CHAPTER VII
HALL AND THERMOELECTRIC STUDIES

7.1 Introduction

The analysis of the electronic properties of selenium chalcogenide layers/films using only conductivity is a complicated process, due to the variety of effects that contribute to the measured values. In order to assist the interpretation of electronic phenomenon in these films, Hall and thermoelectric studies are very much essential. These experiments are performed to determine the carrier concentration and mobility. To get a deeper insight about the conduction mechanisms in tellurium and Se\textsubscript{x}Te\textsubscript{1-x} films, the Hall effect measurements are needed. The details of the Hall effect and thermoelectric power studies carried out on Te and Se\textsubscript{x}Te\textsubscript{1-x} films are presented in this chapter.

In the present investigation, Hall measurements are made on Te, Se\textsubscript{0.7}Te\textsubscript{0.3}, Se\textsubscript{0.5}Te\textsubscript{0.5}, and Se\textsubscript{0.3}Te\textsubscript{0.7}, thin films at different temperatures and the Hall parameters such as Hall coefficient, Hall mobility and carrier concentration are calculated.

Though the initial experiments gave an idea of main physical behaviour of thermoelectricity in many materials, the thermoelectricity has been used as a sophisticated tool for studying electron and phonon scattering in solids. Many workers have studied the thermoelectric properties of different semiconductors [1-4]. But not many results are available with regard to the composition dependence of compound semiconducting films. The present investigation is focussed on the thermopower measurements mainly to get an idea about the thermo e.m.f, thermopower and the type of carriers in Te and selenium telluride films of three different compositions (Se\textsubscript{0.7}Te\textsubscript{0.3}, Se\textsubscript{0.5}Te\textsubscript{0.5}, and Se\textsubscript{0.3}Te\textsubscript{0.7}).
7.2 Theory

7.2.1 Hall Effect

When a current carrying conductor is placed in a magnetic field, a voltage is generated in a direction perpendicular to both the directions of electric and the magnetic fields. In this observation, known as the Hall effect, the charge carriers are deflected to one side of the conductor as a result of Lorentz force experienced by them. A proper analysis of the experimental data will give information regarding the nature of the charge carriers and their densities. The sign of the charge carriers can therefore be determined from the measurement of the polarity of the Hall voltage. From a knowledge of the resistivity ($\rho$) of the sample, developed Hall voltage ($V_H$), current ($I$) through the sample and applied magnetic field ($H$), various Hall parameters can be calculated.

The following equation is used to calculate the resistivity. The sheet resistance ($R_{Sh}$) is given by,

$$R_{Sh} = 4.53 \frac{V}{I}$$

(7.1)

and the resistivity $\rho$ is related as [5]

$$\rho = \frac{R_{Sh}}{d}$$

(7.2)

where $d$ is the thickness of the film. The Hall coefficient ($R_H$) and Hall mobility ($\mu_H$) are calculated using the relations,

$$R_H = \frac{V_H \times d}{\frac{I}{H} \times 10^8 \text{ cm}^3/\text{coulomb}}$$

(7.3)

and
\( \mu_{II} = \frac{R_{II}}{\rho} \text{ cm}^2/\text{V-sec} \) \hspace{1cm} (7.4)

respectively.

The carrier concentration (n) is obtained from the formula

\[
n = \frac{1}{R_{II}} e \hspace{1cm} (7.5)
\]

where 'e' represents the charge of an electron.

### 7.2.2 Thermoelectric power (TEP)

Thermoelectric power is the e.m.f produced per unit temperature difference between the junctions of materials. Among the various transport properties, thermopower is perhaps the most sensitive to distortions of the Fermi surface. The thermoelectric power has been determined using the relation

\[
\text{TEP} = \frac{\Delta V}{\Delta T}, \quad \text{where} \quad \Delta V \text{ is a measure of the voltage produced by the temperature gradient } \Delta T \text{ between two ends of the sample.}
\]

But the variation of TEP with \( \Delta T \) cannot be assumed to be linear and thus the thermo electric power is determined from the slope of \( \Delta V - \Delta T \) curve, i.e., \( \text{TEP} = \frac{d(\Delta V)}{d(\Delta T)} \).

