Chapter-5
Electrical Transport
Properties of SnSe Thin Films

5.1 Introduction

Electrical transport properties of materials play an important role in determining the behavior of solid state devices and thereby their potential for such applications. Study of the electrical conduction is one of the important electrical characteristics of semiconductor material required not only for practical applications but also for the interpretation of various physical phenomena. The profound changes which occur in physical and chemical nature of a material essentially give information through its conductivity data. The study of the variation of electrical resistance with temperature of the material gives an idea of the dominant conduction mechanism of charge carriers involved. Tin selenide find its applications in various electrical and opto-electronic devices. Investigations regarding the electrical behavior of tin selenide thin film have been reported to be strongly depended on deposition conditions [1-9]. For its application in the device fabrication as an active layer it must be thoroughly characterized for electrical transport properties. The investigations of the electrical properties of the grown thin films based on various electrical characterizations methods like Hall Effect measurements and thermoelectric power measurements are presented in this chapter.

5.2 Hall Effect measurement

Hall Effect measurement is a unique tool to provide basic electrical parameters of material needed to find the suitability of its application. The phenomenon in which the production of a voltage difference across an electrical conductor, transverse to an electric current in the conductor placed in a magnetic field perpendicular to the current is known as a Hall Effect [10, 11]. This phenomenon was explained by Edwin H. Hall in 1879 at the Johns Hopkins University. Hall Effect differentiates between positive charges moving in one direction and negative charges moving in the opposite direction. This is a very important feature of the Hall Effect.
The Hall Effect offered the first real proof of the fact that the electric current in metals is carried by moving electrons, not by protons. Hall Effect measurement provides us basic electrical parameters of material needed to find the suitability of its application.

In the present investigation the Hall Effect measurements were made using Lake Shore Hall measurement system (Lake Shore 7504) over a temperature range of 303-393 K under the magnetic field of 3 kG.

5.2.1 van der Pauw method for Hall effect measurement [12]

The theoretical foundation of Hall measurement evaluation for irregularly shaped samples is based on conformal mapping developed by van der Pauw [13, 14]. He showed how the resistivity, carrier concentration and mobility of a flat sample of arbitrary shaped specimen can be determined without knowing the current pattern, if the following conditions are satisfied,

- the contacts are sufficiently small,
- the contacts are at the circumference of the sample
- the sample is homogeneous
- the contact should be ohmic

van der Pauw suggested different geometries such as circular, square, rectangular and cross. The cross structure is generally used for films and other for bulk crystals.

According to the investigations made by Daniel W. Koon [15-18] for different geometries, the preferred geometry is square rather than circle to reduce the effect of contact lead placement errors in measurement of transport parameters such as resistivity and Hall coefficient. The square is the most convenient sample shape to fabricate at the same time it reduces the effect of errors in the van der Pauw method arising from either the size or displacement of contact leads from the edge of the sample. The lead placement in the square sample must be near the corners in order to minimize errors. Square shape geometry for vander Pauw measurement is shown in figure 5.1.

It is easy to show that for four contacts on the boundary of a semi-infinite plane sheet the resistances $R_{12,34}, R_{23,41}$ satisfy the relationship:
\[ \exp\left(\frac{\pi R_{12,34} t}{\rho}\right) + \exp\left(\frac{\pi R_{23,41} t}{\rho}\right) = 1 \] (5.1)

Figure 5.1 (a) Sample geometry for van der Pauw resistivity and Hall effect measurements (b) and (c) Schematic of a van der Pauw configuration used in the determination of the two characteristic resistances \(R_A\) and \(R_B\). (d) Schematic of a van der Pauw configuration used in the determination of the Hall voltage \(V_H\).

By knowing thickness of the sample \(t\), \(R_{12,43}, R_{23,14}\) the above equation can be solved for the resistivity of the material,

\[ \rho = \frac{\pi t}{\ln(2)} \left(\frac{R_{12,43} + R_{23,14}}{2}\right) F \] (5.2)

Where, \( R_{12,34} = \frac{V_{14}}{I_{12}} \) (5.3)

The current \(I\) enters the sample through contact 1 and leaves through contact 2 and \(V_{43} = V_4 - V_3\) is the voltage between contacts 4 and 3. The quantity ‘\(F\)’ is a transcendental function of the ratio,

\[ R_r = \frac{V_{43} I_{23}}{I_{12} V_{14}} = \frac{R_{12,43}}{R_{23,14}} \] (5.4)
or

\[ R_r = \frac{I_{12}V_{14}}{V_{43}I_{23}} = \frac{R_{23,14}}{R_{12,43}} \tag{5.5} \]

Whichever is greater, and \( F \) is obtained by solving the equation,

\[ \frac{R_r - 1}{R_r + 1} = F \cosh \left( \frac{\ln(2)}{2} \ln F \right) \tag{5.6} \]

\( F=1 \), when \( R_r=1 \), which occurs with symmetrical samples like circles or squares, when the contacts are equally spaced and symmetrical.

For each measurement point in a Hall experiment, up to 32 individual resistance measurements are required to be made for both \( A \) and \( B \) type of geometries. Here geometry \( A \) corresponds to \( R_{12,43} \) and \( R_{23,14} \) and geometry \( B \) corresponds to \( R_{41,32} \) and \( R_{34,21} \). Each van der Pauw resistivity requires 8 measurements (terminal interchange and current reversal for both figure 5.1(b and c) and the Hall resistance requires 4 measurements (terminal interchange and current reversal for figure 5.1 d).

The sequence of the measurements is as follows.

- Zero field resistance measurements (8 measurements).
- Hall resistance measurements for +ve magnetic field, +\( B \) (4 measurements).
- Resistivity measurements for +ve magnetic field, +\( B \) (8 measurements).
- Hall resistance for –ve magnetic field, –\( B \) (4 measurements).
- Resistivity measurements for –ve magnetic field, -\( B \) (8 measurements).

