CHAPTER III

ELECTRICAL PROPERTIES OF INDIUM OXIDE, TIN OXIDE AND INDIUM TIN OXIDE THIN FILMS
3.1 Introduction

In this chapter the electrical conductivity of indium oxide, tin oxide and indium tin oxide films is discussed. A variety of techniques\textsuperscript{1-4} are used for the preparation and characterisation of these films. The major work in this field is on its electrical and optical properties. Detailed studies on the electrical property have been reported by Hoffmann et al.,\textsuperscript{5} Samson and Fonstad,\textsuperscript{6} Ray and Banerjee\textsuperscript{7} and Ishibashi et al.\textsuperscript{8} It is found that the film properties strongly depend on the deposition techniques and deposition parameters, such as substrate temperature, oxygen partial pressure, deposition rate and annealing conditions.

3.2 Theory

In a semiconductor the conductivity in the presence of electrons and holes is given by

$$\sigma = (n e \mu_e + P e \mu_h)$$

where \(n\) and \(\mu_e\) are the carrier concentrations and mobility of electrons respectively and \(P\) and \(\mu_h\) are the
corresponding quantities for the holes. In an intrinsic semiconductor the number of electrons is equal to the number of holes. The expressions for the carrier concentration are given by

\[ n_i = N_C \exp \left( \frac{E_F}{k_BT} \right) \quad \ldots \quad (3.1) \]

\[ p_i = N_V \exp \left( \frac{-E_F + E_g}{k_BT} \right) \quad \ldots \quad (3.2) \]

where \( N_C \) and \( N_V \) are the density of states in the conduction band and valance band respectively. \( E_g \) is the forbidden energy gap. \( k_B \) is the Boltzmanns constant and \( T \) is the absolute temperature.

If we assume that the variation of mobility of electrons and holes in the electric field with temperature is small, then the conductivity \( \sigma \) which is proportional to the number of carriers has a variation of the form

\[ \sigma = \sigma_0 \exp (-\Delta E/2k_BT) \quad \ldots \quad (3.3) \]

where \( \sigma_0 \) is a constant, \( \Delta E \) is the activation energy, \( k_B \) is the Boltzmanns constant and \( T \) is the temperature.

But \( \sigma = Ne\mu \)

where \( N \) is the number of charge carriers, \( e \) is the charge and \( \mu \) is the mobility.
3.3 Indium oxide

3.3.1 Experiment

Thin films of $\text{In}_2\text{O}_3$ are prepared using thermal evaporation described in Chapter 2 (Section 2.11). Spectroscopically pure $\text{In}_2\text{O}_3$ powder (99.99% purity) procured from Nuclear Fuel Complex, Hyderabad is used as the source material. Indium oxide powder sintered at a temperature of $800^\circ\text{C}$ for 6 hours and then powdered is evaporated from a tantalum boat. Initially the vacuum chamber is evacu- ated to a base pressure of $10^{-6}$ mbar. Pure oxygen is admitted into the chamber with the high vacuum valve open. A steady state chamber pressure of $10^{-4}$ mbar is rapidly reached by adjusting the needle valve of the plant. Glass slides have been used as substrates on which a calibrated chromel-alumel thermocouple is attached. The substrate is cleaned using procedure described in Chapter 2 (Section 2.9). Inside the bell jar the substrates are subjected to ionic bombardment for 5 minutes before using for actual deposition. The substrate temperature is varied by using a substrate heater. The rate of evaporation is controlled within the range 13-15 nm/min.

The thickness of the film is measured and controlled using the quartz crystal thickness monitor and counterchecked by using the multiple beam interference
technique. The deposited film is subjected to a post-deposition annealing in a muffle furnace for 30 minutes at 350°C. The electrical conductivity of the samples are measured using the conductivity cell and a Keithley Programmable Electrometer (Model No. 617). The ohmic contacts are made by pre-evaporated silver electrodes and using silver paste. Conductivity measurements are done in vacuum (<10^-3 mbar) to eliminate the contamination of the film.

