CHAPTER 7
TRANSPORT PROPERTIES OF ZnX CRYSTALS AND THIN FILMS

7.1 INTRODUCTION

Properties of semiconductors depend on the way they respond to the external force or forces in a given environment. For example, the mechanical, electrical and magnetic properties are the response to the mechanical, electrical and magnetic forces exerted on them. In the recent years there has been tremendous interest in electrical characterization of semiconductors and to relate the various results of measurements to the reliability and performance of the devices made from the semiconductor compounds [1]. Analysis of the various electrical measurements is of great importance in application point of view of the semiconductors.

Despite the considerable interest in photo luminescent and electroluminescent, structural and optical properties of II-VI compounds, few reports have been found for the electrical transport properties of these compounds. This may probably be due to the fact that many of these compounds possess very high resistivity at room temperature.

Electrical properties of II-VI semiconductor crystals as well as thin films are greatly influenced by many parameters [2-25]. Temperature dependence of high field transport of II-VI wide band gap semiconductors is of particular relevance to the large efforts at present in order to produce A.C. and D. C. electroluminescent devices [42]. Electrical resistivity is one of the most important electrical parameter of semiconductors [26-29].

7.2 HALL EFFECT MEASUREMENTS AT VARIOUS TEMPERATURES

7.2.1 HALL EFFECT MEASUREMENT SYSTEM

The Lakeshore 7504 series Hall Effect / Electronic Transport Measurement System has been used to measure the electronic transport properties of electrically conductive
materials [30]. The system consists of advanced integrated hardware and software. The 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.

The system consists of an electromagnet which can produce a magnetic field of maximum 10 kG at 10 cm air gap between two pole pieces of four inch diameter. The magnetic power supply (LS 689) provides necessary current to the magnet. The current and voltage limits of the power supply are 0 to ±72 A and 0 to ±32 V respectively. The gaussmeter (Model – 450) is used for magnetic field measurement.

7.2.2 VAN DER PAUW MEASUREMENT

Electrical properties of the materials play an important role in determining the behavior of solid state devices and thereby their potential for such applications. Hall Effect measurement is an effective tool to provide information about basic material parameters needed to find the suitability of its applications. In the present investigation, the Hall Effect measurement was performed using system (Lakeshore-7504) under magnetic field of ±3kG, from room temperature to 120°C.

The theoretical foundation of the Hall measurement evaluation for irregularly shaped samples is based on the conformal mapping developed by van der Pauw [31-32]. The resistivity, carrier concentration, and mobility of the flat samples of arbitrary shape can be determined without knowing the current pattern, if the following conditions are satisfied

1. The contacts should be sufficiently small
2. The contacts should be at the circumference of the sample
3. The sample should be uniformly thick
4. The sample should not contain isolated holes

Van der Pauw suggested different geometries of the samples 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 Danial W. Koon [33-36] 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 shape is the most convenient sample shape to fabricate, and will reduce the effect of errors in the van der Pauw method arising from either size or the displacement of contact leads from edge of the sample. The lead placement in the square sample must be near to the corners as shown in figure 7.1 (a), to minimize errors.

![Figure 7.1](image)

**Figure 7.1** (a) Sample geometry for van der Pauw resistivity and Hall Effect measurement. (b) & (c) Schematic of van der Pauw configuration used for the determination of the two characteristics resistances $R_A$ and $R_B$. (d) Schmetic of a van der Pauw configuration used in the determination of Hall voltage $V_H$. 
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 following relationship.

\[
\exp\left(-\frac{\pi R_{12,34} t}{\rho}\right) + \exp\left(-\frac{\pi R_{23,41} t}{\rho}\right) = 1
\]  

(7.1)

By knowing thickness of the sample \( t \), \( R_{12,34} \) and \( R_{23,41} \), the above equation can be solved for the resistivity of the material [37,38] and can be written as

\[
\rho = \frac{\pi t}{\ln(2)} \frac{(R_{12,34} R_{23,41})^F}{2}
\]  

(7.2)

where \( R_{12,34} = \frac{V_{34}}{I_{12}} \)  

(7.3)

The current \( I \) enters the sample through contact 1 and leaves through contact 2 and \( V_{34} = V_4 - V_3 \) is the voltage between contacts 4 and 3. \( R_{23,41} \) is similarly defined. The quantity “\( F \)” is a transcendental function of the resistance ratio given as,

\[
R_f = \frac{V_{43} I_{23}}{I_{12} V_{14}} = \frac{R_{12,34}}{R_{23,41}}
\]  