By knowing the thickness ‘\( t \)’ of the sample and measurement of voltage and current with polarity reversal across the contacts, the resistivities for geometries \( A \) and \( B \) can be calculated from the following equation,

\[ \rho_A = \frac{\pi f_\alpha t}{\ln(2)} \left( \frac{V_{12,43}^+ - V_{12,43}^- + V_{23,14}^+ - V_{23,14}^-}{I_{12}^+ - I_{12}^- + I_{23}^+ - I_{23}^-} \right) \tag{5.7} \]

\[ \rho_B = \frac{\pi f_\beta t}{\ln(2)} \left( \frac{V_{34,21}^+ - V_{34,21}^- + V_{41,23}^+ - V_{41,23}^-}{I_{34}^+ - I_{34}^- + I_{41}^+ - I_{41}^-} \right) \tag{5.8} \]

Here \( V_{12,43}^\pm \) means voltage measured between contact 4 and 3 when positive forced current is allowed to pass between contact 1 and 2. Similarly \( I_{12}^\pm \) denotes +ve
forward current measured between contacts 1 and 2. The geometrical factors $f_A$ and $f_B$ are functions of $Q_A$ and $Q_B$, respectively, given by,

$$Q_A = \frac{R_{12,43}^+ - R_{12,43}^-}{R_{23,14}^+ - R_{23,14}^-} = \left(\frac{V_{12,43}^+ - V_{12,43}^-}{I_{12}^+ - I_{12}^-}\right)\left(\frac{I_{23}^+ - I_{23}^-}{V_{23,14}^+ - V_{23,14}^-}\right)$$  \hspace{1cm} (5.9)

$$Q_B = \frac{R_{34,21}^+ - R_{34,21}^-}{R_{41,23}^+ - R_{41,23}^-} = \left(\frac{V_{34,21}^+ - V_{34,21}^-}{I_{34}^+ - I_{34}^-}\right)\left(\frac{I_{41}^+ - I_{41}^-}{V_{41,23}^+ - V_{41,23}^-}\right)$$  \hspace{1cm} (5.10)

The relationship between $f$ and $Q$ is expressed by the transcendental equation,

$$\frac{Q - 1}{Q + 1} = \frac{f}{\ln 2} \cosh^{-1}\left(\frac{1}{2} \exp\left[\ln 2 - \frac{f}{f}\right]\right)$$  \hspace{1cm} (5.11)

The two resistivities must agree to within ±10%. If they do not, then the sample is too inhomogeneous or anisotropic or has some other problem. If they agree, the average resistivity is given by,

$$\rho_{av} = \frac{\rho_A + \rho_B}{2}$$  \hspace{1cm} (5.12)

Similarly with the help of same measurements of voltage and current along with the magnetic field reversal the two Hall coefficients are calculated by the following equations.

$$R_{HC} = \frac{t(m)}{B(T)} \left[\frac{V_{31,42}^+ (+B) - V_{31,42}^- (+B) + V_{31,42}^- (-B) - V_{31,42}^+ (-B)}{I_{31}^+ (+B) - I_{31}^- (+B) + I_{31}^+ (-B) - I_{31}^- (-B)}\right]$$  \hspace{1cm} (5.13)

$$R_{HD} = \frac{t(m)}{B(T)} \left[\frac{V_{42,13}^+ (+B) - V_{42,13}^- (+B) + V_{42,13}^- (-B) - V_{42,13}^+ (-B)}{I_{42}^+ (+B) - I_{42}^- (+B) + I_{42}^+ (-B) - I_{42}^- (-B)}\right]$$  \hspace{1cm} (5.14)

Where $R_{HC}$ and $R_{HD}$ are the Hall coefficients for configuration shown in figure 5.1(d) and its terminal interchange respectively. These two should also agree to within ±10%. If they do not agree, it indicates that the sample is too inhomogeneous or anisotropic or has some other problem. If they agree, then the average Hall coefficient can be calculated by,
\[ R_{Hav} = \frac{R_{HC} + R_{HD}}{2} \quad (5.15) \]

From the average value of resistivity and Hall coefficient the Hall mobility can calculated by,

\[ \mu_H = \frac{|R_{Hav}|}{\rho_{Av}} \quad (5.16) \]

Where \( \rho_{Av} \) is the zero field resistivity.

5.3 Experimental

In the present investigations, the experiment of Hall measurement for pure and off-stoichiometric thin film samples has been conducted with a magnetic field of ±3 kG and at a high temperature range 303-393 K. The main requirement of successful observation and measurement of Hall Effect is to have proper ohmic contacts with the material under test. There are different post preparation techniques to these contacts if they do not show ohmic behavior. These depend mainly on nature of material and contacting metal with bonding paste/agent etc.

The ohmic nature can be confirmed by simply measuring current-voltage characteristics for different combinations of the set of contacts like 1212, 2323, 3434, and 4141. Normally, this four combinations of pair of contacts are supposed to be tested for identifying Ohmic behavior.

5.3.1 Hall effect measurement system

The Lake Shore 7504 Series Hall Effect/Electronic Transport Measurement System [19] is designed to measure electric transport properties of electrically conductive materials. The system consists of advanced, integrated hardware and software. 7504 Series systems are easy to operate using the Lake Shore Hall Measurement System Software. The Hall System Software controls system instrumentation during an experiment and determines sample resistance, resistivity, Hall coefficient, Hall mobility and carrier concentration. The software can control magnetic field during measurements. Variation in temperature is made possible with the help of ASABA DTC temperature controller.
The Lake Shore 7504 Series Hall Effect Measurement System consists of an electromagnet which can produce a magnetic field of maximum $10kG$ with 4 inch air gap between the two pole pieces. The necessary current is being supplied by the magnet power supply (LS 689) with current and voltage limits of 0 to $\pm 72\ A$ and 0 to $\pm 32\ V$ respectively. The Model 450 is an extremely accurate full-featured Gauss meter that covers a wide range of magnetic fields and applications.