3.3.2 Results and Discussion for Indium Oxide

Figure 3.1 shows the variation of ln $R_{sh}$ with thickness of the $\text{In}_2\text{O}_3$ film deposited at substrate temperature ($T_s$) 50, 150, 200, 250 and 300°C. For the film of $T_s = 50\degree C$, a sheet resistance ($R_{sh}$) of 984 KΩ/□ is obtained for a thickness 55 nm. For a film of thickness 190 nm the measured sheet resistance is 36.5 KΩ/□. In the case of $T_s = 150\degree C$ $R_{sh}$ for a film of thickness 80 nm is 490 KΩ/□. For the thickness 200 nm sheet resistance measured is 0.601 KΩ/□. Sheet resistance of 32.859 KΩ/□ at thickness 70 nm is obtained at a substrate temperature 200°C. For the same substrate temperature 0.601 KΩ/□ is obtained at a thickness 190 nm. Increased substrate temperature considerably lowers the sheet resistance. At substrate temperature 250°C, 9.897 KΩ/□ is obtained at
Fig. 3.1 Plot of $\ln R_{sh}$ Vs thickness for In$_2$O$_3$ for substrate temperatures 50, 150, 200, 250 and 300°C.
a thickness 60 nm. Lowest sheet resistance for as-deposited films obtained is at the substrate temperature 300°C. Sheet resistance of 0.601, 0.445, 0.365, 0.164 and 0.134 kΩ/□ are obtained for thickness 70, 95, 125, 150 and 185 nm respectively.

The variation of resistivity of the annealed samples with substrate temperature is plotted in Figure 3.2. Films of thickness 150 nm are used for the study. A minimum resistivity of 0.7 x 10^{-5} Ωm is obtained at a substrate temperature 300°C. Above this substrate temperature (350°C) the resistivity observed is 8 x 10^{-5} Ωm. The highest resistivity 1 x 10^{-2} Ωm is obtained at the substrate temperature 50°C.

In Figure 3.3, the sheet resistance after annealing is plotted as a function of sheet resistance before annealing. The variation of sheet resistance is maximum for films deposited at the substrate temperature 350°C.

The variation of resistivity as a function of temperature is shown in Figure 3.4. A sudden change in resistivity occurs at the temperature region 270-290°C. Above and below this range, the variation of resistivity with temperature is small. For the film of thickness 125 nm the transition takes place at 270°C and for 160 nm the transition is at a higher temperature (290°C).
Fig. 3.2 Plot of log $\rho$ as a function of substrate temperature for In$_2$O$_3$ films.
Fig. 3.3 Plot of annealed sheet resistance as a function of sheet resistance before annealing for In$_2$O$_3$ films.
Fig. 3.4 Variation of resistivity as a function of temperature for In$_2$O$_3$ films.
The dc electrical conductivity is calculated from resistance measurement and by knowing the area and thickness of the film. The temperature dependence of conductivity is given by Arrhenius relation given in equation (3.3), Chapter 3 (Section 3.2).

Figure 3.5 shows the temperature dependence of dc electrical conductivity of In$_2$O$_3$ thin films of thicknesses 51.2, 61.8, 75.2 and 91.4 nm deposited at 50°C. The plot of ln $\sigma$ Vs 1000/T exhibits two straight line regions of different activation energy for the same samples. The values of activation energy $\Delta E_1$ in the lower temperature region (300-380 K) and $\Delta E_2$ in the higher temperature region (380-433 K) are given in Table 3.1. It is seen that at the higher temperature region activation energy $\Delta E_2$ varies considerably with film thickness. In all the samples activation energies $\Delta E_1$ and $\Delta E_2$ decrease with increase in film thickness.

Figures 3.6 and 3.7 show the temperature dependence of dc electrical conductivity of In$_2$O$_3$ thin films deposited at a substrate temperature 250°C and annealed. The plot of ln $\sigma$ Vs 1000/T in the lower temperature region gives the activation energy $\Delta E_1$ and for higher temperature region $\Delta E_2$. The activation energy in region I ($\Delta E_1$) is 0.014 eV and in region II ($\Delta E_2$) is 1.10 eV for a film of thickness 95 nm. The activation
Fig. 3.5 Plot of $\ln \sigma (\Omega \text{m})^{-1}$ Vs $1000/T$ for $\text{In}_2\text{O}_3$ film of thickness 51.2, 61.8, 75.2 and 91.4 nm.
Fig. 3.6 Plot of $\ln \sigma$ vs $1000/T$ in the lower temperature region for In$_2$O$_3$ films of thicknesses 65, 95, 125 and 160 nm.
Fig. 3.7 Plot of $\ln \sigma$ vs $1000/T$ in the higher temperature region for $\text{In}_2\text{O}_3$ films of thicknesses 95, 125 and 160 nm.
energies vary for films of different thicknesses. Variation of activation energy with thickness is given in Table 3.2.

