6 ELECTRICAL PROPERTIES

6.1 Introduction

Electrical conduction in TCO's results because of the presence of defects such as oxygen deficiencies and metallic interstitials. Measurement of various electrical parameters is a requirement for the transparent conducting oxide coatings. The parameters that are considered important are the sheet resistance ($R_{sh}$), resistivity ($\rho$), carrier concentration ($N_H$) and carrier mobility ($\mu_H$). In this chapter a brief account is given about the general concepts of conduction mechanism in the TCO's followed by the description of the determination of various electrical quantities. Hall effect and thermoelectric power measurements have been made on these films to determine the various electrical parameters. The temperature dependence of the $\rho$, $\mu_H$ and $N_H$ is measured for typical samples and the results are discussed.

6.2 Conduction Mechanism

It is well known that all the oxides that have been used for transparent conductors are n-type materials. The n-type conductivity arises because of the presence of defects. These defects are electronic in nature and are created in response to the problem of keeping the crystals neutral over a range of compositions.

If an oxide is fully stoichiometric, it can only be an ionic conductor. Therefore, very high energy should be applied for the process of conduction. But, the oxides used for transparent conductors, in general, are defect solids. The defects may be due to the anion vacancy (oxygen deficiency) or cation vacancy (metallic interstitials) or due to both.

The electrical conductivity is a function of not only the carrier density but also the mobility of the charge carriers. The electrical mobility is limited by various types of scattering mechanisms. That is, when transport takes place through thin specimens, the carriers are subjected to considerable scattering by the boundary surfaces in addition to the normal
bulk scattering. This additional scattering will reduce the effective carrier mobility below the bulk value. The observed electron mobility has contributions from various kinds of scattering such as neutral impurity scattering ($\mu_n$), surface scattering ($\mu_{ss}$), the electron-electron scattering ($\mu_e$), the acoustic lattice scattering ($\mu_a$), optical lattice scattering ($\mu_o$), ionized impurity scattering ($\mu_i$) and finally the grain boundary scattering ($\mu_g$).

In a wide band gap semiconductor, the contributions due to $\mu_n$, $\mu_{SS}$, $\mu_e$, $\mu_a$ and $\mu_o$ are less significant [1]. Since, the carrier concentration of transparent conducting oxide thin films is usually very high, the scattering due to ionized impurity is expected to play a crucial role in limiting the carrier mobility. If the samples are polycrystalline in structure, the contribution of grain boundary scattering may also be considered important. Roy et al [2] have given an expression to determine the grain-boundary-limited mobility by the relation

$$\frac{1}{\mu_{\text{eff}}} = \frac{1}{\mu_s} + \frac{1}{\mu_g} \quad (6.1)$$

where $\mu_s$ is the corresponding mobility in a single crystal where no grain boundary is present at the same concentration. Islam and Hakim [3] have calculated the contributions due to grain boundary (using equation 6.1) and ionized impurity scattering to the carrier mobility at different concentrations in degenerate SnO$_2$ films by the process worked out by Csavinszky [4]. They have observed that these two processes, the grain boundary scattering and the ionized impurity scattering are predominant in the two different ranges of concentrations. One way to verify the contributions due to ionized impurity scattering to the carrier mobility is to link the mean free path of the carriers (evaluated electrically) with the average grain size (determined from structure calculations). The mean free path ($l$) of the carriers can be calculated using the following formula [5]:

$$l = \frac{\hbar}{2e} \left( \frac{3N_H}{\pi} \right)^{1/3} \mu_H. \quad (6.2)$$
If the mean free path of the carriers is considerably lower than the average grain size at a high carrier concentration of the order of $10^{26}$ m$^{-3}$, one may expect ionized impurity scattering to be the dominant scattering mechanism. Otherwise, grain boundary scattering could be identified as the factor limiting the carrier mobility of the films.

6.3 Resistivity Measurements

Various experimental methods have been used for the calculation of resistivity. Among them, the techniques commonly employed are the four probe and square probe array methods. The film resistivity is commonly characterized by the normalized parameter called the sheet resistance ($R_{sh}$) expressed in $\Omega/\square$, which is related to resistivity by

$$R_{sh} = \frac{\rho}{d_f} \quad (6.3)$$

where $\rho$ is the resistivity of a film of thickness $d_f$.

