuum Coating Unit (model 12-A4) at different substrate temperatures. The glass substrates were thoroughly cleaned in detergent, chromic acid, double distilled water and trichloroethylene. The vacuum was kept at 10^{-4} Pa and the rate of deposition was maintained at 2 nms^{-1}. The films prepared at 150°C were found to be uniform, porous free and well adherence with the glass substrates. The thickness of the thin film was measured by forming interference fringes [GOSWAMI] and it was found to be 0.2 μm.

The X-ray diffraction pattern for the thin film was recorded in JEOL JDX 8030 X-ray diffractometer using Cu Kα radiation. The optical spectra was recorded in the wavelength region 400 to 2000 nm using UV-VIS-NIR spectrophotometer (HITACHI V-3400). The electrical conductivity measurements were carried out from 300 to 118 K by the van der Pauw technique in a liquid nitrogen cryostat. The electrical contacts were made using high purity silver paste (Eltecks corporation, Bangalore). The photoconductivity measurements were carried out at room temperature by a two probe technique on freshly prepared films using a halogen lamp source.

3. Results and discussion

3.1 Structural properties

The X-ray diffraction pattern was recorded for the as prepared film and for the film annealed at 300°C for two hours. The XRD pattern for the as prepared film (Fig.1a) did not show any peak and indicates the poor crystalline nature of the film. Fig.1b shows the XRD pattern of the film annealed at 300°C. A well resolved X-ray peak corresponding to the (111) plane is observed. It reveals that the SnSe films annealed at 300°C have a strong preferred orientation and their crystallites are perpendicular to (111) plane. A similar preferred orientation of (111) plane in SnSe films was observed by BHATT et al. and by DANG TRAN QUAN in the thin films grown by the vacuum evaporation technique and by SINGH & BEDI in SnSe thin films prepared by a hot wall epitaxy method. Whereas TEGHIL et al. observed preferred orientations in the (011) and (200) crystallographic planes in the SnSe films prepared by laser ablation method. However, JOHN et al. have reported the preferred orientation in the (400) plane for films grown by reactive evaporation. The various preferred orientations reported for SnSe films indicate that the deposition technique plays an important role for the orientation of SnSe thin film formation.

3.2 Optical properties

The optical absorption coefficient α is determined using the relation

$$a = \frac{1}{t}\ln\left(\frac{1}{T}\right)$$

where t is the thickness of the film and T is the transmittance. The relation between the absorption coefficient and the photon energy hν is

$$a\,h\mathbf{n} = A\left[h\mathbf{n} - E_g \pm E_p\right]^n$$

where E_p is the phonon energy and E_g is the energy gap. In a direct transition ($E_p = 0$), n is equal to 0.5 and 1.5 for allowed and forbidden transitions respectively. For indirect transitions, n is equal to 2 for allowed transitions and 3 for forbidden transitions.
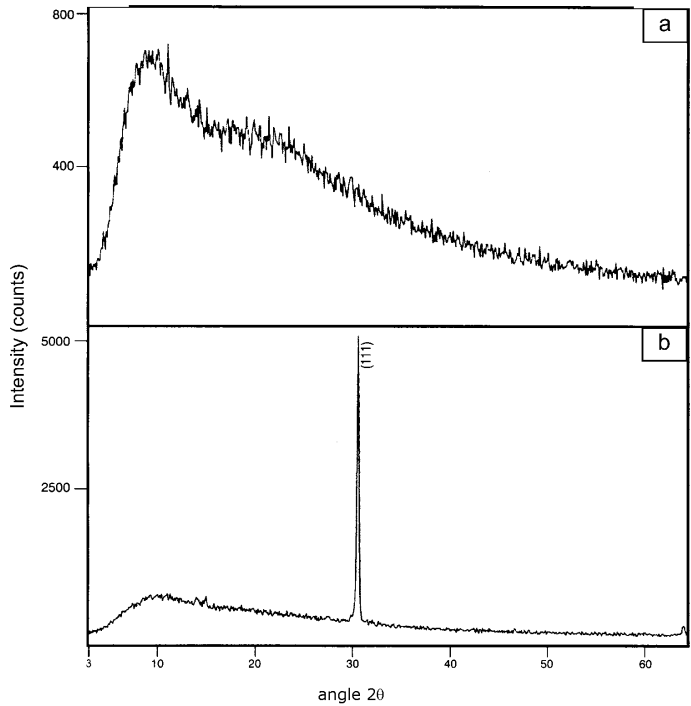

