CHAPTER - 3

ELECTRICAL CHARACTERIZATION

OF

CdSe THIN FILMS
3.1 INTRODUCTION:

The electrical characterization of any material is very important because it gives an idea about various important parameters related to the material. On the basis of these parameters, the applications of the grown semiconductors can be decided. With this view, the electrical and thermoelectric properties of CdSe thin films deposited by thermal evaporation technique in present investigations (as discussed in Chapter 2) have been carried out. The details of various experimental techniques used for these characterization and the results obtained during these investigations have been discussed in the following sections.

3.2 TYPE OF CONDUCTIVITY:

It is always essential to know the type of carriers effective for conduction in grown material. In present investigations also, it is necessary to find out the type of conductivity involved in CdSe thin films. For this purpose, the simplest, but standard technique viz. Hot Probe Method has been used.

3.2.1 Hot Probe Method:

The hot probe method basically involves the measurement of thermo emf. If a metal is connected at its two ends with a second metal and if one of the junction is heated, a voltage is developed across the open ends of the second metal. The same concept is applicable in the case of semiconductors when connected to metal at its ends. A schematic circuit diagram for the measurements of thermoelectric voltages for semiconductor is shown in Fig. 3.1.

If metal contacts are applied to the two ends of a semiconductor rod and if one junction is maintained at higher temperature with respect to the other, a potential difference is developed between the two ends. This thermoelectric voltage is produced partly. The reasons for this are:
Fig. 3.1 Schematic circuit for the measurement of thermoelectric voltage in semiconductors.
(a) The majority carriers in the semiconductor diffuse from hot end to the cold end due to the temperature gradient thereby giving a potential difference across the semiconductor. This voltage builds up to a value such that the return current, just balances the diffusion current when a steady state is reached.

(b) The contact potential takes place between the metal and the semiconductor provided the contacts are non-ohmic.

Predicting that the metallic contacts to the semiconductors are ohmic as checked at primary stage, we can say that the voltage measured due to the temperature gradient across the semiconductor is due to only the transport of majority carriers from one end to the other end of the semiconducting specimen. Thus, we can find out the type of the majority carriers in the semiconductor by observing the polarity or sign of the measured thermo emf.

In case of n-type semiconducting specimens, the type of the conductivity can be determined by using the hot probe method in two different ways.

As shown Fig. 3.2(a), when the probe-connected to the positive terminal of voltmeter is heated and contacted to the semiconductor, the charge carriers - predominantly electron - flow towards negative terminal - being the cold end of the semiconductor. As a result, the deficiency of majority carriers gets created at the hot end of the semiconductor. This will give rise to the thermo emf generated across the semiconductor - the measure of which is the positive sign of the voltage in the external circuit. Similarly, the probe connected to the negative terminal of the voltmeter - is heated and connected to the semiconductor, the direction of the observed voltage is reversed. As shown in Fig. 3.2(b), in case of p-type semiconductors, when the probe-connected to the positive terminal of the voltmeter - is heated, the charge carriers - predominantly holes - flow towards the negative terminal due to the setting up of temperature gradient giving rise to the generation of thermo emf.
Fig. 3.2 Schematic circuit for the measurement of thermo-emf in
(a) n - semiconductor
(b) p - semiconductor.
This will give rise to the negative voltage in the external circuit. Similarly, when the probe-connected to the negative terminal of voltmeter is heated, direction of the voltage is reversed.

3.2.2 Determination of the Type of Conductivity:

The above discussed technique has been used to determine the type of conductivity in CdSe thin films deposited in present investigations. Here, the positive terminal was heated and brought into contact with the film. The resultant voltage observed in the external circuit was found to have a positive sign. This directly indicates that the grown CdSe films possess n-type conductivity. This is attributed to the fact that because of the higher vapor pressure of cadmium, the films are having an excess of cadmium content, which is verified by EDAX. Several research workers have also obtained the same type of conductivity.\textsuperscript{1-14}

3.3 ELECTRICAL RESISTIVITY OF CdSe THIN FILMS AT ROOM TEMPERATURE:

The electrical properties of semiconductor thin films are greatly influenced by many parameters such as crucible nature and configuration, source material and source temperature, substrate nature and substrate temperature, residual pressure, film thickness, rate of deposition etc. The thickness of the films plays an important role in determining the resistivity of the films. CdSe thin films having different thicknesses were deposited on glass substrates using thermal evaporation technique for the study of variation in electrical resistivity with film thickness, in present investigations.