### Table 3.2 Variation of activation energy for In$_2$O$_3$ film deposited at 250°C

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$\Delta E_1$ (eV)</th>
<th>$\Delta E_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>0.022</td>
<td>-</td>
</tr>
<tr>
<td>95</td>
<td>0.014</td>
<td>1.10</td>
</tr>
<tr>
<td>125</td>
<td>0.013</td>
<td>1.00</td>
</tr>
<tr>
<td>160</td>
<td>0.008</td>
<td>0.79</td>
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</table>
Figures 3.8 and 3.9 represent the dc electrical conductivity characteristics of In$_2$O$_3$ thin films prepared at 300°C and annealed. From the ln $\sigma$ Vs 1000/T graph, in the lower temperature region the activation energy $\Delta E_1$ for thickness 82, 123 and 150 nm are determined. The values of activation energy 0.030, 0.024 and 0.022 eV are obtained for the thicknesses 82, 123 and 150 nm respectively. In the upper temperature region (550-600 K) the values of activation energy $\Delta E_2$ for the same films have been determined (Figure 3.9). The activation energies obtained for 123 and 150 nm films are 0.39 and 0.32 eV respectively.

For highly conducting transparent films, thickness is an important parameter. The as-deposited films of indium oxide show a decrease in sheet resistivity with thickness. Mirzapour et al.\textsuperscript{9} have reported that in indium oxide thin films sheet resistance decreases with thickness up to a value of 600 nm. Jeong et al.\textsuperscript{10} also observed that a decrease in sheet resistance up to a value of 200 nm and above that value there was a gradual increase in sheet resistance. The present study shows a minimum sheet resistance nearly at a thickness 200 nm.

The low sheet resistance of the as-deposited film is due to the presence of In and other suboxides. Many workers have reported\textsuperscript{11,12} the dissociation of indium
Fig. 3. A plot of $\ln \sigma$ vs $1000/T$ for In$_2$O$_3$ films of thicknesses 82, 123 and 150 nm in the lower temperature region.
Fig. 3.9 Plot of $\ln \sigma$ Vs $1000/T$ for $\text{In}_2\text{O}_3$ films of thicknesses 123 and 150 nm in the higher temperature region.
oxide during vacuum evaporation into InO, In$_2$O, In and O$_2$. The as-deposited films are dark in colour which also indicates the lower oxidation state. The as-deposited films consist of the above species leading to the formation of non-stoichiometric composition with the above species embedded into the In$_2$O$_3$ lattice matrices. The resulting oxide layer could be considered to have a concentration of impurity or doping agents.

Substrate temperature has a prominent role in the sheet resistance. Higher substrate temperature always enhances the conductivity of the films.\cite{13} The decrease in carrier density is the evidence of oxidation of the deposited In and/or InO$_x$ films. Since higher substrate temperature accelerates oxidation in vacuum, grain size in the film becomes larger as the substrate temperature is higher. The decrease in resistivity up to 300°C of the substrate temperature means the existence of structural imperfection in the film, oxygen vacancies and excess of atoms acting as charged donor centres.\cite{14} There may be a high density of ionised impurity centres in the film caused by oxygen vacancies and excess indium atoms.

The variation of sheet resistance after annealing is greater for the films of higher initial sheet resistance. The disappearance of interstitial indium atoms and oxygen vacancies leads the film to better stoichiometry.
The plot of resistivity Vs temperature in Figure 3.4 shows a sudden transition at temperature range 270-290°C which is due to the crystallization of indium oxide film. Similar behaviour has been reported for indium oxide thin films by Muranaka.\textsuperscript{15} For continuous film the heat released with crystallization of grain is transferred to the neighbouring grains, and causes crystallization. The crystalline nature increases with increase in thickness.