The thermoelectric power measurements are important to find out the nature of the charge carriers i.e., electrons or holes. For a n-type semiconductor, the electron flow will be from the hot end to the cold end. If the hot end of the semiconductor is connected to the live point of the digital multimeter and cold end is connected to the reference point, then the positive polarity will be displayed by the digital multimeter. This happens because, with respect to the cold end, the hot end is depleted of carriers. The reverse phenomena occurs for p-type semiconductor.
7.3 Measurements

7.3.1. Hall Effect

The four-probe method of Van der Pauw has been used to measure the electrical resistivity of the films of Te and Se$_x$Te$_{1-x}$ of three different compositions. In order to achieve a good ohmic contact, gold is evaporated at the periphery of the samples and contacts are made using conductive silver paste. Copper - constantan thermocouple is used to measure the temperature.

A digital Hall measurement set-up (MMR Technology INC., U.S.A.) is used for the Hall studies. The measurements are made under a pressure of 1.3 Pa. Temperature dependence of carrier concentration, mobility and resistivity are studied in the temperature range 300 - 450 K.

7.3.2 Thermoelectric Effect

The thermo e.m.f measurement jig (Fig.7.1) consists of two copper blocks separated by a distance of 3 cm and mounted on an asbestos sheet. One of the copper blocks, acting as the hot junction, is fitted with a stripe heater while the other one serves as the cold junction. Two spring loaded pure copper rods of equal length (5 cm) and diameter (3 mm) are made to form a junction along with the sample placed over the copper blocks. The coated side of the film faces the copper rod. Two copper - constantan thermocouples are used to measure the temperatures of both the cold and hot junctions. The temperature is measured by a digital multimeter. The entire TEP setup is placed inside a stainless steel container. One of the junctions (hot junction) is heated slowly. The developed e.m.f. is measured by a digital multimeter. The whole experiment is carried out under a pressure of 1.3 Pa.
FIG. 7.1. EXPERIMENTAL JIG FOR THERMOELECTRIC POWER MEASUREMENTS:
V-Voltage Leads; Th₁ and Th₂-Thermocouples; H-Heater Leads; S-Sample.
7.4 Results and Discussion

7.4.1 Hall effect

Figs. 7.2 to 7.4 show the variation of Hall mobility (\(\mu_H\)) with absolute temperature for Te and \(\text{Se}_x\text{Te}_{1-x}\) films of different thicknesses. In \(\text{Se}_{0.5}\text{Te}_{0.5}\) and \(\text{Se}_{0.3}\text{Te}_{0.7}\) films (Fig.7.3 and 7.4), the nature of the plot is found to be linear, thus following the Conwell-Weisskopf relationship [6]. In Te and \(\text{Se}_{0.7}\text{Te}_{0.3}\) films, the nature of the plot does not appear to depend linearly on \(T^{-3/2}\) [7] but, the trend indicates that different types of scattering centres are active at different temperature ranges. The mobility is governed by intercrystalline grain boundaries [8].

The variations of carrier concentrations (n) with temperature are shown in Figs. 7.5 to 7.7 for Te and \(\text{Se}_x\text{Te}_{1-x}\) films of different thicknesses. In Te, \(\text{Se}_{0.7}\text{Te}_{0.3}\) and \(\text{Se}_{0.5}\text{Te}_{0.5}\) films (Figs 7.5 to 7.7) the carrier concentration increases only weakly with temperature and we could not find a significant dependence on thickness. In \(\text{Se}_{0.3}\text{Te}_{0.7}\) (Fig. 7.7) films it is interesting to see that n shows a maximum and decreases with increase of thickness.

Figs 7.8 to 7.10 show the variation of Hall coefficient (\(R_H\)) with absolute temperature for Te and \(\text{Se}_x\text{Te}_{1-x}\) films of different thicknesses. In \(\text{Se}_{0.5}\text{Te}_{0.5}\) and \(\text{Se}_{0.7}\text{Te}_{0.3}\) (Fig.7.9 and 7.10) films the curves initially show an increase and then decreases with increase of temperature. In Te and \(\text{Se}_{0.3}\text{Te}_{0.7}\) (Fig.7.8 and 7.9) films it is observed that, with the increase of temperature, \(R_H\) decreases slowly, attaining a minimum and then increase very sharply with further increase in temperature.