In practice, there are several methods which can be used for determination of the electrical resistivity. The choice of the technique depends upon many parameters like the size and the shape of the sample, preparation of the sample, type of the sample etc. The electrical resistivity of CdSe thin
films at room temperature has been investigated in present investigation using a standard van der Pauw method.

3.3.1 van der Pauw Method:

The van der Pauw method is useful to determine the electrical resistivity of the specimen having irregular shape and larger size\(^{[74]}\).

The basic requirements of the method are:

(i) The contacts should be at the circumference of the sample;
(ii) The size of the contacts should be negligibly small as compared to that of the sample;
(iii) The contacts should be ohmic;
(iv) The sample should be very thin as compared to its area;
(v) Surface of the sample should be singly connected i.e. the sample should be free from steps and discontinuities;
(vi) The sample should be flat so that the sample surface and contacts lie in the same plane and
(vii) The applied field should be low so that break down does not occur.

If the contacts are not taken perfectly, the observed results may be associated with some error. This error will be proportional to the dimensions of the contact i.e.

\[
\frac{\Delta \rho}{\rho} = \alpha \frac{d^2}{D^2}
\]

where \( \rho \) is resistivity of the sample,
\( \Delta \rho \) is the change in resistivity,
\( d \) is the size of the contact and
\( D \) is the size of the sample.
The extent of this error depends upon:

(i) Distance of the contact from circumference
(ii) Extension of contact on the surface
(iii) Distance between contact.

The general circuit diagram used to measure the resistivity is shown in Fig. 3.3.

The resistance $R_{AB,CD} = R_1$ can be defined as

$$R_1 = \frac{\text{Potential difference between contacts D and C}}{\text{Current through contacts A and B}}$$

or as the potential difference $V_D - V_C$ per unit current flowing between points A and B. Here, the current enters the sample through contact A and leaves it through contact B.

Similarly, resistance $R_{BC,DA} = R_2$ can be written as

$$R_2 = \frac{\text{Potential difference between contacts A and D}}{\text{Current through contacts B and C}}$$

It is observed that the equation

$$\exp\left(\frac{-\pi R_1 d}{\rho}\right) + \exp\left(\frac{-\pi R_2 d}{\rho}\right) = 1$$

holds good for semiconductors.

Here $\rho$ is the specific resistivity of the semiconducting material and $d$ is the thickness of the sample.

Simplification of above equation yields
Fig. 3.3 Circuit diagram for resistivity measurement through van der Pauw method.
\[ \rho = \frac{\pi d}{2 \ln 2} \left( R_1 + R_2 \right) f \left( \frac{R_1}{R_2} \right) \]  

(3.2)

Fig. 3.4 shows the relationship between \((R_1/R_2)\) and \(f(R_1/R_2)\).

### 3.3.2 Results and Discussions:

The electrical resistivity of CdSe thin films having different thicknesses was investigated using van der Pauw technique. The results of such measurements for one representative case (for film thickness = 9000 Å) are given Table 3.1. Using the values of \(R_1\) and \(R_2\) from this table and equation (3.2), the resistivity was calculated and found to be around 5.40 ohm·cm. Similar measurements have been carried out for the films having different thicknesses and the resistivity was calculated. The variation of resistivity with film thickness has been shown in Fig. 3.5. From this variation it is quite apparent that the resistivity of thin films decreases with increase in thickness of the films. This conclusion match well with the results reported by several workers\(^{41,44,46,47}\).

### 3.4 ELECTRICAL RESISTIVITY OF CdSe THIN FILMS AT HIGH TEMPERATURE:

The variation of the electrical resistivity of the material with temperature gives an idea about the energy gap as well as the activation energy of charge carriers. The study of the variation of resistivity of CdSe thin films with temperature was carried out using the standard van der Pauw technique (as discussed in the previous section).