Arvin\textsuperscript{16} has reported activation energy of 0.87 eV and 0.67 eV for In\textsubscript{2}O\textsubscript{3}. Sundaram and Bhagavat\textsuperscript{17} report the activation energy of 0.007 eV for region I and 0.205 eV for region II. The values of activation energy obtained in the present study is 0.007 eV and 0.032 eV at lower and upper temperature regions respectively for a film of 91.4 nm, deposited at room temperature.

3.4 Tin oxide

3.4.1 Experiment

Thin films of tin oxide have been prepared by using the electron beam gun described in Chapter 2 (Section 2.11). Spectroscopically pure (99.99\% of purity) tin oxide powder procured from Nuclear Fuel Complex, Hyderabad, is pressed into pellets. These pellets are sintered in air at 800°C in a muffle furnace and then
allowed to cool. These are then used as the source material for evaporation from the electron beam gun. The evaporation conditions are as follows: (1) a vacuum of $2 \times 10^{-5}$ mbar, (2) an accelerating voltage 6 KV, (3) electron beam current of 10-15 mA. Glass slides have been used as the substrates. The substrate temperature is varied using the substrate heater. The temperature of the substrate is measured using a chromel-alumel thermocouple placed on the substrates. The rate of evaporation is 13-15 nm/min. The time of evaporation is 15 minutes. The thickness of the films are monitored by quartz crystal thickness monitor. The thickness is counterchecked by the multiple beam interference technique. Annealing of the films have been carried out in a muffle furnace at a temperature 450°C for 3 hours. The electrical conductivity is measured using the Keithley Electrometer (Model No. 617) and the conductivity cell in vacuum.

3.4.2 Results and Discussion for Tin Oxide

The variation of sheet resistance with thickness for tin oxide film deposited at 300 and 350°C are plotted in Figure 3.10. For the film deposited at 300°C the sheet resistance is greater than that of the films of substrate temperature 350°C. The films deposited at a temperature
Fig. 3.10 Plot of variation of sheet resistance with thickness for SnO₂ films.
<200°C are found to be amorphous and are having very high resistivity ($\approx 10^6 \Omega \text{m}$).

Figure 3.11 is the plot of resistivity Vs substrate temperature for tin oxide film having thickness 300 nm. In the case of substrate temperature 50°C resistivity obtained is $0.80 \times 10^{-2}$ Ωm and at $T_s = 100°C$ it is decreased to $0.6 \times 10^{-2}$ Ωm. At $T_s = 150°C$ the resistivity becomes $0.28 \times 10^{-2}$ Ωm. In the temperature range 200–350°C the resistivity shows only a slight change and the value of resistivity at 300°C is $0.06 \times 10^{-2}$ Ωm.

Figure 3.12 shows the temperature dependence of dc electrical conductivity of SnO$_2$ thin films deposited at 150°C. The plot of ln $\sigma$ Vs 1000/T exhibits a straight line region indicating an activation energy. The activation energy $\Delta E$ obtained for the sample of thicknesses 120, 160, 210 and 240 nm are 0.55, 0.40, 0.35 and 0.31 eV respectively. This shows that the activation energy decreases with increase in thickness.

Temperature dependence of dc electrical conductivity of thin films of SnO$_2$ evaporated at a substrate temperature 350°C is shown in Figure 3.13. The plot of ln $\sigma$ Vs 1000/T gives a straight line. The activation energies calculated from the straight line regions is listed in Table 3.3.
Fig. 3.11 Plot of resistivity vs substrate temperature for SnO$_2$ films.
Fig. 3.12 Plot of $\ln \sigma$ vs $1000/T$ for SnO$_2$ films of thicknesses 120, 160, 210 and 240 nm.
Fig. 3.13 Plot of $\ln \sigma$ Vs $1000/T$ for SnO$_2$ films of thicknesses 100, 120, 150 and 180 nm.
Table 3.3 Variation of activation energy with thickness for SnO$_2$ films deposited at 350°C

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Activation energy ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.240</td>
</tr>
<tr>
<td>120</td>
<td>0.108</td>
</tr>
<tr>
<td>150</td>
<td>0.084</td>
</tr>
<tr>
<td>180</td>
<td>0.072</td>
</tr>
</tbody>
</table>

Figure 3.14 is the plot of ln $\sigma$ Vs 1000/T for SnO$_2$ thin films deposited at various substrate temperatures (50-350°C). The sample thickness is 300 nm. From the slope of the straight lines activation energy $\Delta E$ is determined. The variation of activation energy $\Delta E$ with substrate temperature is shown in Figure 3.15.