(7.4)

OR

\[
R_f = \frac{I_{12} V_{14}}{V_{43} I_{23}} = \frac{R_{23,14}}{R_{12,43}}
\]  

(7.5)

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

\[
\frac{R_e - 1}{R_e + 1} = \frac{F}{\ln(2)} \arccosh\left(\exp\left[\frac{\ln(2)}{2F}\right]\right)
\]  

(7.6)

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

For each measurement points 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 \( R_{12,34} \) 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 figures 7.1 (b) and (c) and the Hall resistance requires 4 measurements (terminal interchange and current reversal for above figure 7.1 (d). The sequence of measurement is as follows.

Hall resistance measurements for +ve magnetic field, +B (4 measurements)

1. Zero field measurements (8 measurements)
2. Resistivity measurement for +ve magnetic field, +B (8 measurements)
3. Hall resistance measurements for –Ve magnetic field, -B (4 measurements)
4. Resistivity measurement for –ve magnetic field, -B(8 measurements)

In present investigations the experiment has been conducted with a magnetic field of ±3 kG. 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 equations [37, 38]

\[
\rho_A = \frac{\pi f_A[m, \text{cm}]}{\ln(2)} \left( \frac{V_{12,43}^+ - V_{12,43}^- + V_{23,14}^+ - V_{23,14}^-}{I_{12}^+ - I_{12}^- + I_{23}^+ - I_{23}^-} \right) \Omega m, \Omega cm \tag{7.7}
\]

\[
\rho_B = \frac{\pi f_B[m, \text{cm}]}{\ln(2)} \left( \frac{V_{34,21}^+ - V_{34,21}^- + V_{41,23}^+ - V_{41,23}^-}{I_{34}^+ - I_{34}^- + I_{41}^+ - I_{41}^-} \right) \Omega m, \Omega cm \tag{7.8}
\]

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

\[
Q_A = \left( \frac{R_{12,43}^+ - R_{12,43}^-}{R_{23,14}^+ - R_{23,14}^-} \right) = \left[ \frac{V_{12,43}^+ - V_{12,43}^-}{I_{12,43}^+ - I_{12,43}^-} \right] \left[ \frac{I_{23,14}^+ - I_{23,14}^-}{V_{23,14}^+ - V_{23,14}^-} \right] \tag{7.9}
\]
$Q_B = \begin{bmatrix} R_{34,21}^+ - R_{34,21}^- \\ R_{41,23}^+ - R_{41,23}^- \end{bmatrix} = \begin{bmatrix} V_{34,21}^+ - V_{34,21}^- \\ I_{34}^+ - I_{34}^- \end{bmatrix} \begin{bmatrix} I_{41}^+ - I_{41}^- \\ V_{41,23}^+ - V_{41,23}^- \end{bmatrix}$ \hspace{1cm} (7.10)

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

$$\frac{Q-1}{Q+1} = \frac{f}{\ln 2} \cosh^{-1}\left(\frac{1}{2} \exp\left[\frac{\ln 2}{f}\right]\right)$$ \hspace{1cm} (7.11)

The two resistivities must agree to within ±10% of accuracy. 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

$$\rho_{av} = \frac{\rho_A + \rho_B}{2} [\Omega m, \Omega cm]$$ \hspace{1cm} (7.12)

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

$$R_{HC} = \frac{t(m)}{B(T)}\left[\frac{V_{31,42}^+ (B) - V_{31,42}^- (B) + V_{31,42}^-(B) - V_{31,42}^+ (B)}{I_{31}^+ (B) - I_{31}^- (B) + I_{31}^- (B) - I_{31}^+ (B)}\right] \left[m^3 C^{-1}\right]$$ \hspace{1cm} (7.13)

$$R_{HD} = \frac{t(m)}{B(T)}\left[\frac{V_{42,13}^+ (B) - V_{42,13}^- (B) + V_{42,13}^- (B) - V_{42,13}^+ (B)}{I_{42}^+ (B) - I_{42}^- (B) + I_{42}^- (B) - I_{42}^+ (B)}\right] \left[m^3 C^{-1}\right]$$ \hspace{1cm} (7.14)

where, $R_{HC}$ and $R_{HD}$ are the Hall coefficients for configurations shown in figure 7.1 and its terminals interchange respectively. These two values should also agree 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 the equation

$$R_{Hav} = \frac{R_{HC} + R_{HD}}{2} \left[m^3 C^{-1}\right]$$ \hspace{1cm} (7.15)

From the average value of resistivity and Hall coefficient, the Hall mobility can be calculated using the equation
\[ \mu_H = \frac{[R_{Hv}]}{\rho_{av}} \left[ m^2 V^{-1} S^{-1} \right] \] (7.16)

where \( \rho_{av} \) is the zero field resistivity.

