CHAPTER-5
OPTICAL AND ELECTRICAL PROPERTIES

5.1. INTRODUCTION

A detailed investigation on the optical and electrical properties of semiconductor materials both in bulk and thin film becomes essential for their effective application in optoelectronic devices, solar cells, etc. The absorption of energy by semiconductors, enhances transport of charge carriers and its absorbed energy delivery to the external loads. A careful study on the optical and transport properties of the semiconductors synthesized by various techniques is therefore necessary. These properties of SnS$_x$Se$_{1-x}$ films are of much interest due to their alloying nature and applications in holography and optoelectronic devices [1-4].

5.2. OPTICAL PROPERTIES OF SnS$_x$Se$_{1-x}$ FILMS

5.2.1. Review on SnS$_x$Se$_{1-x}$ Films

Engelken et.al. [5] have reported the optical behaviour of electrodeposited SnSe thin films. A moderately strong absorption edge was observed at wavelengths less than 1000 nm. The plot of \([h\nu (A-A_0)]^{0.5} \) vs \( h\nu \), was reasonably linear and when extrapolated to zero absorbance, yielded a bandgap values between 0.85 and 0.95 eV. Plots of \([h\nu (A-A_0)]^{2} \) vs \( h\nu \), corresponding to direct transitions, showed no constant pattern and unreasonably high bandgap values.

Mitchell [6] reported that SnSe single crystals grown by chemical vapour deposition were always p-type and exhibited optical absorbance “cut off energies” of 0.90 and 0.86 eV, corresponding to two different polarizations. A direct transition was observed at 1.2 eV. The spectrum of the annealed film had been shifted toward shorter wavelengths and exhibited a smaller sub-bandgap
absorbance. A bandgap, $E_g \approx 0.95$ eV before annealing and $E_g \approx 1.30$ eV after annealing was observed. Dang Tran Quan [1] examined the intrinsic absorption edge of the SnSe film synthesized by solid state reaction at 300 K in terms of a direct transition using the equation of Bardeen et al. [7]. A bandgap of $1.195 \pm 0.005$ eV was estimated and it was found to be in the same order as the energy gap (1.210 eV) of evaporated SnSe films [8]. Bhatt et al. [9] have calculated the absorption coefficient ($\alpha$) and it had been plotted as a function of radiation energy $h\nu$. $\alpha$ decreased up to $3.07 \times 10^3$ cm$^{-1}$ at 1.01 eV and then increased to about $2.5 \times 10^4$ cm$^{-1}$. This was attributed to the varying surface condition of the films [10]. The ionization energy $E_i$ of the impurity was found out from the graph and was equal to 0.15 eV. The variation of optical bandgap with thickness of the film was found to be decreased with increasing thickness. The variation was explained in terms of quantum size effect.

A pronounced absorption edge was evident in the vicinity of 700-800 nm for all the electrodeposited SnS samples synthesized by electrodeposition [11]. The indirect nature of optical transition in SnS was reconfirmed [12]. The $E_g$ values were obtained in the range 1.35 – 1.43 eV. A bandgap of about 1.51 eV was observed for a chemically deposited tin (II) sulphide films by Pramanik et al. [13]. Zainal et al. [14] have obtained $E_g$ value of 0.9 to 1.1 eV for electrodeposited SnS thin films. Vacuum evaporated SnS films have yielded an $E_g$ value of 1.48 eV [15]. This is larger than the published values and is attributed to the presence of $Sn_2S_3$ (1.9 eV) and SnS$_2$ (2.3 eV), though their diffraction peaks were not confirmed by X-ray diffraction. The absorption coefficient near the fundamental absorption edge was larger than $2 \times 10^4$ cm$^{-1}$ [15]. Ristov et al. [4] found that it was possible to vary the optical bandgap from 2.04 eV to 1.08 eV by changing the degree of crystallinity. The optical absorption edge [16-18], unpolarized infrared transmission [19] and reflectivity [19,20] spectra of SnS had been reported. It is believed that the energy band structure calculations may add to the understanding of the basic processes involved in the absorption of electromagnetic radiations by a semiconductor and subsequent carrier
The transmission of single crystals of $\text{SnS}_{(1-x)}\text{Se}_x$ was measured at 300°K and 77°K. The square root of the absorption coefficient in this region was found to be a linear function of photon energy which indicated that the absorption was due to indirect transition of electrons from the valence band to conduction band [39].