The most widely used method for measuring resistivity in the $10^{-5}$ to $10^1$ $\Omega$m range is the four-point probe technique. As shown in fig. 6.1 provided the probe spacings $r_1$, $R_1$ and $R_2$ are each far greater than the thickness of film, and if $I$ is the current passing between the outer points, then potentials $V_C$ at C and $V_D$ at D are given by [6]

$$V_C = \frac{\rho}{2 \pi} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \quad (6.4)$$

$$V_D = \frac{\rho}{2 \pi} \left( \frac{1}{R_1} - \frac{1}{R_2} \right). \quad (6.5)$$

For equal probe spacing ($s$), as used in this work, $r_1 = s$, $r_2 = 2s$, $R_1 = 2s$ and $R_2 = s$; therefore

$$\rho = 2\pi s \frac{V}{I} \quad (6.6)$$

where $V$ is the potential difference between points C and D, i.e. $V = V_C - V_D$. 

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Fig. 6.1 Four-point Probe Arrangement for Measuring the Sheet Resistance of Cadmium Oxide Thin Films.
A useful simplification of the collinear four-probe relation obtained for a thin specimen \((d_f \ll s/2)\) is

\[
\rho = 4.532 \frac{V}{I} df = R_{sh} df \quad (6.7)
\]

In the square-probe method, it is given by [3]

\[
\rho = 9.03 \frac{V}{I} df = R_{sh} df \quad (6.8)
\]

In the present investigation, both the techniques have been used for the resistivity calculations.

### 6.4 Hall Effect Studies

When a conductor is placed in a magnetic field perpendicular to the direction of current flow, a field or voltage is developed across the specimen in the direction perpendicular to both the electric and magnetic field and the resulting field is called as the Hall field or Hall voltage. The Hall voltage arises under the influence of Lorentz force which deflects electrons and holes in the direction normal to both the electric and magnetic fields, the direction of electrons and holes being opposite. Thus the magnitude and sign of Hall voltage facilitates the determination of the density and nature of the majority carrier dominant in the films respectively.

Thin film samples of 1 square cm area prepared by spray pyrolysis are used to carry out the Hall studies. Current of few milliamperes is passed by means of dc Aplab power supply between the two diagonally opposite contact points of the sample, namely 1 and 3 (Fig. 6.2). On applying a magnetic field of a few kG, a Hall voltage is developed across 2 and 4, which is measured using a vernier potentiometer set up possessing a sensitivity of 0.1 μV.

The Hall coefficient \((R_H)\) has been determined using the formula,

\[
R_H = \frac{V_H}{I B} \frac{df}{X 10^8 \text{ cm}^3/\text{Coulomb}} \quad (6.9)
\]
Fig. 6.2 Circuit diagram for Hall Effect Measurements of Cd0 Thin Films.
where $V_H$ is the Hall voltage, $d_f$ is the film thickness, $I$ is the input current and $B$ is the magnetic field. The carrier concentration ($N_H$) can be calculated from the Hall coefficient by the relation,

$$N_H = \frac{1}{R_H e}$$  \hspace{1cm} (6.10)

where $e$ is the electronic charge. Knowing the values of $N_H$ and $\rho$, the electron mobility ($\mu_H$) may be estimated from

$$\mu_H = \frac{1}{N_H e \rho}.$$  \hspace{1cm} (6.11)

6.5 Figure of Merit

The suitability of the transparent conducting films for various applications is judged by their figure of merit, $\phi(\lambda)$, which can be calculated for thin films using Haacke’s formula [7] as

$$\phi(\lambda) = \frac{T(\lambda)^{10}}{R_{sh}}$$  \hspace{1cm} (6.12)

where $T(\lambda)$ is the transmittance at wavelength $\lambda$.

6.6 Thermoelectric Power (TEP) Measurements

Thermoelectric power is the emf produced per unit temperature difference between the two junctions of materials. From the TEP measurements, the Fermi energy ($E_F$) can be calculated by using the equation [8]

$$E_F = kT \left( -\frac{Q e}{k} - A \right)$$  \hspace{1cm} (6.13)

where $k$ is the Boltzmann’s constant, $Q$ is the thermoelectric power in $\mu V/K$, $e$ is the electronic charge and $A = 4$ for carrier scattering by ionized impurities.

6.7 Experimental Details

As-deposited cadmium oxide thin films formed by DC reactive magnetron sputtering are annealed in air for about thirty minutes at a temperature of 400°C (Section 3.3.2). Then the samples are used for different
studies. To carry out the Hall studies on CdO samples deposited at various timings, four contacts are made in the samples of $1 \times 10^{-4}$ m$^2$ area using a conductive silver paste at the periphery of the samples, since silver is found to be a suitable ohmic contact material with CdO. The measurements are carried out at room temperature under a magnetic field of 7.67 KГ and passing a current of a few mA with an accuracy of ±0.01 mA through the films. The Hall voltage is measured using a vernier potentiometer set-up possessing a sensitivity of 0.1 μV/div. For CdO films deposited at different substrate temperatures, samples of area $1.5 \times 10^{-4}$ m$^2$ are used for measurements under a vacuum of 1.33 Pa. Temperature dependence of Hall studies are performed for a typical sample of thickness 160 nm coated at $T_s = 550 \, ^\circ\text{C}$ under a magnetic field of 7 KГ and passing a current of 3(±0.01) mA through the samples in the range 304-349 K.