The instrument provides easy-to-use front panel programming and a vacuum fluorescent alphanumeric display. This alphanumeric format allows for message-based front panel operation. Most operations can be performed and monitored through the front panel keypad and message display. The Model 450 measures fields in either Gauss ($G$) or Tesla ($T$). The Gauss meter measures both DC and AC magnetic field values. In DC operation, the display shows the DC field at the probe with the sign (orientation) followed by the appropriate field units. In AC operation, the display shows a Peak or RMS value for the field at the probe.

The high temperature experiments were carried out with the help of ASABA DTC temperature controller coupled with Cr-Al thermocouple. The block diagram of high temperature Hall Effect measurement with sample holder is shown in figure 5.2, 5.3 and 5.4.
A temperature sensor mounted close to the sample provides a much more accurate measure of the actual sample temperature. The temperature sensor (Al-Cr thermocouple) on the sample insert is used to control the temperature.

Figure 5.3 Sample holder.

Figure 5.4 Lake shore-7504 complete Hall Effect measurement system.
Following are the general features of Hall measurement system. (*L.S.HMS 7504*),

- Measures Hall voltage, resistance, magnetoresistance, and current-voltage characteristics with one system.
- Allows contact characterization by measuring current-voltage (I-V) curves in most configurations.
- Measurement configurations capable of measuring samples with resistances ranging from mΩ to hundreds of MΩ.
- Varies magnetic field to determine the effects on materials.
- Calculates resistivity, Hall coefficient, carrier concentration and mobility.
- Reduces measurement time with a fully integrated, automated computer data collection system which makes measurements and calculates results.
- Displays real-time feedback of processed measurement data in both graphical and/or tabular format as the experiment is taking place.
- Controls, monitors, and changes instrument settings throughout the experiment using Hall System Software. The software includes individual instrument drivers for complete on-screen, virtual front panel control and operation of all instrumentation.
- Allows users to write custom programs in Visual **BASIC** or other languages to access the Hall System Software using the Object Linking and Embedding (OLE) interface.
- Produces more accurate, repeatable measurements by actively monitoring, controlling, and stabilizing magnetic flux density (field). It also produces excellent field stability with water cooled magnet coils, feedback control, high quality sensors, and advanced electronics.

### 5.3.2 Results and discussion

First of all, the films having different thicknesses, having different substrate temperatures and having different stoichiometry were prepared on glass slides with 1 × 1 cm² area for electrical measurements. The ohmic contacts were then prepared using silver paste and copper wire. These contacts were made dry properly and then all the contacts were tested for their ohmic nature. The ohmic nature of contacts for the films with different thicknesses is shown in figure 5.5. It is seen that for all films, all four resistance values vary almost linearly in the current range ±1 to ±2 μA.
After the confirmation of the ohmic nature, the experiment has been conducted for Hall measurements to study the effect of thickness on the electrical properties such as resistivity, carrier concentration, Hall mobility and Hall coefficient using standard technique known as van der Pauw method for SnSe thin films of different thicknesses with a magnetic field of ±3 kG and for a high temperature range of 303-393 K.

The results thus obtained by these measurements, for all these four SnSe thin films with 3 kG magnetic field at room temperature are tabulated in the table 5.1.

**Table 5.1** Room temperature Hall parameters of SnSe thin films of different thickness.

<table>
<thead>
<tr>
<th>Film thickness</th>
<th>Resistivity ($\Omega \cdot cm$)</th>
<th>Carrier concentration ($cm^{-3}$)</th>
<th>Hall coefficient ($cm^2/C$)</th>
<th>Mobility ($cm^2/Vs$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 kÅ</td>
<td>4.80x10^8</td>
<td>2.13x10^14</td>
<td>8.93x10^1</td>
<td>4.80x10^2</td>
</tr>
<tr>
<td>10 kÅ</td>
<td>5.40x10^9</td>
<td>3.13x10^13</td>
<td>2.27x10^3</td>
<td>6.98x10^2</td>
</tr>
<tr>
<td>12 kÅ</td>
<td>6.85x10^11</td>
<td>3.04x10^13</td>
<td>8.54x10^3</td>
<td>2.26x10^2</td>
</tr>
<tr>
<td>15 kÅ</td>
<td>1.82x10^13</td>
<td>5.52x10^13</td>
<td>1.31x10^4</td>
<td>1.66x10^5</td>
</tr>
</tbody>
</table>
The variation of the Hall parameters of films of different thicknesses i.e. Resistivity ($\rho$), Carrier concentration ($\eta$), Hall mobility ($\mu$) and Hall coefficient ($R_H$) with temperature are represented graphically in figures 5.6, 5.7, 5.8, and 5.9.

**Figure 5.6** Variation of resistivity as a function of temperature for SnSe thin films of different thickness.

**Figure 5.7** Variation of carrier concentration as a function of temperature for SnSe thin films of different thickness.
Figure 5.8 Variation of Hall coefficient as a function of temperature for SnSe thin films of different thickness.