Optical absorption of flash evaporated SnSSe thin films were obtained in the wavelength range 200 nm to 1500 nm at room temperature [25]. It was noted that the bandgap energy increased with increased substrate temperature and at higher temperature the value approaches 1.53 eV for the bulk material. It was observed that the increase in the substrate temperature led to an improvement in crystallinity of the films.

In the present work, the optical properties of electrodeposited and brush plated SnSe, SnS and SnS$_{0.5}$Se$_{0.5}$ thin films are studied. The following studies are carried out: (a) the bandgap of electrodeposited and brush plated SnSe, SnS and SnS$_{0.5}$Se$_{0.5}$ thin films is measured; (b) the optical constants of refractive index 'n', and extinction coefficient 'k' are evaluated.

5.2.2. Bandgap Evaluation
(i) From Optical Absorption Studies

Semiconductors with controlled bandgap is of immense interest due to their applications in opto-electronic devices and photoelectrochemical solar cell fabrication. The semiconducting films, $\text{SnS}_x\text{Se}_{1-x}$ are used for optical measurements which are coated on SnO$_2$ coated glass plates. The glass slide coated with conducting tin oxide (SnO$_2$) has a sheet resistance of 20 $\Omega$ / cm$^2$ and its thickness is 0.1 $\mu$m. It has been assumed that the film thickness of SnO$_2$ is negligible when compared with semiconductor thickness (> 0.5 $\mu$m). The absorption and transmission properties are studied using double beam spectrophotometer and these spectra area used to calculate their bandgap
variations. A plot of $(\alpha\nu)^{1/2}$ versus $\nu$ yielded a straight line and the intercept of the plot yielded bandgap value of the film.

(ii) From $dT/d\lambda$ Method

Another method of evaluation of bandgap is to draw a graph between differential transmittance for different wavelengths $dT/d\lambda$ and $\nu$ which is very close to the region near absorption edge in the transmittance spectra. A single peak is obtained at a wavelength corresponding to the bandgap. In this work, both the above methods were employed to estimate the bandgap of electrodeposited and brush plated thin films.

5.2.3. SnSe Films

The variation of optical absorbance with wavelength for a SnSe film is shown in Fig. 5.1. The figure shows a constant absorption behaviour upto about 990 nm and then starts increasing. The absorbance data is used to obtain the bandgap for SnSe films. From the Fig. 5.1 (insert), the bandgap is estimated as 1.03 eV at 300 K. This value is in excellent agreement with the reported value [5]. Fig. 5.2 shows the optical transmission (T %) behaviour at different wavelengths ($\lambda$). It is observed that below the absorption edge (i.e) below 1100 nm, the transmittance is very poor and decreases drastically from about 35 % to about 5%. The transmittance above 1100 nm is also medium of about 35 % which shows the excellent absorption property of this SnSe films. The differential of the transmittance values with respect to wavelength $(dT/d\lambda)$ is calculated in the entire spectral region. A curve is drawn between $(dT/d\lambda)$ and $\nu$ in which the peak corresponds to the bandgap of the film. The observed bandgap value is 1.02 eV.

Fig. 5.3 shows the absorption versus wavelength behaviour of the brush plated SnSe film. As the films are thicker compared to electrodeposited films,
Fig. 5.1. Variation of optical absorption with wavelength for the electrodeposited SnSe film (insert) \((\alpha h\nu)^{1/2}\) versus \((h\nu)\) plot

Fig. 5.2. Variation of optical transmittance with wavelength for the electrodeposited SnSe film (insert) \((dT/d\lambda)\) versus \((h\nu)\) plot
Fig. 5.3. Variation of optical absorption with wavelength for the brush plated SnSe film (insert) \((\alpha h\nu)^{1/2}\) versus \(h\nu\) plot.

Fig. 5.4. Variation of optical transmittance with wavelength for the brush plated SnSe film (insert) \((dT/d\lambda)\) versus \(h\nu\) plot.
very broad interference patterns are observed. The bandgap value calculated, from the insert to the figure, is 1.04 eV.

The transmittance curve (Fig. 5.4) of the brush plated film shows a linear variation with wavelength. Though the value is high above 1100 nm, below this region the transmittance value is comparable to that of the electrodeposited films. The $dT/d\lambda$ curve gives a bandgap value of 0.99 eV which is in good agreement with the value calculated from the absorbance curve.