The block diagram for an experimental set up for this characterization is shown in Fig. 3.6. Electrical resistivity measurements have been done in a vacuum chamber. The system was evacuated at 10\(^{-2}\) torr pressure. Using Cr-Al thermocouple and ON-OFF controller, temperature
Fig. 3.4 Relationship between $R_1/R_2$ and $f(R_1/R_2)$.
Table 3.1 Results of measurement of resistivity through van der Pauw method (Film thickness = 9000 Å)

<table>
<thead>
<tr>
<th>Current (I) mA</th>
<th>Voltage (V) Volt</th>
<th>Resistance (R₁) Ohm</th>
<th>Current (I) mA</th>
<th>Voltage (V) Volt</th>
<th>Resistance (R₂) Ohm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>0.104</td>
<td>13000</td>
<td>0.008</td>
<td>0.106</td>
<td>13250</td>
</tr>
<tr>
<td>0.010</td>
<td>0.131</td>
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<td>0.010</td>
<td>0.133</td>
<td>13300</td>
</tr>
<tr>
<td>0.012</td>
<td>0.157</td>
<td>13083</td>
<td>0.012</td>
<td>0.159</td>
<td>13250</td>
</tr>
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<td>0.014</td>
<td>0.183</td>
<td>13071</td>
<td>0.014</td>
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<td>13286</td>
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<tr>
<td>0.016</td>
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<td>0.016</td>
<td>0.213</td>
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<tr>
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<td>13222</td>
<td>0.018</td>
<td>0.238</td>
<td>13222</td>
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<tr>
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<td>0.020</td>
<td>0.267</td>
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<td>0.024</td>
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<td>0.325</td>
<td>13542</td>
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<tr>
<td>0.026</td>
<td>0.345</td>
<td>13269</td>
<td>0.026</td>
<td>0.353</td>
<td>13577</td>
</tr>
</tbody>
</table>

Average R₁ = 13168 ohm

Average R₂ = 13359 ohm
Fig. 3.6 Block diagram of the experimental setup for high temperature characterization.
variation of substrate heater was done to measure resistivity of thin films by van der Pauw technique at different temperatures.

3.4.1 Results and Discussions:

The experimental set up explained above has been used to study the variation of resistivity with temperature at higher temperatures in case of CdSe thin films investigated here. The range of temperature selected in present investigations is from 305 K to 453 K for the film having thickness 9000 Å. The results of this investigations have been given in Table 3.2. The variation of resistivity with temperature has been graphically shown in Fig. 3.7, where a plot of \( \ln \rho \rightarrow 1/T \) shows a non-linear behavior. It is quite evident from Fig. 3.7 that the complete resistivity variation with temperature can be divided into three distinct regions. The region corresponding to low temperatures can be assigned to the transition of carriers from doping levels to the valence band which can be used to calculate the activation energy of charge carriers. This is specifically the case of the extrinsic behavior of the material. The second region can be attributed to the conduction mechanism where a transition from extrinsic to intrinsic mechanism takes place. This results in the reduction of available charge carriers for conduction thereby increasing the resistivity of the material. The third region at high temperature arises mainly due to the transitions of the carriers from the valence band to the conduction band which can be used for evaluation of the energy gap. In this temperature region the thermal energy supplied to the carriers is sufficient to promote them from valence band to the conduction band by overcoming the energy gap.

The activation energy of charge carriers can be related to the temperature dependence of resistivity in semiconducting material as -

\[
E_a = K \left( \frac{\ln \rho}{1/T} \right)
\]  