Figure 5.9 Variation of mobility as a function of temperature for SnSe thin films of different thickness.
Figure 5.6 show that the resistivity of all the films decreases with increasing temperature which indicates the semiconducting behavior of the films. It is observed that, the resistivity decreases almost linearly in the case of thin films having thicknesses 8 kÅ and 10 kÅ. Whereas, resistivity of 12 kÅ thin film is decreasing rapidly with increasing temperature. However, the value of resistivity is decreasing rapidly in temperature range of 308 K to 330 K and changes slowly for the temperature range 330 K to 393 K. The carrier concentration of all the films is found to be increased with the increasing temperature as shown in figure 5.7. It is seen that, initially carrier concentration is found to increase slowly with temperature, however there is a sudden rise is observed above 365 K. Hall coefficient and mobility of all the films decreases with temperature (figure 5.8 and 5.9). This variation of carrier concentration and mobility display the fundamental property of semiconductor that with increase in temperature more carriers are released from their bound states thereby increases the carrier concentration where as the thermal vibrations which are not used in substantial release of charge carriers due to insufficient energy leads to the decrease in the mobility. Further, with increase in carrier concentration, internal scattering of charge carriers increases that reduce the mobility. The positive sign of Hall coefficient for all the films indicates that all the prepared thin films possess holes as a majority charge carrier and thus all the films exhibit $p$–type nature of conductivity.

Figure 5.10 and 5.11 gives variation of room temperature Hall parameters as a function of film thickness. It is seen from figure 5.10 that resistivity is found to be increased from $4.80 \ \Omega.cm$ (8 kÅ) to $68.5 \ \Omega.cm$ (12 kÅ) and then decreases to $18.2 \ \Omega.cm$ (15 kÅ). Whereas, mobility is found to be increased from $480 \ cm^2/V.s$ (8 kÅ) to $698 \ cm^2/V.s$ (10 kÅ) and decrease to $226 \ cm^2/V.s$ (12 kÅ) then again increases to $1660 \ cm^2/V.s$ (15 kÅ). From figure 5.11, it is observed that the value of Hall coefficient increases form $89.3 \ cm^3/C$ to $13400 \ cm^3/C$ with increasing thickness of the films. While carrier concentration is found to be decreased from $2.13 \times 10^{14} \ cm^{-3}$ (8 kÅ) to $3.04 \times 10^{13} \ cm^{-3}$ (12 kÅ) then increase to $5.53 \times 10^{13} \ cm^{-3}$ (15 kÅ). Thus, our results deviate from the general trends of variation in Hall parameters with thickness.
Figure 5.10 Variation of room temperature resistivity and mobility with thickness for SnSe thin films.

Figure 5.11 Variation of room temperature carrier concentration and Hall coefficient with thickness for SnSe thin films.
The temperature dependence of resistivity is expressed by the equation [20],

\[ \rho = \rho_0 \exp \left( \frac{E_a}{kT} \right) \]  

(5.17)

Where, \( \rho \) is the resistivity, \( \rho_0 \) is the pre-exponential factor, \( E_a \) is the activation energy for this thermally activated process, \( k \) is the Boltzmann constant (8.617385 \times 10^{-5} \text{ eV/K} \), and \( T \) is the corresponding temperature.

A plot of \( \ln(\rho) \) vs. \( 1/T \) would be a straight line and we can calculate the activation energy \( (E_a) \) from its slope. This plot for the SnSe thin films of different thicknesses is shown in figure 5.12. The values of activation energy obtained from this plot is found to be 0.18, 0.23, 0.48 and 0.81 \text{ eV} for the films of thicknesses 8, 10, 12 and 15 \text{ kÅ} respectively in the temperature range 303-353 \text{ K}.

**Figure 5.12** Semi-log plot of the resistivity as a function of inverse of temperature for SnSe films of different thicknesses.
The temperature dependent Fermi energy can be calculated using the relation [21-24].

\[ E_F = kT \ln \left( \frac{p}{N_F} \right) \] (5.18)

where \( p \) is the carrier concentration and \( N_F \) is the effective density of states.

The calculated Fermi energy for SnSe films of different thicknesses is plotted against temperature as shown in figure 5.13.

The Hall parameters were also measured for SnSe thin films to study the effect of substrate temperature as well as stoichiometry variation of the films. The variations of these parameters as a function of temperature are shown in following figures (5.15 to 5.18 and 5.24 to 5.27). Before this the ohmic nature of contacts were confirmed and it is shown in figures 5.14 and 5.23. It is seen from figures 5.15 to 5.18 and 5.24 to 5.27 that the results of Hall parameters variations show general trends.

![Figure 5.13](image)

**Figure 5.13** Variation of Fermi energy of SnSe thin films of different thicknesses with temperature.

The results obtained by these room temperature Hall measurements made using 3 kG magnetic field, for all four SnSe thin films deposited at different substrate temperatures are tabulated in the table 5.2.
Figure 5.14  $I - V$ Characteristics of the Pair of ohmic contacts on thermally evaporated $SnSe$ thin films deposited at different substrate temperature.

Table 5.2 Room temperature Hall parameters measured at $3kG$ magnetic field for $SnSe$ thin films deposited at different substrate temperature.

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>Resistivity ($\Omega \cdot cm$)</th>
<th>Carrier concentration ($cm^{-3}$)</th>
<th>Hall coefficient ($cm^2/C$)</th>
<th>Mobility ($cm^2/Vs$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308 K</td>
<td>$5.3989 \times 10^0$</td>
<td>$3.1325 \times 10^{13}$</td>
<td>$2.2689 \times 10^3$</td>
<td>$3.2410 \times 10^2$</td>
</tr>
<tr>
<td>338 K</td>
<td>$2.9879 \times 10^1$</td>
<td>$2.4656 \times 10^{15}$</td>
<td>$4.9317 \times 10^4$</td>
<td>$6.9834 \times 10^3$</td>
</tr>
<tr>
<td>368 K</td>
<td>$1.4559 \times 10^{-1}$</td>
<td>$3.7137 \times 10^{16}$</td>
<td>$8.0100 \times 10^3$</td>
<td>$2.0243 \times 10^3$</td>
</tr>
<tr>
<td>398 K</td>
<td>$8.2715 \times 10^{-2}$</td>
<td>$3.7928 \times 10^{16}$</td>
<td>$1.6808 \times 10^2$</td>
<td>$9.6770 \times 10^3$</td>
</tr>
</tbody>
</table>
Figure 5.15 Variation of resistivity as a function of temperature for SnSe thin films deposited at different substrate temperature.