The effective charge carrier concentration can be computed using the formula

\[ n_e = \frac{1}{R_H e} \] (7.17)

### 7.2.3 EXPERIMENTAL PROCEDURE

The variable temperature Hall effect measurements have been performed on ZnX (X=Se,Te) crystals grown by DVT technique and ZnX (X=Se,Te) thin films deposited by thermal evaporation technique as discussed in earlier chapter. A specially designed sample holder (Scientific Equipments-Roorki) with built in heater and thermocouple was used in this experiment. The sample holder is shown in figure 7.2.

![Figure 7.2 A sample holder with heater and thermocouple.](image)
The ohmic contacts were taken on the samples (crystals and thin films) with conductive silver paste and copper wires. The samples were properly placed on the sample holder and contact wires were carefully attached with the connecting tracks of the holder. In case of the crystals, both ZnSe and ZnTe crystals were properly cleaned to ensure smooth and flat surface area covered with the contact wires. Thin films were deposited on the small glass substrates (area = 1 cm$^2$) so that they can be easily placed on the sample holder.

A temperature controller cum indicator system of ON/OFF type was attached with the sample holder heater circuit to perform the experiment at known and controlled temperatures (from 30°C to 120°C) with an accuracy of ± 1°C. The complete Hall Measurement system along with the high temperature sample holder and temperature controller cum indicator is shown in figure 7.3.

![Figure 7.3](image)

Figure 7.3  A complete Hall Measurement System (Lake Shore 7504) with high temperature sample holder and temperature controller.
Ohmic contacts are required for accurate and error free measurements of Hall Effect to deduce transport properties of semiconducting samples under study. It is recommended that we should test the current–voltage characteristics between the contacts to verify the ohmic behavior of contacts of sample before beginning the Hall measurement experiment. All the samples have been verified for four sets of contacts of the samples for their ohmic nature and then further experiments were performed.

In the first step, I-V measurements were done for the sample using various contacts (R_{12,12}, R_{23,23}, R_{34,34} and R_{41,41}) without applying magnetic field. In the second step, Hall parameters measurements were performed using the van der Pauw method at various magnetic fields (+3kG to -3kG at the interval of 1kG) and at various temperatures (from 30°C to 120°C) for grown crystals and thin films of ZnSe and ZnTe. Here the applied current range suitable for particular sample is manually selected.

7.3 RESULTS AND DISCUSSION

7.3.1 RESULTS OF ZnSe AND ZnTe CRYSTALS GROWN BY DVT TECHNIQUE

7.3.1.1 OHMIC CONTACTS TO ZnSe AND ZnTe CRYSTALS GROWN BY DVT TECHNIQUE

Preparation of Ohmic contact requires special skills and knowledge of band structure of semiconductor and contacting metal. It is all about the finding the suitable metal or alloy or a particular phase of the metal/alloy so that it offers minimum barrier for charge carriers moving across the interface. This can be achieved by using different metals/alloy contacts made by different techniques such as printing, thermal evaporation, sputtering etc. and there may be post preparation treatments in order to obtain near ideal Ohmic nature of contacts. However, it has been observed that these contacts have particular range of current in which Ohmic nature is sustained and outside this limits due to several reasons like high field effects etc. the Ohmicity breaks. In the present case of ZnSe and ZnTe crystals grown by DVT technique, a high conducting silver paste (Elteck-1228C-Bangalore) has been used. The well cleaned crystals with good smooth flat surfaces have been selected by optical microscope and on four corners of each of the sample four copper wires have been attached using the silver paste. They have then been air dried at 50-60°C. As mentioned earlier, all the samples have
then been tested for their Ohmic nature in order to find the linear range of I-V characteristics to select a particular excitation current for Hall effect measurements. Such plots of typical Current-Voltage (I-V) characteristics for ZnSe and ZnTe crystalline samples are shown in figure 7.4 and 7.5 respectively, for set of contacts $R_{12,12}$, $R_{23,23}$ and $R_{34,34}$, $R_{41,41}$. From these figures, it can be seen that the prepared samples of ZnSe and ZnTe possess Ohmic behavior in the current range of fraction of microampere to few tens of microampere and do not require further contact processing e.g. annealing etc.
Figure 7.4  A set of typical I-V characteristics between $R_{12,12}$, $R_{23,23}$, $R_{34,34}$ and $R_{41,41}$ contacts on ZnSe crystal.
Figure 7.5 A set of typical I-V characteristics between $R_{12,12}$, $R_{23,23}$, $R_{34,34}$ and $R_{41,41}$ contacts on ZnTe crystal.
7.3.1.2 TEMPERATURE DEPENDENCE OF TRANSPORT PROPERTIES OF ZnSe AND ZnTe CRYSTALS GROWN BY DVT TECHNIQUE