The activation energy for the film deposited at substrate temperature 50°C is 0.5 eV. Gradually the activation energy decreases with temperature up to 300°C. The minimum value of activation energy obtained for a thickness of 300 nm is 0.01 eV. For the film of substrate temperature 350°C the activation energy obtained is 0.06 eV for a thickness of 300 nm.

Variation of conductivity in heating and cooling cycles on SnO$_2$ film is given in Figure 3.16. The
Fig. 3.14 Plot of $\ln \sigma$ Vs $1000/T$ for SnO$_2$ films of substrate temperatures 50, 100, 150, 200, 300 and 350°C.
Fig. 3.15 Plot of variation of activation energy with substrate temperature for SnO₂ films.
Fig. 3.16 Plot of variation of conductivity in SnO$_2$ films in heating and cooling cycles.
thickness of the film is 120 nm and substrate temperature is 100°C. It is observed that the cooling curve does not retrace the heating curve and the conductivity is found to be increased after the heating and cooling cycle.

The activation energy in tin oxide film is due to the formation of donor levels below the conduction band which increases with the substrate temperature up to 300°C. At 350°C of substrate temperature, these donor levels start decreasing due to better stoichiometry and crystallinity. Das and Banerjee\textsuperscript{18} have obtained activation energy 0.26 eV for electron beam gun evaporated tin oxide films. Sanjines et al.\textsuperscript{19} reports an activation energy of 0.2 eV. Sanjines and Levy\textsuperscript{20} obtained an activation energy of 0.73 eV. Kohnke\textsuperscript{21} obtained activation energy for stannic oxide crystals as 0.72 eV whereas Miloslavski\textsuperscript{22} calculated an activation energy of 0.12 eV in the same temperature region. For electron beam gun evaporated thin films of SnO\textsubscript{2}, Kazmerski and Racine\textsuperscript{23} obtained an activation energy of 0.165 eV. Nishino and Hamakawa\textsuperscript{24} reports an activation energy of 0.023 eV for tin oxide thin films. In the present study, the activation energy is obtained for films deposited at 350°C and having thicknesses 100 and 150 nm are 0.24 and 0.084 eV respectively. Electrical conductivity and ESR studies carried out by Mizokawa and Nakamura\textsuperscript{25} on fine powdered
SnO$_2$ suggest that the material has a double donor level, a shallow one ($\Delta E = 0.3$ eV) originated from the bulk oxygen vacancy and a deep one (1 eV) level due to the surface oxygen vacancy. Samson and Fonstad$^6$ concluded that the doubly ionised oxygen vacancy predominated in SnO$_2$.

3.5 Indium tin oxide (ITO)

3.5.1 Experiment

The tantalum boat is used for evaporation of indium tin oxide (ITO) thin films. The details of the vacuum coating unit is described in Chapter 2 (Section 2.8). Spectroscopically pure indium oxide (99.99% pure) and tin oxide (99.99% pure) procured from Nuclear Fuel Complex, Hyderabad is used as the source material.

The indium oxide powder and tin oxide powder taken in weight percentage proportion (90:10, 80:20, 60:40, 40:60 and 20:80 respectively) are mixed well using a pestle and mortar. Each mixture is sintered in a furnace for 6 hours at a temperature of 800°C. It is evaporated from the tantalum boat at a chamber pressure $2 \times 10^{-5}$ mbar. Glass slides have been used as the substrates. The substrates are cleaned using the process described in Chapter 2 (Section 2.9). The substrate temperature is varied using the substrate heater and the temperature is measured using
a chromel-alumel thermocouple placed over the substrates. The rate of evaporation is controlled within the range 13-15 nm/min. The time of evaporation is 15 minutes. The thickness of the samples and the rate of evaporation is controlled by using the quartz crystal thickness monitor. The thickness is counterchecked using the multiple beam interference technique described in Chapter 2 (Section 2.15). The deposited films are subjected to a post-deposition annealing in air for 30 minutes at a temperature 350°C using the muffle furnace.