In the case of sputtered CdO films, a digital Hall measurement set up (MMR Technology Inc., USA) has been used for the studies. Current of 1 mA is passed through the film under a magnetic field of 3.75 KГ in a vacuum of $10^{-2}$ Torr. Temperature dependence of carrier concentration, mobility and resistivity is studied in the temperature range 300 to 360 K.

For thermoelectric power measurements (TEP), the experimental film is placed on two copper blocks mounted on an asbestos base. Two pure high quality copper rods (3 mm dia) are made to touch the film by spring-loaded pressure contacts to form the junctions at either end of the film. A nichrome heater is fixed in one of the copper blocks for heating. Two copper-constantan thermocouples attached to the ends of the sample serves for the measurement of the temperatures of hot and cold junctions. The whole arrangement is kept inside a stainless steel vessel which is evacuated down to a vacuum of $10^{-1}$ Torr. The temperature of the hot junction is slowly raised and the temperature is measured using a HIL 2665 digital multimeter. The resulting TEP is measured using a DC microvoltmeter with an accuracy of 1 μV. The measurements are made on sprayed CdO samples of area 0.03 m X 0.013 m in the temperature range 304-376 K. TEP measurements have also been carried out on sputtered CdO samples in the temperature range 305-375 K in vacuum (Fig. 6.3).
Fig. 6.3 Experimental Jig for Thermoelectric Power Measurements:
V, Voltage Leads; Th₁ and Th₂, Thermocouples;
H, Heater Leads; S, Sample.
6.8 Results and Discussion

6.8.1 Sprayed CdO Thin Films

6.8.1.1 Dependence of Deposition Timings

Since CdO thin films are prepared at high substrate temperatures, it is found that annealing does not alter the sheet resistance drastically. Hence the as-deposited films are used for various studies. Table 6.1 gives the results of Hall effect measurements obtained in the present investigation for films formed at various deposition timings. The studies indicate that all the films are n-type. The sheet resistance and resistivity are found to decrease with the increase in film thickness. The calculated resistivity values are in good agreement with the observations on CdO films made by earlier workers [9,10]. From the table, it is found that the carrier concentration increases with the increase in film thickness. The decrease in Hall coefficient with the increase in film thickness may be due to the decreasing proportion of oxygen. In other words, it can be stated that the higher carrier concentration in thicker films may be due to the increasing oxygen deficiency in the lattice [11]. Fig. 6.4 gives the variation of the optical transmittance and electrical conductivity with the film thickness. It is seen that as transmittance decreases, the conductivity increases, maintaining the trade-off between transparency and conductivity. The figure of merit at $\lambda = 700$ nm for the films has been evaluated. The values are listed in table 6.1. It is inferred that the film of thickness 270 nm possesses the highest figure of merit.

6.8.1.2 Effect of Substrate Temperature

Hall effect measurements indicate that the films are n-type semiconductors. It is seen that the films possess high carrier concentration and mobility. The decrease in sheet resistance with the increase in substrate temperature is due to the increase in mobility of the charge carriers as a result of increase in preferred orientation as evinced from the structure analysis. The sheet resistance observed for the film deposited at $T_s = 550^\circ C$ is the lowest one among other samples.
Fig. 6.4 Dependence of Transmittance (At $\lambda = 700 \text{ nm}$) and Electrical Conductivity on the Film Thickness Deposited at Various Timings by Spray Pyrolysis.
The mean free path (l) of the carriers has been evaluated, using the formula suggested by Noguchi and Sakata [5], (for $N_H=1.4\times10^{25}/m^3$ and $\mu_H=68\times10^{-4} m^2/Vs$) as 1.6 nm. The crystallite size evaluated from the XRD studies is about 48 nm which is thirty times higher than the mean free path and hence the possibility of scattering due to grain boundary is excluded. Fig. 6.5 shows the variation of mobility with carrier concentration for a typical film of thickness 160 nm. It is observed that the mobility ($\mu_H$) decreases with the increase in carrier concentration ($N_H$). This type of observation leads to the finding of ionized impurity scattering. The contribution of ionized impurity scattering to the carrier mobility at different carrier concentrations in degenerate SnO$_2$ films has been reported in the literature [3]. In the present work, the observed trend is in agreement with the above report. The equation for the mobility in complete degeneracy is of the form [12]

$$\mu_H = (4e/h) (\pi/3) N_H^{-2/3}$$  \hspace{1cm} (6.14)

Fig. 6.5 also depicts the relationships between $\mu_H$ and $N_H$ calculated from the above theory with experimental data obtained from Hall studies. The trend observed is consistent with each other satisfying the fact $\mu_H \propto N_H^{-2/3}$. A similar observation has been made in the case of In$_2$O$_3$ films [5].