Figure 5.16 Variation of carrier concentration as a function of temperature for SnSe thin films deposited at different substrate temperature.
Figure 5.17 Variation of Hall coefficient as a function of temperature for SnSe thin films deposited at different substrate temperature.

Figure 5.18 Variation of mobility as a function of temperature for SnSe thin films deposited at different substrate temperature.
Figure 5.19 Variation of room temperature resistivity and mobility with substrate temperature for SnSe thin films.

Figure 5.20 Variation of room temperature carrier concentration and Hall coefficient with substrate temperature for SnSe thin films.
A plot of $\ln(\rho)$ vs. $1/T$ for the SnSe thin films deposited at different substrate temperatures is shown in figure 5.21. The values of activation energy obtained from this plot is found to be 0.23, 0.40, 0.31 and 0.45 eV for the films deposited at substrate temperature 308, 338, 368 and 398 K respectively in the temperature range 303-353 K.

![Figure 5.21](image)

**Figure 5.21** Semi-log plot of the resistivity as a function of inverse of temperature for SnSe films deposited at different substrate temperatures.

The plot of calculated Fermi energy for SnSe films deposited at different substrate temperatures against temperature is shown in figure 5.22.

![Figure 5.22](image)

**Figure 5.22** Variation of Fermi energy of SnSe thin films deposited at different substrate temperatures with temperature.
The results obtained from Hall measurements, for all these four SnSe thin films deposited with different stoichiometry and with 3kG magnetic field at room temperature are tabulated in the table 5.3.

**Table 5.3** Room temperature Hall parameters measured at 3kG magnetic field for SnSe thin films deposited with different stoichiometry.

<table>
<thead>
<tr>
<th>Film</th>
<th>Resistivity ($\Omega \cdot cm$)</th>
<th>Carrier concentration ($cm^{-3}$)</th>
<th>Hall coefficient ($cm^3/C$)</th>
<th>Mobility ($cm^2/Vs$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe</td>
<td>$5.3989 \times 10^0$</td>
<td>$3.1325 \times 10^{13}$</td>
<td>$2.2689 \times 10^4$</td>
<td>$6.9834 \times 10^4$</td>
</tr>
<tr>
<td>Sn$<em>{0.2}$Se$</em>{0.8}$</td>
<td>$3.9502 \times 10^1$</td>
<td>$1.2057 \times 10^{13}$</td>
<td>$2.1771 \times 10^4$</td>
<td>$2.2855 \times 10^4$</td>
</tr>
<tr>
<td>Sn$<em>{0.3}$Se$</em>{0.7}$</td>
<td>$3.3949 \times 10^2$</td>
<td>$2.0409 \times 10^{13}$</td>
<td>$3.0586 \times 10^4$</td>
<td>$2.5947 \times 10^4$</td>
</tr>
<tr>
<td>Sn$<em>{0.8}$Se$</em>{0.2}$</td>
<td>$2.9869 \times 10^1$</td>
<td>$6.6546 \times 10^{13}$</td>
<td>$4.7969 \times 10^4$</td>
<td>$2.1911 \times 10^4$</td>
</tr>
</tbody>
</table>
Figure 5.24 Variation of resistivity as a function of temperature for SnSe thin films deposited with different stoichiometry.

Figure 5.25 Variation of carrier concentration as a function of temperature for SnSe thin films deposited with different stoichiometry.
Figure 5.26 Variation of Hall coefficient as a function of temperature for SnSe thin films deposited with different stoichiometry.

Figure 5.27 Variation of mobility as a function of temperature for SnSe thin films deposited with different stoichiometry.
Figure 5.28 Variation of room temperature resistivity and mobility with stoichiometry variation ($X=0.2, 0.3, 0.8$) for $Sn_xSe_{1-x}$ thin films.

Figure 5.29 Variation of room temperature carrier concentration and Hall coefficient with stoichiometry variation ($X=0.2, 0.3, 0.8$) for $Sn_xSe_{1-x}$ thin films.
A plot of $ln(\rho)$ vs. $1/T$ for the $SnSe$ thin films deposited with different stoichiometry is shown in figure 5.30. The values of activation energy obtained from this plot is found to be 0.23, 0.29, 0.39 and 0.26 eV for the films $SnSe$, $Sn_{0.2}Se_{0.8}$, $Sn_{0.3}Se_{0.7}$ and $Sn_{0.8}Se_{0.2}$ respectively in the temperature range 303-353 K.

Figure 5.30 Semi-log plot of the resistivity as a function of inverse of temperature for $SnSe$ films of different stoichiometry.

The plot of Fermi energy as a function of temperature for the $SnSe$ thin films with different stoichiometry is shown in figure 5.31.

Figure 5.31 Variation of Fermi energy of $SnSe$ thin films of different stoichiometry temperature.
The positive sign of Hall coefficient for all the films indicates that all the prepared thin films exhibit \( p \) – type nature of conductivity, thus all the films possess holes as a majority charge carrier.