(3.3)
<table>
<thead>
<tr>
<th>Temperature T(K)</th>
<th>1/T (K⁻¹)</th>
<th>Resistivity p (Ωcm)</th>
<th>ln p</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
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<td>11.018</td>
<td>2.400</td>
</tr>
<tr>
<td>308</td>
<td>0.00325</td>
<td>10.936</td>
<td>2.392</td>
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<td>2.361</td>
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<td>323</td>
<td>0.00310</td>
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<td>333</td>
<td>0.00300</td>
<td>6.411</td>
<td>1.858</td>
</tr>
<tr>
<td>343</td>
<td>0.00292</td>
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<td>1.537</td>
</tr>
<tr>
<td>353</td>
<td>0.00283</td>
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<td>0.848</td>
</tr>
<tr>
<td>363</td>
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<td>1.982</td>
<td>0.684</td>
</tr>
<tr>
<td>373</td>
<td>0.00268</td>
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<td>0.605</td>
</tr>
<tr>
<td>383</td>
<td>0.00261</td>
<td>1.800</td>
<td>0.588</td>
</tr>
<tr>
<td>393</td>
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<td>1.784</td>
<td>0.579</td>
</tr>
<tr>
<td>403</td>
<td>0.00248</td>
<td>1.800</td>
<td>0.588</td>
</tr>
<tr>
<td>413</td>
<td>0.00242</td>
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<tr>
<td>423</td>
<td>0.00236</td>
<td>1.822</td>
<td>0.600</td>
</tr>
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<td>433</td>
<td>0.00231</td>
<td>1.738</td>
<td>0.553</td>
</tr>
<tr>
<td>443</td>
<td>0.00226</td>
<td>0.677</td>
<td>-0.390</td>
</tr>
<tr>
<td>453</td>
<td>0.00221</td>
<td>0.397</td>
<td>-0.923</td>
</tr>
</tbody>
</table>
Fig. 3.7 Plot of $\ln \rho$ vs $1/T$ for CdSe thin film at high temperature.
\[ K = \text{Boltzmann constant} \]
\[ = 8.625 \times 10^{-5} \text{eV/K} \]

Equation (3.3) can be written as

\[ E_a = K \text{(Slope)} \text{eV} \tag{3.4} \]

Substituting the slope of the line of region-I in equation (3.4), the activation energy has been calculated and its value has been found to be around 0.44 eV, which agrees with the earlier reports \cite{25,75}. Brodie et al\cite{25} found activation energies ranging from 0.14 eV to 0.53 eV in vacuum evaporated CdSe films. Similarly, the energy gap of semiconducting material can be given as -

\[ E_g = 2K \text{(Slope)} \text{eV} \tag{3.5} \]

where \( E_g = \text{Energy gap of semiconductor} \)

Substituting the value of slope of region-III (of Fig. 3.7) in equation (3.5), the energy gap of CdSe has been calculated in present investigations. It has been seen that this value comes to be around 1.72 eV, is in good agreement with the band gap obtained by optical measurement as well as the previous reports\cite{2,11,23,46,76,84}.

### 3.5 ELECTRICAL RESISTIVITY OF CdSe THIN FILMS AT LOW TEMPERATURE:

The van der Pauw technique discussed above has also been used to investigate the electrical resistivity of CdSe thin films at low temperatures. The method discussed here is used to investigate the dependence of the electrical resistivity of CdSe samples on temperature in the low temperature range.
The cryostat LN-DP is designed specially for the experiments in temperature range 77 K to 303 K. This consists of a sample chamber and a sample holder (Fig. 3.8). The system is portable and very easy to manage. It is designed to fit directly into any of the standard liquid nitrogen (Liquid N₂) storage containers. The system is supplied with a standard 1/2" valve for evacuating and a 1/4" valve for introducing the exchange gas, monitoring vacuum etc.

The sample holder consists of a gold-plated copper assembly, mounted with a standard platinum thermometer (Pt -100), and a heater, which can be used for temperature control. Electrical leads for thermometer and the heater are brought at the top of the cryostat at a D-type 9 pin connector. The samples can be mounted on a rectangular projection (Fig.3.9). Sixteen permanent electrical points are available for the experiments. These are brought out at the top of the cryostat at the D-type 25 pin connector. At a time, four resistivity samples can be mounted on the sample holder. These samples can be mounted with a low temperature conducting Apiezone-N grease.

The four probes for each of the samples were attached using proper solder/silver paste. A low power (10 watt maximum) soldering rod was used for soldering work near the sample holder (otherwise electrical insulation from pin to pin may break down). The samples can be selected using the sample changer SMC-4.