The results of Hall effect measurements on CdO films prepared at different substrate temperatures are given in table 6.2. From a comparison of tables 6.1 and 6.2, it is found that the carrier density is larger in table 6.1 than in table 6.2. The resistivity and mobility also differ by a factor of 3-5. The observed difference in the electrical parameters could be due to the difference in film thickness and the flow rate. Also, for films of lower thicknesses, the preferential growth is along the (111) diffracted plane and for films of higher thicknesses, it is along the (200) diffracted plane as evinced from the structural analysis and this may also be a fact for the observed difference in the electrical properties.

Fig. 6.6 shows the relation between thermoelectric power and temperature for a CdO thin film of typical thickness 160 nm. From the TEP measurements, the Fermi energy ($E_F$) has been calculated taking into account $A = 4$ for ionized...
Fig. 6.5 Variation of Carrier Mobility with Concentration for CdO Thin Film of Typical Thickness 160 nm Formed at $T_s = 550 \, ^\circ$C by Spray Pyrolysis.
Fig. 6.6 Plot of Thermoelectric Power Against Temperature for CdO Thin Film ($d_f = 160$ nm) Produced by Spray Pyrolysis.
impurity scattering. For $T = 304 \, K$ and $Q = 12 \, \mu V \, K^{-1}$, the value of the Fermi energy 0.11 eV is higher than $kT$ (0.03 eV). Hence, CdO is a degenerate semiconductor at room temperature. The effective mass ($m^*$) has been calculated from the relation [5]

$$m^* = \left( \frac{\hbar^2}{8 \, E_F} \right) \left( \frac{3 \, N_H}{\pi} \right)^{2/3} \tag{6.15}$$

and the value of effective mass is found to be 0.44 $m_0$ where $m_0$ is the rest mass of the electron. This value is higher than the value of 0.23 $m_0$ reported for films prepared by direct current reactive sputtering [11].

6.8.2 Sputtered CdO Thin Films

As-deposited films show somewhat high sheet resistance of the order of kΩ. Hence all the samples are annealed in air at 400 °C for 30 minutes. This shows that the conductivity of pure cadmium oxide films is increased by heating in air and this increase in conductivity may be associated with the partial dissociation of the oxide to provide excess cadmium [13].

The results of electrical measurements for the sputtered CdO thin films are listed in table 6.3. The sheet resistance and hence the resistivity of the films are found to be very low. The decrease in resistivity with an increase in substrate temperature is due to the increase in carrier mobility of the films. The high mobility is directly correlated with the decrease in structural defects as evinced from the structural analysis of the sputtered CdO thin films (Chapter 3, table 3.4).

Mean free path has been evaluated by making use of the relation (6.2) for a film of thickness 177.5 nm. The calculated value of mean free path is about 12.63 nm which is considerably lower than the value of the crystallite size (22 nm). Hence, it seems that the contribution due to grain boundary scattering does not play a major role in limiting the mobility of the carriers.

Temperature dependence of electrical parameters for a film of typical thickness 177.5 nm is given in table 6.4. It is observed that the resistivity increases with an increase in temperature which is attributed to the metallic state of the films. Varkey and Fort [14] have observed the
metallic nature of CdO thin films prepared by solution growth at about 450 K. A steady decrease in the value of mobility with increasing carrier concentration suggests that scattering by the ionized donors may be the dominating process limiting the mobility.

Figure of merit calculated for the sputtered cadmium oxide thin films at $\lambda = 600$ nm is also listed in table 6.3. It is interesting to note that $\phi(\lambda)$ obtained for these films is better than that of specimens prepared by spray pyrolysis.

Fig. 6.7 shows the variation of TEP with temperature for CdO film of thickness 163 nm. It is found that the TEP increases with an increase in temperature. The dependence of TEP on temperature and carrier concentration is given by the relation [15]

$$\text{TEP} = \left( \frac{P}{6} + \frac{1}{2} \right) \left( \frac{\pi k T}{h} \right)^2 \frac{8 m^*}{e} \left( \frac{\pi N_H}{3} \right)^{-2/3}$$  (6.16)

where $P$ is the scattering index and $k$ is the Boltzmann's constant. According to this relation, the TEP should decrease with increase in carrier concentration, which is in agreement with the experimental results of sprayed and sputtered CdO samples. In both the cases, the TEP increases linearly with the temperature. Similar results have been observed in arsenic doped tin oxide films [16].