### 5.2.4. SnS Films

The optical absorbance curve for SnS film is shown in Fig. 5.5. The bandgap $E_g$ is obtained by extrapolation of the plot of $(a\nu)^{1/2}$ versus $\nu$ and found to be 1.2 eV as shown in the insert of Fig. 5.5. This value is in good agreement with a reported value of 1.1 – 1.2 eV for SnS film [12]. The presence of interference pattern and the very low value of absorbance confirm the very thin nature of the electrodeposited films. The thickness of the films is about 0.9 $\mu$m. Fig. 5.6 shows the transmittance spectrum of these films which indicate a steep fall in the 'T' value below the absorption edge. The $dT/d\lambda$ curve, shown in Fig. 5.6 (insert) has a peak at 1.18 eV which is in coincidence with the $E_g$ value calculated from the absorption curve.

The absorption and transmission behaviour of the brush plated SnS films are shown in Figures 5.7 and 5.8. The thickness of the films is about 0.8 $\mu$m which is evident from the interference pattern observed from the transmittance curve. The calculated bandgap value is 1.23 eV and 1.16 eV respectively from the $(a\nu)^{1/2}$ vs $\nu$ and $dT/d\lambda$ vs $\nu$ curves.

### 5.2.5. SnS$_{0.5}$Se$_{0.5}$ Films

The optical absorption and transmission studies have also been carried out for both the electrodeposited and brush plated SnS$_{0.5}$Se$_{0.5}$ films. The
Fig. 5.5. Variation of optical absorption with wavelength for the electrodeposited SnS film (insert) $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ plot.

Fig. 5.6. Variation of optical transmittance with wavelength for the electrodeposited SnS film (insert) $(dT/d\lambda)$ versus $(h\nu)$ plot.
Fig. 5.7. Variation of optical absorption with wavelength for the brush plated SnS film (insert) $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ plot.

Fig. 5.8. Variation of optical transmittance with wavelength for the brush plated SnS film (insert) $(dT/d\lambda)$ versus $(h\nu)$ plot.
absorption and transmission spectra for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ films are shown in Fig. 5.9 and 5.10 respectively. The bandgap values calculated are 1.10 eV and 1.12 eV which is the first ever reported value for SnS$_{0.5}$Se$_{0.5}$ thin films. The best agreement between the values calculated from the above calculations is a confirmation of solid solution formation.

This is also confirmed for the brush plated films for which the absorption and transmission curves are shown in Fig. 5.11 and 5.12. The calculated bandgap values 1.12 eV and 1.15 eV support the previous discussion.

Fig. 5.13 shows the variation of bandgap with the composition 'x'. It shows almost linear variation of $E_g$ with 'x'.

5.3. EVALUATION OF OPTICAL CONSTANTS

The estimation of optical constants for semiconducting thin films prepared under variety of techniques is a vital field in the materials research [23]. The optical matching of refractive index reduces reflection losses and enhances transmission and hence increases the efficiency of optoelectronic devices. From the optical spectra, the refractive index (n) and the extinction coefficient (k), are determined. For determining the optical constants, a modified continuous differential descent method is used and is already described in Chapter 2.

5.3.1. SnSe Films

The dispersion of 'n' and 'k' for different wavelengths obtained using the CDD algorithm for electrodeposited SnSe films is shown in Fig. 5.14. The 'n' value is slowly increasing from higher wavelength region towards lower wavelength region. In the region near the absorption edge, the refractive index value reaches 3.0 and then reaches a maximum of about 3.1. The extinction
Fig. 5.9. Variation of optical absorption with wavelength for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ film (insert) $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ plot.

Fig. 5.10. Variation of optical transmittance with wavelength for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ film (insert) $(dT/d\lambda)$ versus $(h\nu)$ plot.
Fig. 5.11. Variation of optical absorption with wavelength for the brush plated SnS$_{0.5}$Se$_{0.5}$ film (insert) \((\alpha h\nu)^{1/2}\) versus \((h\nu)\) plot

Fig. 5.12. Variation of optical transmittance with wavelength for the brush plated SnS$_{0.5}$Se$_{0.5}$ film (insert) \((dT/d\lambda)\) versus \((h\nu)\) plot
Fig. 5.13. Variation of band gap ($E_g$) with film composition ($x$)
(A) Electrodeposited films (B) Brush plated films
coefficient ‘k’ varies from 0.02 to 0.45 as the wavelength decreased from 1500 nm to 400 nm.