The ohmic contacts are made by pre-evaporated silver electrodes and silver paste. The sheet resistance and electrical conductivity are measured using the Keithley Electrometer (Model No. 617) and the conductivity cell. The temperature of the sample during conductivity study is measured using a chromel-alumel thermocouple and a digital multimeter. The conductivity measurements are done in vacuum to eliminate the contamination of the sample.

3.5.2 Results and Discussion for Indium Tin Oxide

Figure 3.17 is the plot of resistivity Vs percentage of tin. The thickness of the films is 150 nm. It is found that the resistivity is lowest when the sample is of 80% In₂O₃:20% SnO₂ by molar concentration. Here the resistivity obtained is 2 x 10⁻³ Ωm. When the molar
Fig. 3.17 Plot of resistivity Vs percentage of tin oxide doping for ITO films.
concentration of SnO₂ increases the resistivity also increases and above 40% of SnO₂ resistivity is $2 \times 10^{-2}$ Ωm. Increased doping does not show considerable change in resistivity. Figure 3.18 is the plot of $R_{sh}$ Vs thickness for ITO thin films deposited at two different substrate temperatures 200 and 250°C. For the film deposited at 200°C the sheet resistance obtained for a thickness 60 nm is 3.5 kΩ/□ which is higher than the sheet resistance of film deposited at 250°C (2.0 kΩ/□). At a thickness of 210 nm, the sheet resistance of the film having substrate temperature 200 nm is 0.21 kΩ/□ and that for a film of substrate temperature 250°C is 0.165 kΩ/□. In both the cases sheet resistance above a thickness 200 nm is nearly a constant. At this thickness ITO thin films obtain a saturation in sheet resistance.

ITO thin films (In₂O₃:SnO₂, 80%:20%) deposited at different substrate temperatures and resistivity is shown in Figure 3.19 which gives the plot of resistivity Vs substrate temperature (Ts). The thickness of the films is 150 nm. At the substrate temperature 50°C the resistivity obtained is $1.4 \times 10^{-2}$ Ωm. Resistivity for the temperatures 150 and 200°C are $4 \times 10^{-3}$ and $2 \times 10^{-4}$ Ωm respectively. A sudden drop from $1.4 \times 10^{-2}$ Ωm to $2 \times 10^{-4}$ Ωm is obtained in the temperature range 50-150°C. Above 150°C the change in resistivity is very small and
Fig. 3.18 Plot of sheet resistance Vs thickness for ITO film deposited at 200 and 250°C.
Fig. 3.19 Plot of resistivity Vs substrate temperature for ITO.
The lowest resistivity obtained is $7 \times 10^{-5}$ $\Omega$m at the substrate temperature $350^\circ$C. In Figure 3.20 resistivity of the sample is plotted as a function of temperature. At the temperature region $270-290^\circ$C a sudden drop in resistivity is obtained. On cooling resistivity remains $10^{-1}$ $\Omega$m.

Figure 3.21 is the plot of $\ln \sigma$ Vs $1000/T$ for the indium tin oxide thin film deposited at $50^\circ$C. The thicknesses of the films are 55, 80, 105 and 147 nm. The graphs show two straight line regions indicating the presence of two activation energies $\Delta E_1$ in the lower temperature region (300-400 K) and $\Delta E_2$ in the higher temperature region (400-450 K). The activation energies of the samples are calculated from the slope of the straight lines. The activation energies $\Delta E_1$ and $\Delta E_2$ for films of different thicknesses are given in Table 3.4.