6.9 Conclusions

The following significant conclusions have emerged from the studies:

(1) Annealing in air causes a drastic change in the sheet resistance of cadmium oxide thin films produced by DC reactive magnetron sputtering.

(2) Hall effect measurements indicate that cadmium oxide films prepared by both the techniques are n-type semiconductors. A very low sheet resistance of about 15 $\Omega/\square$ is obtained for the first time in sputtered Cadmium oxide thin films of typical thickness 177.5 nm. The electrical resistivity obtained for films prepared by spray technique is of the order $10^{-5}$ $\Omega m$, whereas films formed by DC sputtering are found to possess still very low values of the order $10^{-6}$ $\Omega m$. This is due to
Fig. 6.7 Variation of TEP with Temperature for Sputtered CdO Thin Film of Thickness 163 nm.
the high carrier mobility of sputtered CdO thin films. Furthermore, the carrier density observed in sputtered CdO films is very high of the order $10^{26}$ m$^{-3}$.

(3) From the comparison of crystallite size with the evaluated mean free path and from the mobility versus carrier concentration plots, it is inferred that the ionized impurities are responsible for the dominant scattering mechanism to limit the mobility values of the films. The increase in resistivity of sputtered CdO films with the temperature is due to a decrease in the carrier mobility of the films.

(4) The thermoelectric power observed for sputtered cadmium oxide films is found to be lower when compared to the results obtained for sprayed CdO thin films. This is attributed to the higher carrier density of sputtered CdO thin films.
### Table 6.1 Electrical Parameters of CdO Thin Films Prepared at Different Deposition Timings by Spray Pyrolysis.

<table>
<thead>
<tr>
<th>t (s)</th>
<th>df (nm)</th>
<th>$R_{sh}$ (Ω/□)</th>
<th>$\rho$ (10^{-5} Ωm)</th>
<th>$R_H$ (10^{-6} m$^3$/C)</th>
<th>$N_H$ (10^{26} m$^{-3}$)</th>
<th>$\mu_H$ (10^{-4} m$^2$/Vs)</th>
<th>$\phi$ (V$^{-1}$)</th>
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<tr>
<td>4</td>
<td>200</td>
<td>71</td>
<td>1.400</td>
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<td>19.01</td>
<td>1.63</td>
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<td>49</td>
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<td>2.60</td>
<td>18.06</td>
<td>1.66</td>
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<td>-0.022</td>
<td>2.80</td>
<td>17.59</td>
<td>0.52</td>
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### Table 6.2 Electrical Parameters of CdO Thin Films Prepared at Different Substrate Temperatures by Spray Pyrolysis.

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>df (nm)</th>
<th>$R_{sh}$ (10^3 Ω/□)</th>
<th>$\rho$ (10^{-5} Ωm)</th>
<th>$N_H$ (10^{25} m$^{-3}$)</th>
<th>$\mu_H$ (10^{-4} m$^2$/Vs)</th>
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<td>550</td>
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<td>68.29</td>
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Table 6.3  Electrical Parameters of CdO Thin Films Prepared by DC Reactive Magnetron Sputtering at Different Substrate Temperatures.

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>$d_f$ (nm)</th>
<th>$R_{sh}$ ($\Omega/\square$)</th>
<th>$\rho$ ($10^{-6}$ $\Omega$m)</th>
<th>$N_H$ ($10^{26}$ m$^{-3}$)</th>
<th>$\mu_H$ ($10^{-4}$ m$^2$/Vs)</th>
<th>$\phi(\lambda)$ ($10^{-2}$ $\Omega^{-1}$)</th>
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<tr>
<td>30</td>
<td>146.0</td>
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<td>2.35</td>
<td>100.48</td>
<td>2.90</td>
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Table 6.4  Temperature Dependence of Electrical Parameters of CdO Thin Films of Typical Thickness 177.5 nm Prepared by DC Reactive Magnetron Sputtering.

<table>
<thead>
<tr>
<th>$T_s$ (K)</th>
<th>$\rho$ ($10^{-6}$ $\Omega$m)</th>
<th>$N_H$ ($10^{26}$ m$^{-3}$)</th>
<th>$\mu_H$ ($10^{-4}$ m$^2$/Vs)</th>
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References