The constant current source CCS-10 is ideal for powering wide range of transducers and also for many other purposes like four probe resistivity measurements, where a stable but variable constant current is the basic requirement. The constant current source CCH-1000 has been specially designed for its use as a heater supply for a 30-40 ohm heater. It is capable of supplying a maximum of 25 watts of power to the heater, which is adequate for cryogenic purpose.
Fig. 3.8 The cryostate LN - DP, used in low temperature resistivity measurements.
Fig. 3.9 The sample holder used in low temperature resistivity measurements.
The samples were mounted on the sample holder and the electrical connections were taken properly. After cleaning the 'O' ring joint, the sample holder was inserted in the sample chamber and the clamp was tightened gently. The pumping valve was closed, after evacuating the sample chamber to a vacuum of the order of at least 10-2 torr. The entire assembly was inserted and fixed in a liquid nitrogen container. At a time, four different specimens can be mounted on the sample holder. The temperature of these specimens can be raised from 77 K to room temperature in a step of 5 K and the developed voltage across their inner leads can be measured, for a constant current passed through the outer leads of the specimen. The schematic diagram of the experimental setup used in the present investigation has been shown in Fig. 3.10. The experimental set up for the same is shown in Fig. 3.11. After the experiment, the entire assembly is pulled out and system is allowed to come to room temperature before the sample chamber is opened.

### 3.5.1 Results and Discussions:

The van der Pauw method discussed earlier has also been used to study the behavior of the electrical resistivity of CdSe thin films at low temperature ranging from 223 K - 300 K. The experimental set up explained above has been used for these investigations. The results obtained for CdSe thin films have been given in Table 3.3. From this table it is quite apparent that as the temperature decreases, the resistivity increases, as expected according to the semiconducting behavior of cadmium selenide. The graphical representation of the results given in Table 3.3 has been shown in Fig. 3.12 which is again depicting a non-linear behavior. This non-linear behavior has also been attributed to the hopping of carriers, the presence of exciton mechanism etc.\cite{85-87}.
Fig. 3.10 Schematic diagram of the low temperature resistivity measurements.
Fig. 3.11  Photograph of the actual set up for low temperature measurement.
Table 3.3 Results of low temperature resistivity measurements

<table>
<thead>
<tr>
<th>Temperature T(K)</th>
<th>1/T (K⁻¹)</th>
<th>Resistivity p (ohm·cm)</th>
<th>ln p</th>
</tr>
</thead>
<tbody>
<tr>
<td>223</td>
<td>0.00448</td>
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</tr>
<tr>
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<td>2.974</td>
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<td>235</td>
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<td>2.939</td>
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<td>0.00400</td>
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<td>300</td>
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<td>2.246</td>
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</table>
Fig. 3.12  Plot of $\ln \rho$ vs $1/T$ for low temperature range.
3.6 MEASUREMENTS OF HALL PARAMETERS:

The van der Pauw technique described earlier has been modified to determine the type of conductivity, mobility and carrier concentration of the CdSe thin films. This modification, shown in Fig. 3.13, facilitates the measurement of voltage developed across by passage of current between the diagonally opposite contacts.

3.6.1 Experimental Set up:

The sample, for this measurement, is kept in a known magnetic field produced by an electromagnet (type EMPS-5, Omega Electronics, Jaipur). This magnetic field modifies the path of electrons and produces the Hall voltage. These results were used for the evaluation of mobility and carrier concentration. A photograph of experimental set up is shown in Fig. 3.14.

Knowing the values of difference in resistance ($\Delta R$), magnetic field ($\Delta B$) and thickness of the sample $t$, the mobility of carriers was evaluated using the equation

$$\mu = \frac{t}{\Delta B} \frac{\Delta R}{\rho}$$

(3.6)

where $\rho$ is the room temperature resistivity of the sample.

The Hall coefficient can be calculated using the formula

$$R_H = \mu_H \rho$$

(3.7)

and carrier concentration, can be calculated using the relation

$$n = \frac{1}{R_H e}$$

(3.8)
Fig. 3.13  Circuit diagram for Hall effect measurements.
Fig. 3.14  Actual experimental set up for the Hall effect measurement.
From the sign of the Hall coefficient, the nature of the charge carriers in the deposited samples can be ascertained.