7.4.2 Thermoelectric Power

The negative polarity shown by digital multimeter while connecting its live and reference points to the hot and cold junctions of the semiconductor
FIG. 7.2. VARIATION OF MOBILITY ($\mu_H$) WITH TEMPERATURE FOR Te THIN FILM
FIG. 7.3. VARIATION OF MOBILITY ($\mu_H$) WITH TEMPERATURE FOR $\text{Se}_{0.5}\text{Te}_{0.5}$ THIN FILMS.
FIG. 7.4. VARIATION OF MOBILITY ($\mu_H$) WITH TEMPERATURE FOR $\text{Se}_{0.7}\text{Te}_{0.3}$ and $\text{Se}_{0.3}\text{Te}_{0.7}$ THIN FILMS
FIG. 7.5. CARRIER DENSITY ($n$) Vs. TEMPERATURE PLOT OF Te THIN FILM
FIG. 7.6. CARRIER DENSITY (n) Vs. TEMPERATURE PLOT OF $\text{Se}_{0.5}\text{Te}_{0.5}$ THIN FILM
FIG. 7.7. CARRIER DENSITY (n) Vs. TEMPERATURE PLOT OF
Se$_{0.7}$Te$_{0.3}$ and Se$_{0.3}$Te$_{0.7}$ THIN FILMS
FIG. 7.8. HALL COEFFICIENT Vs. TEMPERATURE PLOT OF Te THIN FILM
FIG. 7.9. HALL COEFFICIENT Vs. TEMPERATURE PLOT OF Se$_{0.5}$Te$_{0.5}$ THIN FILM
FIG. 7.10. HALL COEFFICIENT Vs TEMPERATURE PLOT OF
Se$_{0.7}$Te$_{0.3}$ and Se$_{0.3}$Te$_{0.7}$ THIN FILMS
respectively indicates its charge carriers to be of p-type. Similar observation has been made by Chakraborty et al [9] in bulk antimony selenide.

Thermo e.m.f. has been measured for Te and three different compositions of $\text{Se}_x\text{Te}_{1-x}$ films ($\text{Se}_{0.7}\text{Te}_{0.3}$, $\text{Se}_{0.5}\text{Te}_{0.5}$ and $\text{Se}_{0.3}\text{Te}_{0.7}$). Te thin film of typical thickness 88 nm is used for the TEP measurement. Fig. 7.11 shows the variation of thermo e.m.f. with temperature. The increase in thermo e.m.f. is noticed with the increase of temperature and the variation is also linear. The thermoelectric power is calculated from the slope of the plot (Fig. 7.11) as $210 \mu \text{V K}^{-1}$.

The variation of thermo e.m.f. with temperature for $\text{Se}_x\text{Te}_{1-x}$ thin films of three different compositions of typical thicknesses 110, 129 and 138 nm respectively are shown Figs. 7.12 and 7.13. It is observed that the plots are linear. The thermopower for these films are calculated as 100, 90 and $75 \mu \text{V K}^{-1}$ respectively.

In selenium telluride films of three different compositions ($\text{Se}_{0.7}\text{Te}_{0.3}$, $\text{Se}_{0.5}\text{Te}_{0.5}$ and $\text{Se}_{0.3}\text{Te}_{0.7}$), the decrease of thermoelectric power observed in the present investigation is mainly due to the increase of tellurium percentage.

The thermopower versus temperature plots (Figs. 7.11 to 7.13) shows an increase in TEP with increase in temperature of the hot junction. This linear increase in thermopower is due to the fact that as the temperature gradient increases, creation of electron–hole pair increases and thus there is an increase in the concentration of majority carriers. Similar results were observed by Volklein and Kesslser [10] in antimony films and Damodaradas et al [11] in tellurium thin films.
FIG. 7.11. THERMO EMF Vs. TEMPERATURE PLOT OF Te THIN FILM (d = 88 nm).
FIG. 7.12. THERMO EMF Vs. TEMPERATURE PLOT OF Se₀.₅Te₀.₅ THIN FILM
(d = 110 nm).
FIG. 7.13. THERMO EMF Vs. TEMPERATURE PLOT OF $\text{Se}_{0.7}\text{Te}_{0.3}$ ($d = 129 \text{ nm}$) and $\text{Se}_{0.3}\text{Te}_{0.7}$ ($d = 138 \text{ nm}$) THIN FILMS
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