The variation of n and k values with wavelength for brush plated SnSe is shown in Fig. 5.15. As the films developed by the brush plating are of higher thickness the refractive index values are found to be higher. The steep increase in ‘n’ is observed exactly at 1050 nm which is the absorption edge. The extinction coefficient curve shows the same trend.

5.3.2. SnS Films

The dispersion of n and k with wavelength is shown in Fig. 5.16. The value of refractive index starts increasing near 1100 nm which corresponds to the absorption edge of SnS. The evaluated value of refractive index is less than the SnSe. The value of ‘k’ decreases with wavelength and the variation is similar to those obtained for SnSe thin films. The k values are very low of the order of 0.1 revealing the very thin nature of the electrodeposited SnS films. This is supported by the high transmittance values and lower absorption values reported earlier in Fig. 5.5 & Fig. 5.6. The n and k values of brush plated SnS film are shown in Fig. 5.17. The ‘n’ values are high of about 3.7 below the absorption edge and is about 3.0 at the absorption region which is located at 1100 nm for SnS films. This value is close to the ‘n’ value of 3.5 for SnS single crystal [17].

5.3.3. SnS_{0.5}Se_{0.5} Film

The variation of the values of ‘n’ and ‘k’ for the electrodeposited SnS_{0.5}Se_{0.5} film is shown in Fig. 5.18. The ‘n’ values vary in the range of 2.5 – 4.5 which shows the same trend as the end members (i.e.) SnS and SnSe. The increasing trend of ‘n’ starts at about 1100 nm which coincides with the absorption edge value already reported in previous section. The k values are very low in the order of 0.1.
Fig. 5.14. Variation of refractive index (n) and extinction coefficient (k) with wavelength for the electrodeposited SnSe film.

Fig. 5.15. Variation of refractive index (n) and extinction co-efficient (k) with wavelength for the brush plated SnSe film.
Fig. 5.16. Variation of refractive index (n) and extinction coefficient (k) with wavelength for the electrodeposited SnS film.

Fig. 5.17. Variation of refractive index (n) and extinction coefficient (k) with wavelength for the brush plated SnS film.
Fig. 5.18. Variation of refractive index (n) and extinction coefficient (k) with wavelength for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ film.

Fig. 5.19. Variation of refractive index (n) and extinction coefficient (k) with wavelength for the brush plated SnS$_{0.5}$Se$_{0.5}$ film.
Fig. 5.19 shows the n and k values for the brush plated film. The n value is found increasing at about 1100 nm and the value is about 3.25. The extinction coefficient curve shows a maximum near the 1000 nm region.

5.4. ELECTRICAL PROPERTIES

The studies on the transport properties of SnSe and SnS have attracted attention due to their high potentials in photoelectrochemical cells. The electrical properties of SnSe, and SnS thin films have been studied by several researchers [24-39]. However, thin films based on SnS$_x$Se$_{1-x}$ have not been studied in detail with respect to their electrical properties. The electrical properties of this system is found to depend on the various deposition parameters, i.e., bath pH, temperature, molarity of the constituent species and annealing conditions of the films. Hence, a study of electrical conductivity of these alloy films is an important aspect.

The present study deals mainly with the electrical conductivity of these films and their related semiconductor parameters.

5.4.1. Review on SnS$_x$Se$_{1-x}$ Films

The electrical properties of SnSe films deposited by flash evaporation onto glass, mica and KCl substrates are reported [40]. The films deposited on KCl substrates showed a lower resistivity than those deposited on glass and mica substrates. The films were found to be p-type in nature. Hall mobility and carrier concentration were observed to increase with increasing temperature. At room temperature, the resistivity, the Hall mobility and the carrier concentration were found to be 80 ohm cm, 59 cm$^2$V$^{-1}$s$^{-1}$ and $9.5 \times 10^{16}$ cm$^{-3}$ respectively. Thermally stimulated currents (TSC) were measured in the structures containing a monocrystalline SnSe film grown by the Hot Wall Epitaxy (HWE) technique. The result showed a total trap density of the order of $10^{18}$-$10^{19}$cm$^{-3}$. It was observed
that trap density increased with decrease in film thickness [41]. Amorphous SnSe films which possess ovonic type switching properties are fabricated using vacuum deposition techniques [24]. Conductivity, photoconductivity and Hall measurements had been carried out on vacuum evaporated, air heated SnSe films of different thickness in the temperature range 300 K – 85 K to probe into the mechanism of photoconductivity in these films [42]. The average value of the barrier height is found to be in the order of 0.18 eV. The magnitude of the grain boundary potential barrier for different thickness of the film was also estimated from the variation of mobility with temperature and the average value obtained is of the order of 0.17 eV.