Figure 5.19 and 5.20 represents the variation of room temperature Hall parameters as a function of substrate temperature. These figures show that the resistivity is decreasing with increase substrate temperature while mobility is found increasing with substrate temperature. The resistivity is found to decrease with increasing temperature because of decrease in lattice strain value that causes an improvement in crystallinity of the film deposited at higher substrate temperature [25]. At the lower substrate temperatures, deposited films have smaller grain sizes with larger grain boundaries which are highly distorted and thus they have large number of defect states. Therefore films deposited at higher substrate temperatures will have comparatively larger grain sizes which can cause decrease in defect states thereby leads to increase the conductivity of the films [26-28]. Figure 5.28 and 5.29 shows the variation of room temperature Hall parameters as a function of different stoichiometry. It is seen that as the tin content increases and selenium content decreases in the deposited film, the resistivity is found to be increased from 39.50 \( \Omega \cdot \text{cm} \) to 339.5 \( \Omega \cdot \text{cm} \) and then decreases to 29.9 \( \Omega \cdot \text{cm} \) whereas the mobility is found to be increased from 229 cm\(^2\)/V.s to 259 cm\(^2\)/V.s then decreases to 2.19 cm\(^2\)/V.s. However, the carrier concentration and Hall coefficient are found to increase with increasing content of tin in the films.

5.4 Thermoelectric Power Measurement

The thermoelectric effect is one of the most popular laboratory methods to measure the electrical properties like Fermi energy, effective state density and effective mass of carriers of the semiconductors. The thermoelectric effect offers a distinctive advantage over other methods because the measured thermoelectric voltage is directly related to the carrier concentration, which makes the thermoelectric measurement simpler even for low mobility materials [29, 30]. Thermoelectric measurement are therefore, frequently employed in the study of semiconductors as an independent method for determining the sign of charge carriers, effective density of states, the position of Fermi level in semiconductor [31-33] effective mass of the carriers and the scattering mechanism.
In this investigation we use thermoelectric power (TEP) measurement for the study of thermally evaporated SnSe thin films. The TEP measurements on prepared thin films have been carried out using the thermoelectric power measurement setup developed in our laboratory.

According to Hicks [33], Rahman and Ashraf [34] a simple relationship can be obtained for $p$ - type non degenerate semiconductor which directly relates Seebeck coefficient $(S)$ to the carrier concentration ‘$\eta'$ (=\(NA\))[36],

$$S = \left(\frac{k}{e}\right) \left[A + \left(\frac{\ln 2 \left(2\pi m^*_h kT\right)^{3/2}}{nh^3}\right)\right]$$

(5.19)

In this expression, ‘$k$’ is the Boltzmann constant, ‘$e$’ is the electronic charge, ‘$h$’ is the Planck constant, ‘$m_h^*$’ is the effective mass of the charge carrier, ‘$T$’ is the temperature and ‘$A$’ is the scattering coefficient, its value is related to the scattering mechanism and it relates to scattering parameter ‘$s$’ by relation,

$$A = \left(\frac{5}{2} - s\right)$$

(5.20)

It is well known [36-39] that in a non-degenerated semiconductor the carriers are scattered in three different ways (i) by ionized impurities (or defects) (ii) by acoustic phonons or (iii) by optical phonons. For scattering by ionized impurities or defects, the mobility of charge carriers increases with increasing temperature. To analyze the temperature dependence of the thermoelectric power ‘$S$’ of a non-degenerate semiconductor, the expressions given by Mohanchandra and Uchil [40], Goldsmid [35, 41], has been used. This is given as [42-45],

$$S = -\frac{k}{e} \left(\frac{E_F}{A + \frac{E_F}{kT}}\right)$$

(5.21)

In equation 5.20 ‘$A$’ is the scattering coefficient which varies from 0 to 4 depending on the scattering process as discussed above, ‘$s$’ is the scattering parameter and ‘$E_F$’ is the separation of Fermi level from the top of the valance band.

Using the values of ‘$A$’ and the value of ‘$p$ (=\(N_d\))’ carrier concentration from room temperature Hall effect measurements and the values of ‘$S$’ from TEP measurements.
It is well known that the carrier concentration in crystal depends on the $E_F$ [32]. For a small temperature range $E_F$ can be considered as fairly constant. The constant value of $E_F$ implies that the carrier concentration $p$ is not substantially changing with temperature. Therefore, equation 5.19 can be expressed as,

$$S = \frac{k}{e} \left( A + \ln \left( \frac{N_v}{\eta} \right) \right) \quad (5.22)$$

where $N_v$ is the effective density of states in valance band and is given by,

$$N_v = 2 \left( \frac{2\pi m^*_h kT}{\hbar^2} \right)^{3/2} \quad (5.23)$$

Using the value of carrier concentration obtained from Hall Effect measurements $p (=N_A)$, the effective density of states $N_v$ can be calculated with the help of the formula [37, 46],

$$p = N_v \exp \left( -\frac{E_F}{kT} \right) \quad (5.24)$$

Substituting the values of effective density of states in equation 5.23, the effective mass of holes $m^*_h$ was calculated and these values are listed in table 5.3 and it is much closer to the reported value of $m^*_h$ that is $0.15 m_h$ [47].

5.4.1 Thermoelectric power measurement setup

Schematic diagram of experimental setup is shown in figure 5.32. The sample mounting stage is attached with the heaters and both heaters are placed in vacuum chamber with pressure of $10^3$ torr. Two thyristors, which can be controlled individually by temperature controller Eurotherm 2604, are used to provide ac current for the heaters. The same 2604 (multipurpose) controller senses the voltage across thermocouple and voltage across the sample. All electrical connections of the controller are interfaced with computer via RS232. The longitudinal section of the apparatus is shown in figure 5.27 used for the high temperature Seebeck coefficient measurements. It consists of well-insulated 100 Watt cylindrical heaters. The heaters are constructed using nichrom wire and connected to two individual thyristor power supplies which are controlled by the Eurotherm 2604 temperature controller.
In high temperature thermo power measurement setup, one of the key issues is establishing and maintaining a good thermal contact between the sample and the electrical leads, which are measuring the emf, generated from the sample. Hence, for sample mounting two highly conducting copper plates of dimension $35 \times 25 \times 3 \text{ mm}^3$ are brazed on the top of both the heaters (see figure 5.33) and heated with the help of power supply. Holes of $\approx 0.5 \text{ mm}$ diameter are drilled into the two copper plates in order to insert very thin chromal – alumel (type - K) thermocouples.