3.6.2 Results and Discussions:

A modification of the van der Pauw technique described above, has been used to evaluate the type of carriers and their mobility and concentration in cadmium selenide thin films. Hall mobility of the sample was determined by measuring the change in resistance ($\Delta R$), when magnetic field was applied perpendicular to the sample.

The range of magnetic field used here varied from 4.98 K Gauss to 13.05 K Gauss. The results obtained from the Hall effect experiment carried out for CdSe thin films have been given in Table 3.4, for magnetic field 13.05 K Gauss, as a representative case.

The substitution of average resistance and the magnetic field in equation (3.6), (3.7) and (3.8) is used to find out the values of Hall coefficient, mobility of carriers and concentration of carriers and the results have been given in Table 3.5 for different values of the applied magnetic field.

From this table it can be seen that the Hall coefficient has a negative value which is an indication of the fact that the CdSe thin films under present investigations have n-type conductivity which reaffirms the results obtained from the hot probe method. The Fig. 3.15 shows the variation in resistance of the films with the applied magnetic field. The range of mobility is found to be 724 - 820 cm$^2$/volt-sec, which is close to the published as well as the reported data$^{[32,81,88-91]}$. The value of the mobility investigated from Fig. 3.15 comes out to be around 700 cm$^2$/volt-sec, which is in close agreement with the above investigation.
Table 3.4 Results of Hall effect experiment for B = 13.05 KGauss

<table>
<thead>
<tr>
<th>Current (I) (μA)</th>
<th>Hall Voltage (V)</th>
<th>Hall Resistance (R) (Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>5600</td>
</tr>
<tr>
<td>12</td>
<td>-0.068</td>
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<td>-0.198</td>
<td>5824</td>
</tr>
<tr>
<td>36</td>
<td>-0.212</td>
<td>5888</td>
</tr>
<tr>
<td>38</td>
<td>-0.222</td>
<td>5842</td>
</tr>
<tr>
<td>40</td>
<td>-0.235</td>
<td>5875</td>
</tr>
<tr>
<td>42</td>
<td>-0.244</td>
<td>5809</td>
</tr>
<tr>
<td>44</td>
<td>-0.259</td>
<td>5886</td>
</tr>
<tr>
<td>46</td>
<td>-0.268</td>
<td>5826</td>
</tr>
<tr>
<td>48</td>
<td>-0.281</td>
<td>5854</td>
</tr>
<tr>
<td>50</td>
<td>-0.293</td>
<td>5860</td>
</tr>
<tr>
<td>52</td>
<td>-0.305</td>
<td>5865</td>
</tr>
<tr>
<td>54</td>
<td>-0.310</td>
<td>5740</td>
</tr>
<tr>
<td>56</td>
<td>-0.318</td>
<td>5678</td>
</tr>
<tr>
<td>58</td>
<td>-0.325</td>
<td>5603</td>
</tr>
</tbody>
</table>
Table 3.5 Various parameters obtained from Hall effect experiment for CdSe thin films

<table>
<thead>
<tr>
<th>Magnetic field (B)</th>
<th>Hall Coefficient ($R_H$) cm$^2$/col</th>
<th>Mobility ($\mu$) cm$^2$/volt-sec</th>
<th>Carrier Concentration (n) cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.98 Kgauss</td>
<td>-4427</td>
<td>820</td>
<td>$1.41 \times 10^{16}$</td>
</tr>
<tr>
<td>8.79 Kgauss</td>
<td>-3976</td>
<td>736</td>
<td>$1.57 \times 10^{15}$</td>
</tr>
<tr>
<td>11.00 Kgauss</td>
<td>-4107</td>
<td>761</td>
<td>$1.52 \times 10^{15}$</td>
</tr>
<tr>
<td>12.30 Kgauss</td>
<td>-3908</td>
<td>724</td>
<td>$1.60 \times 10^{15}$</td>
</tr>
<tr>
<td>13.05 Kgauss</td>
<td>-4017</td>
<td>744</td>
<td>$1.55 \times 10^{15}$</td>
</tr>
</tbody>
</table>
Fig. 3.15 Variation in the resistance of CdSe thin films with applied magnetic field.
3.7 THERMOELECTRIC POWER MEASUREMENTS:

The absolute Seebeck coefficient, \( ASC \), is defined as the instantaneous rate of change of the absolute Seebeck effect with respect to temperature at a given temperature:

\[
ASC = \left[ \frac{d}{dT} (ASE) \right]_T
\]

The main application of the Seebeck effect is in thermoelectric thermometry. This results from the fact that thermoelectric circuits convert thermal energy into electrical energy. The possibility of using thermoelectric phenomena in the generation of electricity was considered as early as in 1885 by Rayleigh, who first calculated the efficiency of a thermoelectric generator. In the early 1960s a requirement of autonomous sources of electrical power arose from the exploration of space, advances in medical physics and the exploitation of the earth's resources in increasingly hostile and inaccessible locations. Thermoelectric generators are ideally suited to such applications.

Therefore, there is a constant need to develop more and more efficient thermoelectric materials. Hence, since the last decade there has been a worldwide search for new materials with higher thermoelectric figure-of-merit and attempts to improve the thermoelectric properties of the known compounds. Looking to the recent importance of thermoelectric power generation, it is worthwhile to carry out a systematic study of the thermoelectric properties of semiconducting materials.

The thermoelectric figure of merit \( Z \) is defined by

\[
Z = \frac{S^2 \sigma}{\lambda}
\]
where \( S \) is the Seebeck coefficient, 
\( \sigma \) is the electrical conductivity and 
\( \lambda \) is the thermal conductivity.

Further, the quantity \( S^2 \sigma \) or \( S^2/p \), where \( p \) - the resistivity of the material is called the "power factor". Its unit is Watt/cm K².

In present investigations, a systematic measurement of the thermoelectric power of CdSe thin films as a function of temperature has been carried out. In order to study temperature dependence of the thermoelectric power of non-degenerate n-type material, let us consider the expression,

\[
S = -\frac{k}{e} \left[ A + \frac{E_F}{kT} \right] \tag{3.9}
\]

where \( k \) is the Boltzmann constant
\( e \) is the electronic charge
\( A = (5/2 - S) \) is the constant that varies from 0 to 4 depending upon the scattering process.
\( E_F \) is the separation of the Fermi level from the bottom of the Conduction band.

For the small temperature range, \( E_F \) is fairly constant and hence, from equation (3.9), the thermoelectric power \( S \) is plotted against the reciprocal of temperature \((1/T)\), a straight line is expected. From the slope and the intercept of the line, \( E_F \), the energy separation of the Fermi level from the bottom of the conduction band and \( A \), the constant indicating the nature of scattering, can both be determined. \( E_F \) is fairly constant implies that the carrier concentration \( n_e \) is not changing with the temperature. Therefore equation (3.9) can be expressed as
\[ S = -\frac{k}{e} \left[ A + \ln \left( \frac{N_e}{n_e} \right) \right] \]  

where \( N_e \) is the effective density of states given by,

\[ N_e = \frac{2 \pi m^* kT}{h^2} \left( \frac{N_e}{n_e} \right)^{3/2} \]

3.7.1 Experimental Set up:

In present investigations, the thermoelectric power measurements on all the samples of CdSe thin films were carried out with thermopower set up TPSS-200 developed by Scientific Solutions, Mumbai. The experimental set up shown in Fig. 3.16 mainly consists of two blocks:

(a) Sample holder with heaters and pick up probes and

(b) Electronic circuits controlling temperature and temperature gradient across the sample.

(a) Sample holder and pick up probes:

The sample holder consists of two low power heaters A and B (15 W each). The temperature T of the heater A is measured with the help of thermocouple (TC1) and the temperature gradient \( \Delta T \) between A and B is measured by differential temperature sensor (TC2). Both the thermocouples are of K type. The sample under investigation is mounted directly on the heaters and is held by two pick up probes which are of copper (or stainless steel). These probes also measure the Seebeck voltage developed across the two ends of the sample.
Fig. 3.16  Actual experimental set up for thermopower measurement.
(b) **Temperature controlling system:**

This part of the system consists of temperature indicator, proportional controller and two heater control circuits which drive the two heaters A and B. With the help of this electronic control circuits, it is possible to generate a stable temperature gradient between the two heaters. It is possible to control the temperature ranging from 298 K to 573 K and with $\Delta T$ of $\pm 10$ K simultaneously with better than $\pm 1$ K stability. The problem usually encountered in making thermoelectric power measurements are, stray thermal emfs. In the present instrument, it has been eliminated by providing choice of selection of temperature gradient in the range between 1 K to 10 K.