The structure, electronic and optical properties of SnSe films prepared by flash evaporation and hot wall epitaxy techniques onto different substrates have been presented [43]. It was observed that the electrical conductivity and carrier mobility of HWE grown SnSe films are comparatively higher than those obtained by conventional evaporation techniques. Observations revealed that the mobility and carrier concentration showed an increase with increasing thickness [43]. I-V curves obtained for electrodeposited SnSe films [5] were slightly non-linear with a positive $d^2I/dV^2$ but symmetrical. Hot probe measurements indicated that the films were weakly p-type, consistent with Mitchell's results [6]. The $\ln$ (conductance)-$1000/T$ plot exhibits two linear regions with an activation energy of 0.44 eV for the high temperature region and 0.51 eV for the low temperature region.

A method is described, by which the SnS films can be deposited on a glass surface, from aqueous solutions of SnCl₂ and Na₂S or (NH₄)₂S [4]. The conductivity of non-annealed SnS films measured at 20°C and under day light illumination was found to depend on the alkalinity of the SnCl₂ solution. The increase of pH from 3 to 12 led to an increase in conductivity by four orders of magnitude. The films prepared at pH = 3, 10 and 12 with a thickness of 0.1 μm had conductivities of $1 \times 10^{-7}$, $5 \times 10^{-5}$ and $6 \times 10^{-3}$ Ω⁻¹ cm⁻¹ respectively. The $\ln$
(resistance) vs $1/T$ yielded the activation energies of 0.3 eV in the high temperature range and 1.1 eV in the low temperature region. Short-time annealing (for 30 min) at 285°C in open air changed the type of conductivity from p-type to n-type. The donor activation energy $E_d = 0.1$ eV was determined [4]. The electrical characterization of SnS films, synthesized by a chemical method on glass substrates at room temperature (300 K) using an Sn$^{2+}$ salt solution, triethanolamine, ammonia and thioacetamide as the reagents, was studied. The films were found to be amorphous and n-type with an optical energy gap of $2.42 \times 10^{-19}$ J (1.51 eV) [13]. The current-voltage characteristics of the SnS film with silver contacts were found to be linear, suggesting that silver paint forms an ohmic contact to SnS films.

The electrical properties of SnS films prepared by vacuum evaporation method were reported [15]. Vacuum-deposited SnS films exhibit always p-type conduction with a resistivity of $13-20$ $\Omega^{-1}$ cm$^{-1}$, a carrier density of $6.3 \times 10^{14} \sim 1.2 \times 10^{15}$ cm$^{-3}$ and a Hall mobility of $400 \sim 500$ cm$^2$V$^{-1}$S$^{-1}$. The activation energy for conduction was about $0.28 \sim 0.34$ eV, suggesting the presence of deep acceptor levels, in accordance with the results in the literature [12]. Plots of In (conductance) vs $T^{-1}$ for the grey-black Sn$_{1-x}$S ($E_g \sim 1.0 \sim 1.3$ eV) synthesized by the CVD technique [4] indicated activation energies between 0.43 and 0.69 eV. The Sn$_{1-x}$S films exhibited moderate photoconductance with apparent recombination times $\sim 1$ ms. SnS films prepared by electrodeposition technique at room temperature on indium tin oxide coated glass substrates showed p-type nature.

Single crystals of SnS$_{0.5}$Se$_{0.5}$ were used for Hall voltage and resistivity measurements according to Van der Pauw's method [39]. Good electrical contacts were obtained using silver paint or by welding 100 $\mu$ gold wires to the samples. All crystals prepared by distillation and zone refining were p-type with a free hole concentration at room temperature between $10^{17}$ and $5 \times 10^{18}$ cm$^{-3}$ depending on the heat treatment. For SnSe, similar results were reported [36].
The temperature dependence of the hole mobility measured on cleavage plates of SnS$_{0.5}$Se$_{0.5}$ showed that only at high impurity concentrations, the mobility was observed to decrease drastically at low temperatures.