Table 3.4 Variation of activation energy with thickness for ITO films deposited at $50^\circ$C

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$\Delta E_1$ (eV)</th>
<th>$\Delta E_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>0.036</td>
<td>0.417</td>
</tr>
<tr>
<td>80</td>
<td>0.034</td>
<td>0.412</td>
</tr>
<tr>
<td>105</td>
<td>0.028</td>
<td>0.136</td>
</tr>
<tr>
<td>147</td>
<td>0.022</td>
<td>0.132</td>
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</table>
Fig. 3.20 Plot of resistivity Vs temperature for ITO films.
Fig. 3.21 Plot of $\ln \sigma$ vs $1000/T$ for ITO thin films for thicknesses 55, 80, 105 & 147 nm
Plot of $\ln \sigma$ vs $1000/T$ for the samples deposited at 100°C is given in Figure 3.22. The thickness of the samples are 83, 110 and 140 nm. The graph shows two straight line regions. The activation energies of ITO films deposited at 100°C are shown in Table 3.5. The conductivity of the samples increase with thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Activation energy</th>
<th>( \Delta E_1 ) (eV)</th>
<th>( \Delta E_2 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>83</td>
<td></td>
<td>0.032</td>
<td>0.402</td>
</tr>
<tr>
<td>110</td>
<td></td>
<td>0.025</td>
<td>0.380</td>
</tr>
<tr>
<td>140</td>
<td></td>
<td>0.020</td>
<td>0.350</td>
</tr>
</tbody>
</table>

Figure 3.23 is the plot of $\ln \sigma$ vs $1000/T$ for indium tin oxide thin films deposited at 200°C. The conductivity of the samples of thicknesses 70, 120, 150, 180 and 200 nm with temperature are shown. For the films of thicknesses 70, 120, 150 and 180 nm the activation energy is very small in the lower temperature region. The curves in the higher temperature region are not regular in shape and it is very difficult to determine the activation energy.
Fig. 3.22 Plot of \( \ln \sigma \) vs \( 1000/T \) for ITO films of thicknesses 83, 110, and 140 nm.
Fig. 3.23 Plot of $\ln \sigma$ vs $1000/T$ for ITO films of thicknesses 70, 120, 150, 180 and 200 nm.
DC electrical conductivity of ITO films of substrate temperature 250°C is shown in Figure 3.24. A plot of ln σ Vs 1000/T for films of thickness 110, 150, 180 and 210 nm are given. Conductivity of the samples increase with film thickness. At this substrate temperature films of thicknesses 110, 150, 180 and 210 nm show a straight line region with a positive slope, indicating metallic nature of the samples. In the higher temperature region the shape of the curves are irregular.

Figure 3.25 is the plot of ln σ Vs 1000/T for ITO thin film deposited at 300°C and annealed for different time intervals. Curves A, B and C correspond to an annealing time 1, 2 and 3 hours respectively. The thickness of the sample is 110 nm. For the film annealed for 1 hour the ln σ Vs 1000/T curve has irregular shape. For the film of thickness 110 nm and annealed for 2 hours a straight line region is obtained with a positive slope. Curve C also shows the same nature. It is noted that as the annealing time is increased the conductivity decreases. The values of conductivity at room temperature for ITO films of thickness 110 nm are 5.4 x 10^5, 2.9 x 10^5, 2.4 x 10^5/Ω/m for annealing time 1, 2 and 3 hours respectively.
Fig. 3.24 Plot of ln $\sigma$ vs $1000/T$ for ITO films of thicknesses 110, 150, 180 and 210 nm.
Fig. 3.25 Plot of $\ln \sigma$ vs $1000/T$ for ITO films for different annealing times.
Change in dc electrical conductivity with temperature for the unannealed samples have been studied in the lower temperature (300-500 K). The plot of $\ln \sigma$ vs $1000/T$ for samples deposited at substrate temperature 50, 250 and 300°C are shown in Figure 3.26. The thicknesses of the samples are 130 nm each. The curves show a straight line region without considerable slope. The electrical conductivity of these films are unaffected upto a temperature 500 K. But the conductivity at room temperature is higher for the films of higher substrate temperatures. The room temperature conductivities are $5.4 \times 10^1$, $3.6 \times 10^5$ and $4.42 \times 10^5$/n/m for films of substrate temperature 50, 250 and 300°C respectively.

In all the cases sheet resistance shows thickness dependence. The carriers liberated from substitutional tin (Sn$^{4+}$) increases carrier density. Increase in thickness improves film crystallinity which results in decreasing donor sites trapped at the dislocation or point defect aggregates. Shigesato and Paine\textsuperscript{26} suggest that increase in carrier density with increasing film thickness is associated with increasing oxygen vacancy. This increase in electrically active oxygen vacancy is caused by vacuum deposition.