Fig. 1: X-ray diffraction spectra of tin selenide thin films: (a) as prepared and (b) annealed at 300° C for 2 hours
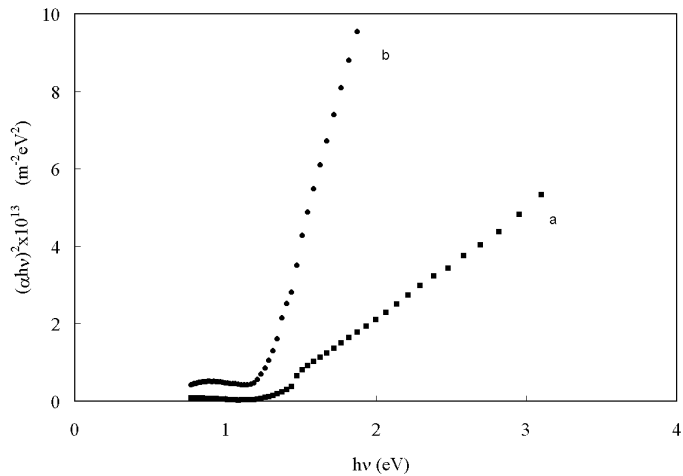

Fig. 2: Plots of $(\alpha h\nu)^2$ versus hν for SnSe thin films (a) as prepared and (b) annealed at 300°C

A plot of $(\alpha h\nu)^2$ as a function of hν is shown in Fig. 2 and it is linear in the strong absorption near the fundamental absorption edge. Since the value of α is in the order of 10^6 m^{-1} and the absorption coefficient is measured at room temperature, the presence of exciton bands is not likely to be possible. Therefore, the absorption is from a band to band transition [DANG

TRAN QUAN; JOHN et al; SMITH] and it is only due to an allowed direct transition from the top of the valence band to the bottom of the conduction band at the center of the Brillouin zone. The band gap energy value determined for the direct transition is 1.26 eV for the as prepared film. The band gap energy reported by various workers for SnSe thin films together with our value is given in Table 1 for comparison. On annealing the sample at 300°C for 2 hours, the band gap energy decreases and is found to be 1.23 eV. It is also evident from Fig.2 that the optical transmission coefficient of the annealed film is lower than that of the unannealed film. The observed decrease in the band gap energy and the decrease in the optical transmission spectra can be related to the improvement in the crystallinity of the annealed films. A similar decrease in optical transmission spectra of the annealed films was observed by NAIR et al. in their chemically deposited CdSe thin films. The band gap energy should decrease with annealing if the effect was indeed a quantum size effect [GRAY MODES et al]. The sintering of small particles during annealing lead to increasing connectivity between particles and eventually to grain growth. The validity of the above argument is supported by the improvement in the crystallinity as seen from the XRD pattern.

Sl. No.	Method of deposition	Band gap energy (eV)	Nature of transition	Reference
1.	Vacuum	1.26	direct	present work
2.	Vacuum	1.21	direct	DANG TRAN QUAN
3.	Reactive evaporation	1.21	direct	JOHN et al
4.	Laser ablation	0.94	direct	TEGHIL et al
5.	Vacuum	0.935	indirect	BHATT et al
6.	Electrodeposition	1.30	indirect	ENGELKEN et al

Table 1: SnSe band gap energy reported by various workers

3.3 Electrical properties

The electrical conductivity of the as deposited films has been measured by the van der Pauw technique in the temperature range 300 to 118 K and a plot of $\ln(\sigma)$ versus $10^3/T$ is shown in Fig.3. The Arrhenius behaviour is observed in the range 298 to 268 K, 268 to 193 K and 193 to 148 K in the regions I, II and III respectively. In these three linear regions, the activation energy is found to be 223 meV, 106 meV and 18 meV. Below 148 K the conductivity is almost constant indicating the freezing of charge carriers. Two different activation energies of 0.09 eV and 0.06 eV in the temperature region 150 to 300 K are reported for the SnSe thin films prepared by laser ablation [TEGHIL et al].