The sample and the electronic circuits have been installed into one single unit. The use of low power heaters and electronic controllers make the operation very easy and Seebeck coefficient of the samples can be very conveniently measured.

### 3.7.2 Results and Discussions :

The results of the thermopower measurements on CdSe thin films carried out using the above discussed experimental set up have been given in Table 3.6.

The Seebeck coefficient calculated at each temperature shows a negative value and remains negative over the entire temperature range which again is a confirmation of n-type conductivity of CdSe thin films developed in the present investigations.

The variation of Seebeck coefficient with temperature has been shown in Fig. 3.17. The slope and the intercept of the graph have been used to find out the value of $N_e$ and effective mass $m_e^*$ using the relations,
### Table 3.6 Results of Seebeck experiment

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (K⁻¹)</th>
<th>V (mV)</th>
<th>S (V/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316</td>
<td>0.00316</td>
<td>-0.062</td>
<td>-0.0000124</td>
</tr>
<tr>
<td>321</td>
<td>0.00312</td>
<td>-0.078</td>
<td>-0.0000156</td>
</tr>
<tr>
<td>326</td>
<td>0.00307</td>
<td>-0.092</td>
<td>-0.0000184</td>
</tr>
<tr>
<td>331</td>
<td>0.00302</td>
<td>-0.120</td>
<td>-0.0000240</td>
</tr>
<tr>
<td>336</td>
<td>0.00298</td>
<td>-0.154</td>
<td>-0.0000308</td>
</tr>
<tr>
<td>341</td>
<td>0.00293</td>
<td>-0.202</td>
<td>-0.0000404</td>
</tr>
<tr>
<td>346</td>
<td>0.00289</td>
<td>-0.265</td>
<td>-0.0000530</td>
</tr>
<tr>
<td>351</td>
<td>0.00285</td>
<td>-0.320</td>
<td>-0.0000640</td>
</tr>
<tr>
<td>356</td>
<td>0.00281</td>
<td>-0.365</td>
<td>-0.0000730</td>
</tr>
<tr>
<td>361</td>
<td>0.00277</td>
<td>-0.409</td>
<td>-0.0000818</td>
</tr>
<tr>
<td>366</td>
<td>0.00273</td>
<td>-0.448</td>
<td>-0.0000896</td>
</tr>
<tr>
<td>371</td>
<td>0.00270</td>
<td>-0.490</td>
<td>-0.0000980</td>
</tr>
<tr>
<td>376</td>
<td>0.00266</td>
<td>-0.537</td>
<td>-0.0001074</td>
</tr>
<tr>
<td>381</td>
<td>0.00262</td>
<td>-0.570</td>
<td>-0.0001140</td>
</tr>
<tr>
<td>386</td>
<td>0.00259</td>
<td>-0.607</td>
<td>-0.0001214</td>
</tr>
<tr>
<td>391</td>
<td>0.00256</td>
<td>-0.637</td>
<td>-0.0001274</td>
</tr>
<tr>
<td>396</td>
<td>0.00253</td>
<td>-0.666</td>
<td>-0.0001312</td>
</tr>
</tbody>
</table>
Fig. 3.17 Graph of $S$ vs $1/T$ for CdSe thin film.
\[ N_e = \frac{n_e}{e^{-\frac{E_f}{kT}}} \] (3.12)

and

\[ m_e^* = \frac{(N_e)^{2/3} \hbar^2}{(2)^{2/3} (2\pi k T)^{1/2}} \] (3.13)

In the present investigations, \( N_e \) comes out to be \( 2.35 \times 10^{18} \text{ cm}^{-3} \) and the value of the effective mass has been carried out \( 1.72 \times 10^{-31} \text{ kg} \). This effective mass has been compared with the electron mass and its value has been investigated as

\[ \frac{m_e^*}{m_e} = 0.19 \]

Which fairly matches with the standard data\[^{[80,89,92-95]}\].
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