After confirmation of ohmic behavior of contacts on samples, Hall effect measurements were carried out. Different operating typical conditions of the Hall measurement system parameters and geometrical parameters of the samples are tabulated in table 7.1 and 7.2 for ZnSe and ZnTe crystals respectively. Zero field resistivity and resistivity at 3 kG magnetic field of ZnSe and ZnTe crystals at various temperatures (303K to 383K) are shown in figures 7.6 and 7.7 respectively. It shows the effects of magnetic field as well as temperature on resistivity for both types of crystals. There is a significant decrease in resistivity, with both magnetic field and temperature for both the crystals of ZnSe and ZnTe. This confirms the semiconducting behavior of the grown crystals. Various Hall parameters like Hall coefficient, carrier density and mobility are measured for both the crystals at magnetic field of 3 kG and at different temperatures (303K to 383K). The variations of these parameters with temperature at magnetic field of 3 kG are shown in figures 7.8, 7.9 and 7.10 for ZnSe and ZnTe crystals. The positive sign of Hall coefficient variation with temperature (Figure 7.8) shows that the holes are the majority carrier which dominates the transport properties in the entire temperature range of measurement. Carrier density and mobility variations with temperature (Figure 7.9 and 7.10) display the fundamental property of semiconductors that with increase in temperature more carriers are released from their bound states and thereby increases the carrier density 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.
<table>
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<td>Sample Thickness</td>
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<td>Sample Length</td>
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<td>Depletion Layer Correction</td>
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<td>Field Step</td>
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<td>Current Reversal</td>
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Table 7.1 Sample and Hall measurement system parameters for ZnSe crystals.
### Sample parameters

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### Measurement Parameters

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<td>Geometry Selection</td>
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</table>

Table 7.2 Sample and Hall measurement system parameters for ZnTe crystals.
Figure 7.6  Variation of zero field resistivity of ZnSe and ZnTe crystals with temperature.

Figure 7.7  Variation of resistivity of ZnSe and ZnTe crystals at 3kG with temperature.
Figure 7.8  Variation of Hall Coefficient of ZnSe and ZnTe crystals at 3kG with temperature.

Figure 7.9  Variation of Carrier Density of ZnSe and ZnTe crystals at 3kG with temperature.
7.3.2 RESULTS OF ZnSe and ZnTe THIN FILMS DEPOSITED BY THERMAL EVAPORATION TECHNIQUE

7.3.2.1 OHMIC CONTACTS TO THERMALLY EVAPORATED ZnSe AND ZnTe THIN FILMS

Ohmic contacts to the deposited thin films of both ZnSe and ZnTe samples were prepared by conducting silver paste as described above. Plots of I-V characteristics of ZnSe thin films of various thicknesses deposited at different substrate temperatures are shown in figure 7.11 and figure 7.12, while figures 7.13 and 7.14 represent I-V characteristics for ZnTe thin films. From the figures 7.11 to 7.14, it can be seen that all contacts on prepared samples possess Ohmic nature and they do not require any further contact treatment. It can be observed that for all thin film samples the linear range of current extends only up to few nano-amperes for ZnSe thin films and that up to few microamperes in case of ZnTe thin films. This range is normally observed to be expanding by two to three orders of magnitude for thicker films and for films that are deposited at elevated substrate temperatures in case of both ZnSe and ZnTe thin films.
Figure 7.11  Plots of I-V characteristics for ZnSe thin films of 1000Å and 2000Å deposited at various substrate temperatures.
Figure 7.12  Plots of I-V characteristics for ZnSe thin films of 3000Å and 5000Å deposited at various substrate temperatures.
Figure 7.13  Plots of I-V characteristics for ZnTe thin films of 1000Å and 2000Å deposited at various substrate temperatures.
Figure 7.14  Plots of I-V characteristics for ZnTe thin films of 3000Å and 5000Å deposited at different substrate temperatures.
7.3.2.2 TRANSPORT PROPERTIES OF ZnSe THIN FILMS