The Arrhenius plot can yield the different levels, which are responsible for the different donor and acceptor levels. In polycrystalline thin films at low temperatures in addition to bulk conductivity, grain boundary effects also have to be considered. Following the methods of SETO JOHN, the grain boundary effect is analysed and found to be negligible. Next, the possibility of hopping conduction is analysed. At low temperatures, all the trap states are filled and conduction occurs through the variable range hopping of the electrons in the localised states at the Fermi levels. The GREAVES conductivity expression for variable range hopping (VRH) model applicable to low temperature is

$$\boldsymbol{s}\, T^{1/2} = C \exp\left(-\frac{T_0}{T}\right)^{1/4}$$

where C and T_o are constants related to the density of localised states $N(E_F)$ by

$$T_0 = \frac{16\boldsymbol{a}^3}{kN(E_F)}$$

where α^{-1} is the measure of the spatial extension of the wave function exp(-αx) associated with the localised states. A plot of $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ is drawn and shown in Fig. 4. In the temperature range 158 to 198 K, it is found to be a straight line and it indicates the validity of hopping conduction mechanism. This is in good accordance with MOTT's VRH process. The slope of this curve gives the value of T_o, equal to 6.35 x 10^7 K.
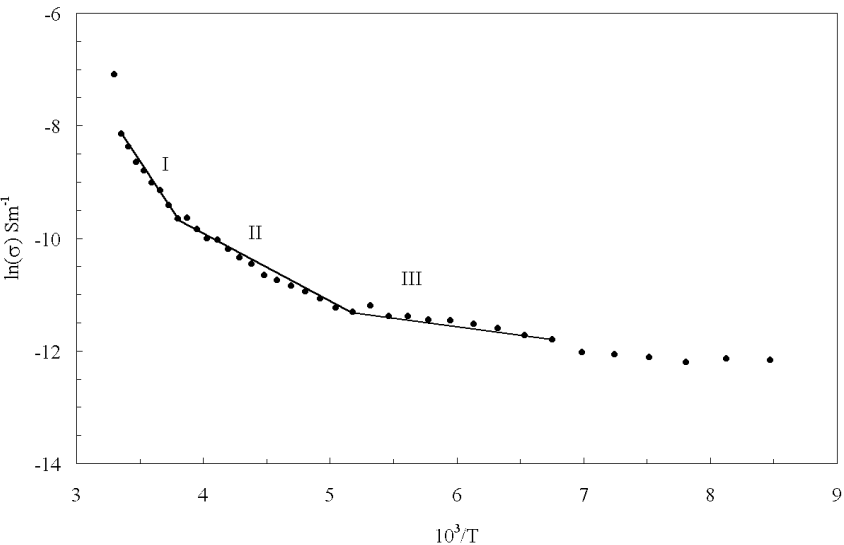

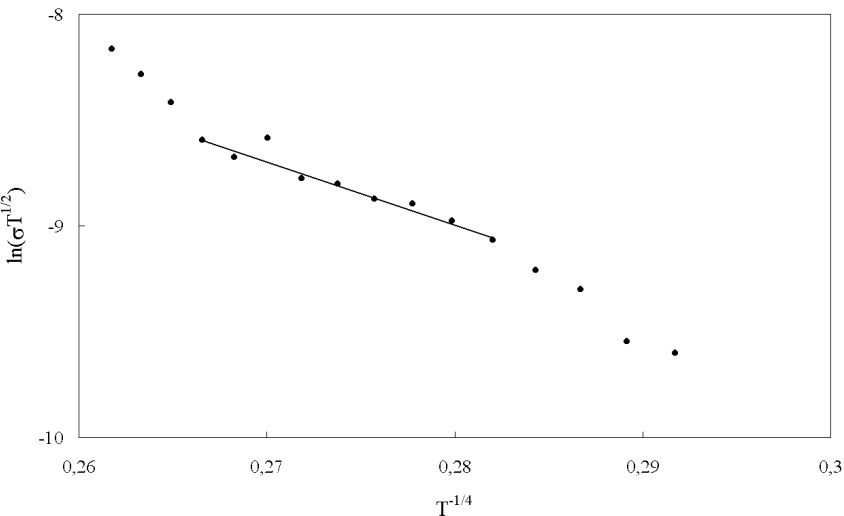Fig. 3: Reciprocal temperature dependence of electrical conductivity for SnSe thin films

Fig. 4: A plot of $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ showing hopping conduction in SnSe thin films