**Figure 5.32** Block diagram of TEP.

**Figure 5.33** Experimental setup for TEP measurement with Pressure contacts.

In order to establish good thermal contact, the sample is mounted on these two copper blocks. For this purpose, author employs spring loading mechanism made up of silver wires that are situated on the top of the copper blocks, which can be finely
adjusted. This ensures that both thermo–emf and temperature difference are measured at the same point and very close to the sample ends. Both the pressure contacts sense the generated emf due to temperature gradient that can be stored in the computer memory connected via RS232 cable and operated with the help of software ‘iTools’. Accurate temperature setting, its control and measurement are critical for investigation of the Seebeck coefficient (S). One needs to know not only the absolute temperature at which the measurement is taken but also the temperature gradient along the length of the sample – an accurately determined gradient while studying the Seebeck effect. Temperature of the heaters and hence of both the copper plates are controlled by a Eurotherm 2604 temperature controller that sets and maintains the operational point to within ±0.5 K over the range of temperature extending up to 800 K, and this temperature is measured by K type Cr – Al thermocouples. This type of thermocouple remains stable and is resistant to oxidation at least up to 1000 K. Since the entire system is placed in a vacuum chamber with pressure of 10\(^{-3}\) torr, the influence of the heat loss is eliminated and there is negligible temperature drift during the measurement. Also the same metal wires for both voltage leads are brought out of the vacuum chamber using a specially designed feed through to eliminate any artifacts due to dissimilar junction.

5.5 Experimental

The SnSe thin films with the area of 1 × 1 cm\(^2\) having different thicknesses and deposited at different substrate temperatures along with different stoichiometry have been prepared for the TEP measurements. For this purpose, the samples of deposited SnSe thin films have been placed on the sample mounting stage. Before that, the sample mounting stage was cleaned with acetone. Sample was then placed on a piece of mica sheet that was kept on the copper plates to avoid the direct contact between mounting stage and sample. Two ends of sample are connected to the electrical leads with the two taper-ended pressure contacts. The sample is positioned by placing its ends on the copper blocks and pressed with the taper-ended strips. The measurements are taken in the temperature range of 308 to 423 K. The temperature difference (\(\Delta T\)) between the ends of the sample was kept around 5 K. The current for the heater is
regulated by the controller (connected with the computer) to ensure the desired value of $\Delta T$. When the emf voltage ($V$) is generated for particular temperature gradient, the controller senses it. The computer program records the value of emf($V$) when the temperature controller acquires additional delay of three minutes after $\Delta T$. Then Seeback coefficient is evaluated by the equation $S = \Delta V/\Delta T$. The obtained data can be stored by selecting data logging facility of the software.

### 5.5.1 Results and discussion

The variation of Seebeck coefficient (thermoelectric power)'$S'$ as a function of temperature in the range of 308 to 423 $K$ for all four thin films having different thicknesses is shown in figure 5.34. Here it is seen that the sign of Seebeck coefficient is positive for all the SnSe thin films in entire studied temperature range. The positive sign of '$S'$ confirms the $p$ – type nature of conductivity as it was seen in the Hall effect results. The average value of thermo power is found to be increasing with increasing film thickness.

![Figure 5.34 Variation of thermoelectric power ($S$) as a function of temperature for SnSe thin films of different thicknesses.](image)

137
The equation 5.19 and equation 5.21 suggest that if thermoelectric power \((S)\) is plotted against the reciprocal of temperature that gives a straight line \([37, 40, 48]\) as shown in figure 5.35. From the slope of this line the value of Fermi energy ‘\(E_F\)’ \([37, 48]\) can be determined and it is found to be 0.13, 0.10, 0.079 and 0.066 \(eV\) for SnSe thin films of thickness 8, 10, 12 and 15 \(k\AA\) respectively. Thus Fermi energy decreases with increasing thickness of the film. The scattering parameter’s can be obtained from the intercept on y-axis.

![Figure 5.35](image)

**Figure 5.35** Variation of thermoelectric power \((S)\) as a function of reciprocal of temperature for SnSe thin films of different thicknesses.

The values of effective density of states \((N_V)\) and effective mass \((m_b^*)\) can be determined using equations 5.23 and 5.24 respectively. These calculated values of \(N_V\), \(m_b^*\), the carrier concentration from room temperature Hall effect measurement and obtained values of other thermopower parameters for SnSe thin films of different thicknesses from above analysis are shown in table 5.4.

**Table 5.4** Thermopower parameters for SnSe thin films of different thickness

<table>
<thead>
<tr>
<th>Thick. of film</th>
<th>Carrier density (p) ((cm^{-3})) ((RT HE))</th>
<th>Effective density of states (N_V) ((cm^{-3}))</th>
<th>Effective mass (m_b^*(kg))</th>
<th>(m_b^*/m_h)</th>
<th>Fermi energy (E_F) ((eV))</th>
<th>Scatt. Para.((s))</th>
<th>Scatt. Coeffi. ((A))</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 (k\AA)</td>
<td>2.13x10^{13}</td>
<td>2.84x10^{16}</td>
<td>1.14x10^{-12}</td>
<td>0.013</td>
<td>0.131</td>
<td>8.93x10^{-4}</td>
<td>2.4991</td>
</tr>
<tr>
<td>10 (k\AA)</td>
<td>3.13x10^{13}</td>
<td>1.35x10^{17}</td>
<td>1.48x10^{-13}</td>
<td>0.002</td>
<td>0.100</td>
<td>8.01x10^{-4}</td>
<td>2.4992</td>
</tr>
<tr>
<td>12 (k\AA)</td>
<td>3.04x10^{13}</td>
<td>5.95x10^{14}</td>
<td>4.01x10^{-13}</td>
<td>0.005</td>
<td>0.079</td>
<td>7.52x10^{-4}</td>
<td>2.4993</td>
</tr>
<tr>
<td>15 (k\AA)</td>
<td>5.52x10^{13}</td>
<td>6.62x10^{14}</td>
<td>9.20x10^{-14}</td>
<td>0.001</td>
<td>0.066</td>
<td>7.16x10^{-4}</td>
<td>2.4993</td>
</tr>
</tbody>
</table>
The same TEP study and analysis has been carried out for the SnSe thin films deposited at different substrate temperature and also for films deposited with different stoichiometry.