As there are no reports available on SnS$_{0.5}$Se$_{0.5}$ in thin film form, the electrical properties of these films prepared by electrodeposition and brush plating are reported for the first time.

**5.4.2. Studies on Electrical Properties**

The electrical properties of tin chalcogenide films (SnSe, SnS and SnS$_x$Se$_{1-x}$) prepared by electrodeposition and brush plating technique are studied in a vacuum of $10^{-4}$ torr. The current-voltage characteristics are studied in the temperature range 300-450 K. The temperature is measured using calibrated chromel-alumel thermocouple.

The electrical characterization of electrodeposited and brush plated semiconducting films by resistance measurements is complicated by the fact that the film must be removed from the conducting substrate without damage prior to any measurement.

The chalcogenide films are removed from the conductive substrate by attaching a plate to the surface of the film using an epoxy. After the epoxy is dried for ten hours, the epoxy and the tin chalcogenide film comes away with the plate when force is applied between the plate and the substrate. Crack and pin-hole free films of area 0.5 to 1.0 cm$^2$ are removed from tin oxide coated glass substrates. Thickness of typical films used for the electrical studies are in the range of 1.2 to 2.5 $\mu$m. Contacts to the semiconductor films are made with silver paste to obtain low resistance ohmic contacts [13]. The current-voltage characteristics show a linear behaviour suggesting that silver paint forms ohmic contact to SnS$_x$Se$_{1-x}$ films.
5.4.3. SnSe Films

The effect of temperature on electrical conductivity ($\sigma$) of SnSe films is studied. Fig. 5.20 & 5.21 show the variation of $\ln \sigma$ with inverse absolute temperature for a typical electrodeposited and brush plated SnSe vacuum annealed films respectively. The conductivity of the SnSe films is found to increase from $10^{-11}$ to $10^{-8}$ mho cm$^{-1}$ as the temperature increases for the electrodeposited SnSe films and from $10^{-10}$ to $10^{-7}$ mho cm$^{-1}$ for the brush plated films. Thermal activation energy ($E_a$) of electrical conduction is estimated using the conductivity relation, $\sigma = \sigma_0 \exp (-E_a / kT)$ using a least square fit method. The activation energy of the SnSe is estimated as 0.45 eV for the electrodeposited SnSe film and 0.43 eV for the brush plated film. This value is in good agreement with the reported value of 0.44 eV for SnSe films [5] prepared by electrodeposition technique. The observed value of 0.45 eV is nearly half of the optical bandgap value which confirms the presence of a deep acceptor level in p-type SnSe films.

In the present work, the reduction in the film resistivity is caused by annealing the SnSe films at high temperatures (250°C) in vacuum. Annealing causes an improvement in grain size which reduces the carrier scattering at the grain boundaries.

5.4.4. SnS Films

The effect of temperature on the electrical conductivity of SnS films is studied. The variation of $\ln \sigma$ with $1/T$ for electrodeposited and brush plated SnS films annealed in vacuum is shown in Fig. 5.22 and Fig. 5.23. It is observed from the Fig. 5.22 that the conductivity increases from $10^{-7}$ mho cm$^{-1}$ to $10^{-6}$ mho cm$^{-1}$ as the temperature increases from 300 to 450 K for electrodeposited films.
Fig. 5.20. Variation of $\ln \sigma$ with inverse absolute temperature for the electrodeposited SnSe film

Fig. 5.21. Variation of $\ln \sigma$ with inverse absolute temperature for the brush plated SnSe film
Fig. 5.22. Variation of $\ln \sigma$ with inverse absolute temperature for the electrodeposited SnS film.

Fig. 5.23. Variation of $\ln \sigma$ with inverse absolute temperature for the brush plated SnS film.
Fig. 5.23 shows the variation of $\ln \sigma$ with $1/T$ for a brush plated SnS film annealed in vacuum. The conductivity is found to vary from $10^{-7}$ mho cm$^{-1}$ to $10^{-5}$ mho cm$^{-1}$ as the temperature increases from 300 to 450 K.

The activation energy is estimated to be 0.46 eV for electrodeposited and 0.44 eV for brush plated films which are in good agreement with the values reported for SnS films prepared by other techniques [11]. The brush plated films show higher conductivity compared to the electrodeposited films due to their high thickness.