In present study, the van der Pauw method has been used. Various measurement parameters like current forced, magnetic field, contact geometry, current reversal field reversal with the step of field, zero field resistivity etc. were set using software. After proper setting of these parameters the sample assembled on the sample holder placed between the pole magnets, undergo the execution of the Hall measurement process. The Ohmic contacts to the samples placed under Hall measurement system were confirmed by simply measuring their current voltage characteristics as described above.

7.3.2.2.1 THICKNESS DEPENDENT TRANSPORT PROPERTIES

Figures 7.15 to 7.19 show the variation of zero field resistivity, resistivity at 3kG, Hall coefficient, carrier density and mobility with thickness of ZnSe thin films deposited at different substrate temperatures when measured over the temperature range 303-393 K.

Following observations can be easily made from these figures

1. Resistivity of all thin film samples decreases with increasing thickness. This may be because of the fact that thicker films are normally continuous having large number of bigger oriented grains. This growth tendency is enhanced at elevated substrate temperatures as reflected by the decreasing resistivity values shown in the figures 7.15 and 7.16.

2. The sign of the Hall coefficient remains positive for all the samples of ZnSe thin films and its magnitude remains in the range of $12-1.49 \times 10^4$ cm$^3$C$^{-1}$ (Fig.7.17). This indicates that all the prepared films possess holes as a majority charge carrier and thus all the films exhibit p-type semiconducting nature. Also the majority carrier type reversal is not observed in the studied range of temperature i.e.303-393K. It is further found that the magnitude of Hall coefficient decreases monotonically with the increase in film thickness as well as the substrate temperature.

3. Majority charge carrier density i.e. hole density in case of all the deposited thin films of ZnSe increases with the thickness of the films up to $1.4 \times 10^{17}$ cm$^{-3}$ as shown in the figure 7.18.

4. Charge carrier mobility for all the deposited thin films of ZnSe decreases with increasing film thickness(Fig.7.19)
Figure 7.15  Variation of zero field resistivity of ZnSe thin films deposited at different substrate temperatures with film thickness.
Figure 7.16 Variation of resistivity (3kG) of ZnSe thin films deposited at different substrate temperatures with films thickness.
Figure 7.17 Variation of Hall Coefficient for ZnSe thin films deposited at various substrate temperatures with films thickness.
Figure 7.18  Variation of Carrier Density of ZnSe thin films deposited at various substrate temperatures with films thickness.
Figure 7.19  Variation of Mobility of ZnSe thin films deposited at various substrate temperatures with films thickness.
7.3.2.2 SUBSTRATE TEMPERATURE DEPENDENT TRANSPORT PROPERTIES

Variation of various Hall effect parameters like resistivity, Hall coefficient, carrier density and mobility of ZnSe thin films with the film thickness has been studied. Figures 7.20 to 7.24 show the variation of zero field resistivity, resistivity at 3kG, Hall coefficient, carrier density and mobility with substrate temperature for ZnSe thin films of different thickness when measured over the temperature range 303-393 K. Following observations can be easily made from these figures:

1. Resistivity of all thin film samples decreases with increasing substrate temperature as shown in the figures 7.20 and 7.21. This is because of the decrease of the lattice strain value that causes an improvement in crystallinity of the films deposited at higher substrate temperatures [20]. At the lower substrate temperatures, deposited films will have smaller grain sizes with larger grain boundaries which are highly distorted and thus they have large number of defect states. Therefore the films deposited at higher substrate temperatures will have comparatively larger grain sizes which can cause decrease in the defect states and thereby leads to increase the conductivity of the films [39-41].

2. The values of Hall coefficient and carrier mobility decreases with the increase in substrate temperature as shown in figure 7.22 and 7.24.