**Figure 5.36** Variation of thermoelectric power (S) as a function of temperature for SnSe thin films deposited at different substrate temperature.

**Figure 5.37** Variation of thermoelectric power (S) as a function of reciprocal of temperature for SnSe thin films deposited at different substrate temperature.
Figure 5.36 show the variation of thermoelectric power \( (S) \) as a function of temperature for \( SnSe \) thin films deposited at different substrate temperature and the variation of thermoelectric power \( (S) \) as a function of reciprocal of temperature for \( SnSe \) thin films deposited at different substrate temperature is shown in figure 5.37. Similarly the variation of thermoelectric power \( (S) \) as a function of temperature and reciprocal of temperature for the films of \( SnSe \) deposited with different stoichiometry are shown in figure 5.38 and 5.39 respectively.

**Figure 5.38** Variation of thermoelectric power \( (S) \) as a function of temperature for \( SnSe \) thin films deposited with different stoichiometry.

**Figure 5.39** Variation of thermoelectric power \( (S) \) as a function of reciprocal of temperature for \( SnSe \) thin films deposited with different stoichiometry.
In both the case the Fermi energy and scattering parameter have been determined using plot of \( S \) vs. \( 1/T \) and the values of effective density of states \( (N_V) \) and effective mass \( (m_h^*) \) have also been determined using equations 5.23 and 5.24 respectively. The obtained results for SnSe thin films deposited at different substrate temperature and films deposited with different stoichiometry are shown in table 5.5 and 5.6.

**Table 5.5** Thermopower parameters for SnSe thin films deposited at different substrate temperature.

<table>
<thead>
<tr>
<th>Substrate temp.</th>
<th>Carrier density ( p ) (cm(^{-3}) (RT HE))</th>
<th>Effective density of states ( N_V ) (cm(^{-3}))</th>
<th>Effective mass ( m_h^* ) (kg)</th>
<th>( m_h^*/m_h )</th>
<th>Fermi energy ( E_F ) (eV)</th>
<th>Scatt. Para.(s)</th>
<th>Scatt. Coeffi. (( A ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>308 K</td>
<td>3.13 x10(^13)</td>
<td>1.48x10(^17)</td>
<td>1.54x10(^{-33})</td>
<td>0.002</td>
<td>0.100</td>
<td>8.01 x10(^{-4})</td>
<td>2.4991</td>
</tr>
<tr>
<td>338 K</td>
<td>2.47 x10(^13)</td>
<td>5.69x10(^16)</td>
<td>1.82x10(^{-22})</td>
<td>0.020</td>
<td>0.082</td>
<td>7.54 x10(^{-4})</td>
<td>2.5000</td>
</tr>
<tr>
<td>368 K</td>
<td>3.71 x10(^10)</td>
<td>6.94x10(^17)</td>
<td>9.72x10(^{-32})</td>
<td>0.011</td>
<td>0.076</td>
<td>7.34 x10(^{-4})</td>
<td>2.4993</td>
</tr>
<tr>
<td>398 K</td>
<td>3.79 x10(^10)</td>
<td>5.83x10(^17)</td>
<td>8.65x10(^{-32})</td>
<td>0.095</td>
<td>0.072</td>
<td>7.31 x10(^{-4})</td>
<td>2.4993</td>
</tr>
</tbody>
</table>

It is seen from the results that all the films show semiconductor behavior as the thermoelectric power in both the cases remains positive throughout the entire temperature range. The Fermi energy is found to decrease with increasing substrate temperature as well as increasing stoichiometric proportion of Sn in the film. The value of scattering coefficient \( (A) \) is found to be around 2.5 for all the films.

**5.6 Conclusions**

Here the electrical transport properties have been obtained using two different methods i.e. Hall effect and Thermo power measurements. The final overall conclusions drawn from above study are listed below.

- The decrement in resistivity of the films with increasing temperature indicates the typical semiconducting behaviour of SnSe thin films.
The positive sign of Hall coefficient from Hall effect results suggest the $p$ – type semiconducting nature of thermally evaporated $SnSe$ thin films. Hence holes are considered as majority carriers in deposited thin films.

From temperature dependent resistivity, activation energy has been calculated for all the thin films and it is found to be increased with increasing in thickness and substrate temperature.

The charge carrier density is found to increase with increase in temperature while the mobility of charge carrier is found to be decreased with increasing temperature.

The effect of thickness and substrate temperature on Hall parameters can be successfully explained based on film is crystalinity.

It is seen from the thermopower measurement results for all the films that films posseses $p$ – type semiconducting nature which supports the Hall effect results.

The steady increase of thermopower with temperature indicates the typical nature of semiconductor.

Fermi energy of $SnSe$ thin films have been calculated using TEP data and it is found that the value of Fermi energy decreases with increasing film thickness as well as substrate temperature.

The value of scattering coefficient is found to be around 2.5 for all the deposited $SnSe$ thin films.

From the obtained parameters we can say that deposited $SnSe$ thin films are suitable for fabrication of Schottky diode and other devices.

References