5.4.5. SnS$_{0.5}$Se$_{0.5}$ Films

The variation of conductivity at room temperature for SnS$_{0.5}$Se$_{0.5}$ films is estimated and represented in Fig. 5.24 and Fig. 5.25 for the electrodeposited and brush plated films respectively. It is found that the conductivity of the film varies linearly with composition in the range $10^{-10}$ to $10^{-6}$ mho cm$^{-1}$. The activation energy of SnS$_{0.5}$Se$_{0.5}$ is calculated as 0.51 eV for electrodeposited and 0.53 eV for brush plated film.

Table 5.1 shows the electrical parameters like cross plane resistivity, mobility of holes and diffusion coefficient for SnS$_x$Se$_{1-x}$ ($x = 0.0, 0.5$ and $1.0$) films prepared by electrodeposited and brush plated techniques. Because of cross plane resistivity is higher for electrodeposited than brush plated films, the mobility of holes and diffusion coefficient are found to be lower.

It has been found from hot probe studies that the SnS$_x$Se$_{1-x}$ films prepared by both techniques exhibited p-type nature of semiconductors. Both electrodeposited and brush plated SnSe films are stoichiometric in nature and hence the resistivity is somewhat higher. As the percentage of SnSe in SnS$_x$Se$_{1-x}$ films increases, the film resistance also increases due to the incorporation of more Se in the film. Another interesting observation is that the conductivity
Fig. 5.24. Variation of $\ln \sigma$ with inverse absolute temperature for the electrodeposited $\text{SnS}_x\text{Se}_{1-x}$ film (where $x = 0, 0.5$ and $1$)
Fig. 5.25. Variation of $\ln \sigma$ with inverse absolute temperature for the brush plated $\text{SnS}_x\text{Se}_{1-x}$ film (where $x = 0, 0.5$ and 1)
### Table 5-1

Electrical properties of electrodeposited and brush plated SnS\(_{x}\)Se\(_{1-x}\) films

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample</th>
<th>Cross plane resistivity ((\rho)) (\Omega) cm</th>
<th>Mobility of holes ((\mu_H)) (\text{cm}^2\text{V}^{-1}\text{s}^{-1})</th>
<th>Diffusion coefficient ((D_p)) (\text{cm}^2\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SnSe films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrodeposited</td>
<td>20</td>
<td>4.5</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Brush plated</td>
<td>6.0</td>
<td>14</td>
<td>0.35</td>
</tr>
<tr>
<td>2.</td>
<td>SnS films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrodeposited</td>
<td>18</td>
<td>4.7</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Brush plated</td>
<td>10</td>
<td>20</td>
<td>0.52</td>
</tr>
<tr>
<td>3.</td>
<td>SnS(<em>{0.5})Se(</em>{0.5}) films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrodeposited</td>
<td>15</td>
<td>9.0</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Brush plated</td>
<td>5.0</td>
<td>30</td>
<td>0.77</td>
</tr>
</tbody>
</table>
values are in the intermediate range for the SnSe and SnS values. It confirms the solid solution formation.

5.5. SUMMARY AND CONCLUSION

The optical and electrical properties of SnS$_x$Se$_{1-x}$ (where $x = 0, 0.5$ and $1$) films are studied. As the electrodeposited films are thinner compared to brush plated films, good interference patterns are observed. A slight shift is only observed for SnS$_{0.5}$Se$_{0.5}$ solid solution films as the S content increases in the films prepared by both electrodeposition and brush plating. The optical constants $n$ and $k$ estimated using a modified continuous differential descent method and their variation with wavelength are studied.

Electrical properties of SnSe, SnS and SnS$_{0.5}$Se$_{0.5}$ films are studied in vacuum in the temperature range 300 to 450 K. It is found that the conductivity of the film varies linearly with composition in the range $10^{-10}$ to $10^{-6}$ mhos cm$^{-1}$. The exact value of the conductivity depends on the solid solution film composition. As the percentage of SnSe in SnS$_x$Se$_{1-x}$ film is increased, the film resistance also increases due to the incorporation of more Se in the film. The conductivity values are in the intermediate range for the end components which confirm the solid solution formation. Thermal activation energies of the films are estimated and the results are discussed.
REFERENCES