3. Majority charge carrier density i.e. hole density in case of all the deposited thin films of ZnSe increases with the substrate temperature of the films up to $1.4 \times 10^{17} \text{cm}^{-3}$ as shown in the figure 7.23.
Figure 7.20 Variation of zero field resistivity for ZnSe thin films of different thicknesses with their substrate temperature.
Figure 7.21  Variation of resistivity (3kG) for ZnSe thin films of different thicknesses with their substrate temperature.
Figure 7.22 Variations of Hall Coefficient for ZnSe thin films of different thicknesses with their substrate temperature.
Figure 7.23  Variation of Carrier Density for ZnSe thin films of different thickness with their substrate temperature.
Figure 7.24  Variation of Mobility for ZnSe thin films of different thicknesses with their substrate temperature.
7.3.2.2.3 TEMPERATURE DEPENDENT TRANSPORT PROPERTIES

Hall parameters have been measured at various temperatures from 303K to 393K. Figure 7.25(a),(b),(c) to figure 7.29 shows the variation of different Hall parameters with the temperatures for ZnSe thin films of different thicknesses deposited at different substrate temperatures. It can be seen from figure 7.25(a),(b),(c) and 7.26 that as the temperature increase, films become more conductive and resistivity decreases due to increase in grain size and reduction in defects as discussed above. Similarly, Hall coefficient and mobility decreases with temperature and carrier density increases with temperature.

![Figure 7.25 (a)](image)

**Figure 7.25 (a)** Temperature variation of zero field resistivity for ZnSe thin films of various thicknesses deposited at 303K.
Figure 7.25 (b),(c) Temperature variation of zero field resistivity for ZnSe thin films of various thicknesses deposited at 373K and 448K
Figure 7.26  Temperature variation of resistivity (3kG) for ZnSe thin films of various thicknesses deposited at different substrate temperatures.
Figure 7.27 Temperature variation of Hall coefficient for ZnSe thin films of various thicknesses deposited at various substrate temperatures.
Figure 7.28  Temperature variation of Carrier Density for ZnSe thin films of various thicknesses deposited at various substrate temperatures.
Figure 7.29  Temperature variation of Mobility for ZnSe thin films of various thicknesses deposited at different substrate temperatures.
7.3.2.3 TRANSPORT PROPERTIES OF ZnTe THIN FILMS

7.3.2.3.1 THICKNESS DEPENDENT TRANSPORT PROPERTIES

Hall parameters have been measured at different temperatures, as explained earlier, for ZnTe thin films of various thicknesses deposited at different substrate temperatures. Resistivity (zero field and 3kG), Hall-coefficient, carrier density and Hall mobility variations of ZnTe thin films with temperature are shown in figure 7.30 to figure 7.34 respectively. Following observations can be made easily from these figures.

1. Resistivity of all ZnTe thin films have been found to be decreasing in the range 3-9.44x10² Ω.cm as thickness of the films increases as shown in figure 7.30-7.31.

2. The sign of the Hall coefficient remains positive for all the samples of ZnTe thin films and its magnitude remains in the range of 3-9.44x10² cm³C⁻¹(Fig.7.32). This indicates that all the prepared films possess holes as a majority charge carrier and thus all the films exhibit p-type semiconducting nature. Also the majority carrier type reversal is not observed in the studied range of temperature i.e.303-393K. It is further found that the magnitude of Hall coefficient decreases monotonically with the increase in film thickness as well as the substrate temperature.

3. Majority charge carrier density i.e. hole density in case of all the deposited thin films of ZnTe increases with the thickness of the films from 2.52x10¹⁶ to 4.66x10¹⁸ cm⁻³ as shown in the figure 7.33.

4. Charge carrier mobility for all the deposited thin films of ZnTe decreases from 5.90x10² to 4.66 (cm² /V.Sec) with increasing film thickness (Fig.7.34).
Figure 7.30  Variation of resistivity (Zero Field) of ZnTe thin films with film thickness measured at different temperatures.
Figure 7.31 Variation of resistivity (3kG) of ZnTe thin films with film thickness measured at different temperatures.
Figure 7.32  Variation of Hall Coefficient of ZnTe thin films with film thicknesses measured at different temperature.
Figure 7.33 Variation of carrier density of ZnTe thin films with film thicknesses measured at different temperature.
Figure 7.34 Variation of Hall mobility for ZnTe thin films with film thicknesses measured at different temperature.
7.3.2.3.2 SUBSTRATE TEMPERATURE DEPENDENT TRANSPORT PROPERTIES

Variation of various Hall effect parameters like resistivity, Hall coefficient, carrier density and mobility of ZnTe thin films with the film thickness has been studied. Figures 7.35 to 7.39 show the variation of zero field resistivity, resistivity at 3kG, Hall coefficient, carrier density and mobility with substrate temperature for ZnSe thin films of different thickness when measured over the temperature range 303-393 K. Following observations can be easily made from these figures:

1. As observed in the case of ZnSe thin films, resistivity of all ZnTe thin film samples decreases with increasing substrate temperature as shown in the figures 7.35 and 7.36.