3. 4 Photoconductivity

3. 4. 1 Steady state photoconductivity

Fig. 5 shows the voltage dependence of the dark current and of the photocurrent recorded for the as deposited SnSe thin films for different light intensity levels (a-600 lux, b-1800 lux and c-3000 lux) at room temperature. The photocurrent is obtained by subtracting the dark current from the total current measured. The dark current as well as the photocurrent increases linearly with the increase in voltage in the region studied (0-30 V). The photocurrent increases with the increase in photo illumination level and it is due to the generation of more number of free charge carriers. The slope of the current-voltage characteristics curve also increases with increase in the illumination level F and obeys the power law

$$I_{ph} \propto F^g$$

where γ is a constant and its value determines whether the recombination process is monomolecular or bimolecular. For bimolecular process, $\gamma=0.5$ and for monomolecular process $\gamma=1$. If the value of γ lies between 0.5 and 1, it represents the continuous distribution of localised states [ALBERT ROSE]. In the present study, it is found that the value of γ lies between 0.54 and 0.60 for SnSe thin films and it indicates the presence of the continuous distribution of localised states. A similar behaviour of γ has been reported in $AgInTe_2$ by SHUKLA et al, in Te-Se-Sb based glass systems by SHIMAKAWA et al and in $Sb_{15}Ge_{10}Se_{75}$ by MANN et al, which are known to have a wide distribution of localised states. The dark conductivity and the total conductivity observed for the light intensity of 3000 lux are 5.56 x 10^{-9} Sm^{-1} and 7.50 x 10^{-9} Sm^{-1} respectively. The photosensitivity of the film is determined using the relation S = σ_{ph}/σ_d and found to be 0.17, 0.27 and 0.35 for the intensities of 600 lux, 1800 lux and 3000 lux respectively.
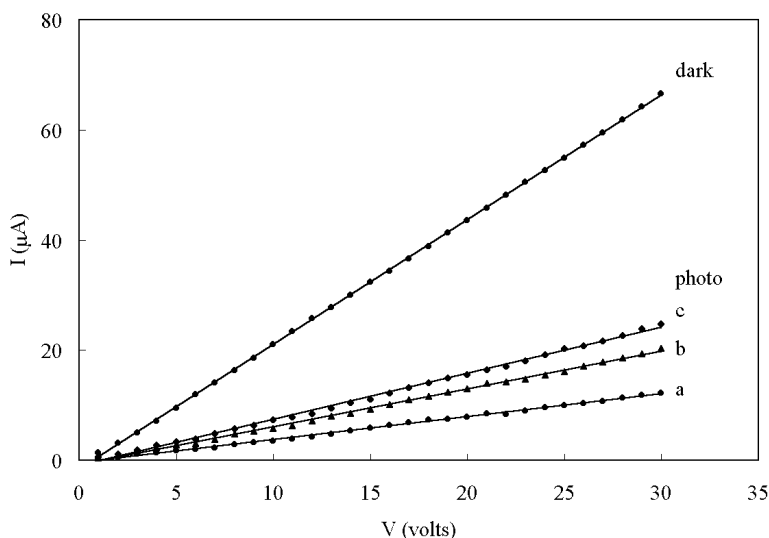

Fig. 5: Dark current and photocurrent as a function of voltage at different levels of illumination (a-600 lux, b-1800 lux and c-3000 lux) in SnSe thin films

3. 4. 2 Transient photoconductivity

Transient photoconductivity measurements are carried out by illuminating the thin film using unpolarised white light and recording the current simultaneously. Then the light is turned off and the decay current is followed. Fig. 6 shows the transient photoconductivity curve observed at room temperature for the intensity of 3000 lux. On illumination, the conductivity increases at first and then saturates.

The long photocurrent rise time and slow decay process observed in the SnSe thin film samples is due to the presence of the deep localised gap states in these materials. The slow decay process is a function of time and it can be described using the differential lifetime τ_d [FUHS, MEYER] The lifetime for such a slow decay process can be written as