2. The values of Hall coefficient and carrier mobility decreases with the increase in substrate temperature as shown in figure 7.37 and 7.39.

3. Majority charge carrier density i.e. hole density in case of all the deposited thin films of ZnTe increases with the substrate temperature of the films up to $1.4 \times 10^{17}$ cm$^{-3}$ as shown in the figure 7.38.
Figure 7.35  Variation of resistivity (Zero Field) for ZnTe thin films of different thickness with substrate temperature measured in the temperature range 303-393K.
Figure 7.36  Variation of resistivity (3kG) for ZnTe thin films of different thickness with substrate temperature measured in the temperature range 303-393K.
Figure 7.37  Variation of Hall coefficient for ZnTe thin films of different thickness with substrate temperature measured in the temperature range 303-393K.
Figure 7.38  Variation of carrier density for ZnTe thin films of different thickness with substrate temperature measured in the temperature range 303-393K.
Figure 7.39  Variation of mobility for ZnTe thin films of different thickness with substrate temperature measured in the temperature range 303-393K.
7.3.2.3.3 TEMPERATURE DEPENDENT TRANSPORT PROPERTIES

The Hall measurement experiment was performed at various temperatures in the range 303K to 393K at the interval of 10K. Figure 7.40 to figure 7.44 shows the variation of different Hall parameters with temperature for ZnTe thin films of various thicknesses deposited at various substrate temperatures. Significant variations in different Hall parameters were observed with temperature.

It can be seen from figure 7.40 and 7.41 that as the temperature increases, films become more conductive and resistivity decreases due to increase in grain size and reduction in defects as discussed above. Similarly, Hall coefficient (fig.7.42) and mobility (fig.7.44) decreases with temperature carrier density increases with temperature (fig. 7.43).
Figure 7.40  Variation of resistivity (Zero Field) with temperature for ZnTe thin films of different thicknesses.
Figure 7.41  Variation of resistivity (3kG) with temperature for ZnTe thin films of different thicknesses.
Figure 7.42  Variation of Hall coefficient with temperature for ZnTe thin films of different thicknesses.
Figure 7.43  Variation of carrier density with temperature for ZnTe thin films of different thicknesses.
Figure 7.44 Variation of Mobility with temperature for ZnTe thin films of different thicknesses.
7.4 CONCLUSIONS

In present investigation ZnX (X=Se and Te) crystals grown by Direct Vapor Transport (DVT) technique have been used. The grown crystals were sufficient in size to prepare samples out of them for transport properties study using variable temperature Hall effect measurements. Few good crystals with flat signing surfaces have been selected using optical microscope. As the grown crystals have irregular shape with almost uniform thickness, van der Pauw geometry for Hall effect measurement has been selected for further measurements. Silver contacts occupying minimum surface area were prepared carefully to eliminate contact placement error. For all the crystals of ZnX, these Ohmic contacts have been found giving linear current-voltage relationship and from these the force current values for Hall measurement were decided. To eliminate further various measurement errors, the Hall measurements were carried out by current and magnetic field reversals and averaged values of various Hall parameters have been determined. Similar steps have been followed for the square shaped thin film samples of ZnSe and ZnTe deposited by thermal evaporation technique. Table 7.3, 7.4 and 7.5 reports the summary of all measured Hall parameters of ZnSe and ZnTe crystals, ZnSe thin films and ZnTe thin films respectively, along with few data collected from the published literature.

From the literature it is found that DVT technique is very rarely used technique to grow II-VI compound semiconductor crystals because it yields in to growth of relatively smaller crystals than other techniques like Bridgemen technique etc. Therefore, transport property data of such crystals have not been found and here we have compared such data obtained from the measurements made on crystals grown by other techniques. All the grown crystals of ZnSe and ZnTe possess holes as majority carriers as the sign of Hall coefficient remains positive throughout the temperature range of measurement. The resistivity, Hall mobility and Hall coefficient have been found decreasing where as carrier concentration has been found decreasing with increasing temperature in the range 303-393K. This variation is in good agreement with the reported data in the literature as shown in the table 7.3.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (Ω.cm)</th>
<th>Hall Coefficient (Cm³C⁻¹)</th>
<th>Carrier concentration (cm⁻³)</th>
<th>Mobility [cm²/(VS)]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe Crystal</td>
<td>1</td>
<td>10⁴</td>
<td>10⁶ to 10⁸</td>
<td>10⁴</td>
<td>ZnSe, melt growth with excess Zn of 3 to 9.3 mol% [52]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10⁻¹</td>
<td></td>
<td></td>
<td>ZnSe, melt growth with excess Te [54].</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>ZnSe, PVT technique. [53]</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>ZnSe crystals, decrease with temperature from 0 to 350 (K) [50]</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>10¹ - 10³</td>
<td>10⁻¹ - 10²</td>
<td>10¹⁵ - 10¹⁶</td>
<td>Present work, ZnSe crystals PVT technique</td>
</tr>
<tr>
<td>ZnTe Crystal</td>
<td>1</td>
<td>10⁴</td>
<td></td>
<td></td>
<td>ZnTe, Vapor Phase growth, Resistivity decreases with temperature [25].</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10¹</td>
<td></td>
<td></td>
<td>ZnTe melt growth with excess Te [54].</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>10¹⁰ to 10¹⁶</td>
<td>60-1800</td>
<td>ZnTe, grown by vertical Bridgmann method, Increase in temperature increases carrier concentration [47].</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10¹ to 10³</td>
<td>10¹³ to 10¹⁶</td>
<td>46 to 537</td>
<td>ZnTe grown from vertical Bridgemann method, increasing temperature decreases mobility and increases carrier concentration [22].</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td></td>
<td>800 to 40</td>
<td>ZnTe crystals[50]</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>10⁻¹⁻¹⁻²</td>
<td>10⁰⁻¹⁻¹⁻¹⁻⁰⁻¹⁻¹⁻⁰⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻�</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.3 Reported and measured Hall parameters of ZnSe and ZnTe crystals.
Table 7.4 Reported and measured Hall parameters of ZnSe thin films
<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (Ω·cm)</th>
<th>Hall Coefficient (cm²·C⁻¹)</th>
<th>Carrier concentration (cm⁻³)</th>
<th>Mobility [cm²/(VS)]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe Thin Films</td>
<td>1</td>
<td></td>
<td>4×10^{16}</td>
<td>40-1000</td>
<td>ZnTe:N films, MBE, 2000Å [49]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>10^{14} to 10^{15}</td>
<td>5 – 60</td>
<td>ZnTe films, Brush plating technique at 0.9V potential on conducting glass and titanium substrates at different temperatures [46].</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10⁴ -10⁵</td>
<td></td>
<td></td>
<td>ZnTe thin films, Electrodeposition (0.65V), 3000Å, Au coated Cu substrate [56].</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>10^{19}</td>
<td></td>
<td>ZnTe films, Thermal evaporation tech. Glass/silicon substrate, 220 to 1700Å thickness [57].</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>10⁹ -10²</td>
<td>10⁹-10²</td>
<td>10^{16}-10^{18}</td>
<td>590-33</td>
</tr>
</tbody>
</table>

Table 7.5 Reported and measured Hall parameters of ZnTe thin films
Apart from the thermal evaporation technique, there have been verities of techniques adopted to deposit thin films of ZnSe and ZnTe and few such data of transport properties measurements on these thin films are also compared with the results of present investigation.

It is found that the measured data of transport properties in case of ZnSe and ZnTe crystals and thin films are in good agreement with the reported data as shown in table 7.4 and 7.5. They also show the similar trend of decreasing resistivity, carrier concentration and mobility along with increasing Hall coefficient in the temperature range of measurement i.e. 303-393K. The temperature variation of mobility, in a limited range of temperature, is in good agreement with such measurements made in the similar range and it is found that at higher temperature optical phonon scattering is dominant.

For thin films of ZnSe and ZnTe, the thickness and substrate temperature variation of Hall parameters have been investigated in the temperature range 303-393K. It is found that with increasing thickness and substrate temperature the sign of Hall coefficient remains positive indicating that the majority carriers are holes and there is no conductivity type reversal in the measured range of temperatures. All Hall parameters have been found improving as thickness of the films and substrate temperature are increasing because of the fact that thicker films are continuous films ending their growth with smoother surfaces as substrate temperature is increased as evident from the AFM data given in chapter-6.
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