$$t_d = -\left(\frac{1}{I'_{ph}} \frac{dI_{ph}}{dt} \right)^{-1}$$

where I'_{ph} is the maximum photocurrent at t=0 for a given applied voltage. The decay time observed for the vacuum deposited SnSe thin film is found to be time dependent and the relation between $\ln \tau_d$ and $\ln t$ is shown in Fig. 7. A straight line graph is observed and this linear behaviour confirms the non-exponential decay process involved in the SnSe thin film samples. It shows that the decay law is hyperbolic. The extrapolation of the curve at t=0, gives the value of the carrier life time and it is found to be 1.6 second. The straight line in Fig. 7, obeys a power law of the form t^{-n}, with $n = d(\ln t_d / \ln t)$ and the value of n is found to be 1.23.
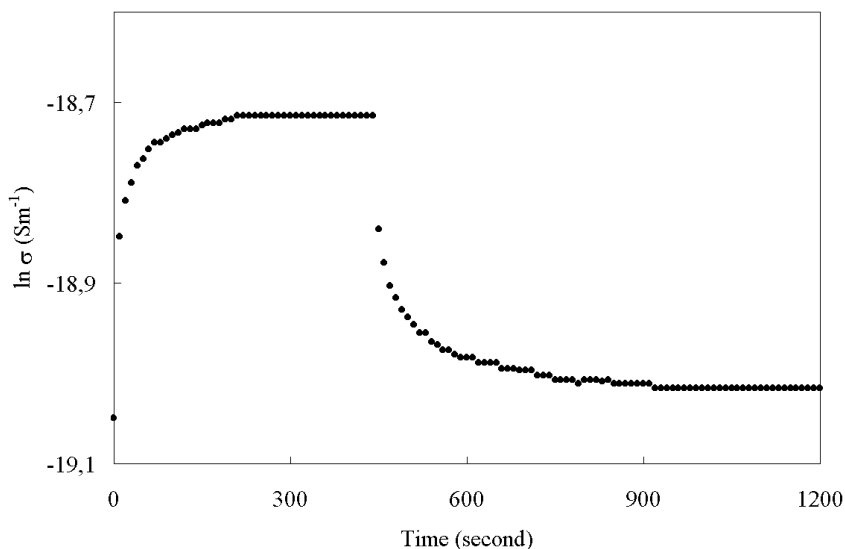

Fig. 6: Decay of photo conductivity as a function of time at room temperature in SnSe thin films

4. Conclusion

Structural, optical, electrical and photoelectrical characteristics of SnSe thin films prepared by vacuum deposition technique have been studied. The deposition parameters are optimised to yield uniform and well adhering films. The as prepared SnSe thin film is found to be poor

in crystalline nature and annealing the film at 300°C for 2 hours improves the crystallinity. Optical studies reveal that SnSe has a direct band gap energy of $E_g = 1.26$ eV and the indirect band gap is improbable. The conductivity measurements show that in the region 158 to 198 K, SnSe exhibits variable range hopping conduction. The steady state photoconductivity studies indicate that there is a continuous distribution of localised states. The photosensitivity increases with increasing illumination level in SnSe thin films. The photo decay process in this vacuum deposited film reveals the presence of deeper localised states and the carrier life time is found to be 1.6 second.
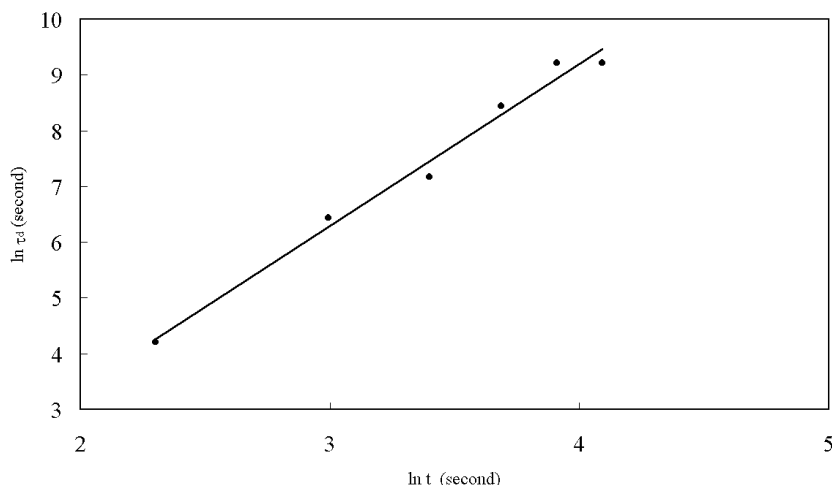

Fig. 7: A plot of $\ln \tau_d$ versus $\ln$ t showing the non-exponential decay in SnSe thin films

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