The increase in resistivity on annealing is caused by the decrease in oxygen vacancies due to oxidation\textsuperscript{27} In the
Fig. 3.26 Plot of \( \ln \sigma \) vs \( 1000/T \) for ITO film deposited at 50, 250 and 300°C.
case of In$_2$O$_3$ or ITO the non-stoichiometric films are formed rich in Sn or In which is evident from XRD study. These excess free carriers cause a low resistivity of the as-deposited film. On annealing the films become stoichiometric with the disappearance of these carriers with increase in resistivity.

When the substrate temperature is varied the initial decrease in resistivity may be attributed to the improved crystalline nature of the films. The crystalline nature may reduce the grain boundary scattering mechanism. The increase in carrier density may be understood from the relation

\[ N = N_0 \exp(-q\phi/KT) \]

where $N_0$ is the carrier density in the absence of grain boundary and $\phi$ is the grain boundary potential. The increase in resistivity at higher substrate temperature may be due to the better stoichiometry of the films.

The increase in substrate temperature may lead to oxygen deficient films resulting in an increase in carrier density. When tin is added to indium oxide, the carrier density further varies for any particular substrate temperature due to the availability of more tin to become ionised and donate electrons. In ITO lattice
tin substitutes for indium as Sn$^{4+}$ gives rise to an additional electron for conduction. But it is not necessary that all the tin ions are efficient in generating conduction electrons. The preferred valence state depends on the deposition conditions.

It may be noted that no rigorous electronic band structure calculation is available for indium oxide. Fan and Goodenough\textsuperscript{14} proposed a model to explain the physical properties of ITO as shown in Figure 3.27. According to this model the conduction band is mainly from In:5s electrons and the valance band from O$^{2-}$:2p electrons. The doubly charged oxygen vacancies and the singly charged tin are represented as donor levels with low ionisation energies. At high density of the dopants, the conduction band merges with the donor levels.

The electrical conduction in ITO films may be better explained if one considers the phenomena of insulator metal transition. The conduction electrons are donated to the ITO by the oxygen vacancies and the dopant tin. When the donor concentration reaches a critical density ($n_c$) for the insulator metal transition, the donor states merge with the conduction band. The critical density can be estimated from using the Mott's criterion.\textsuperscript{29}$$n_c^{1/3} a_0^* \approx 0.25$$where $a_0^*$ is the effective Bohr radius.
Fig. 3.27 Schematic energy band model for ITO.
The schematic density of states diagram is shown in Figure 3.28. If the donor concentration is above the Mott critical density the Fermi level is within the conduction band. The exact position of the Fermi level is determined by the highest occupied states in the conduction band. If the electron concentration is not much higher than the Mott critical density, the Fermi level is of the order of $kT$. Due to the tailing of the Fermi-Dirac distribution function

$$f_{FD}(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

and the electron scattering effects, the Fermi level is not sharply defined. These circumstances yield that all the conduction band electrons contribute to the electrical conductivity.

At high electron densities ($10^{20}/cm^3$) such as those normally present in ITO films, the Fermi level is high up in the conduction band. The function $(-df/dE)$ in Figure 3.28 is sharp and the semiconductor is said to be highly degenerate exhibiting the metallic properties. Thus all the conduction electrons have approximately the same energy $E_F$ and the conductivity depends mainly on the properties of the fermi surface electrons and not on the total number of electrons in the conduction band.
Fig. 3.28  Schematic density of states diagram for a semiconductor doped to various extents.

(a) Undoped intrinsic material (non-degenerate)

(b) Donor levels within the band gap (non-degenerate to slightly degenerate)

(c) Above the Mott critical density (degenerate)

(d) Highly doped material (degenerate)
Thus the electrical conductivity mechanism of metals is reasonably valid for indium tin oxide. Similar to indium oxide, indium tin oxide also exhibits a double donor level in the conduction band. In the low temperature region the donor level is shallow and in the high temperature region it is sharp. Hoffmann et al.\(^5\) have reported the activation energies as 0.035 and 0.045 eV in region I and II respectively. Huang\(^30\) have reported an activation energy 8.6 x 10\(^{-6}\) eV for thermally evaporated indium tin oxide films.

Investigations on doped indium oxide films for conductivity by Nath et al.\(^23\) obtained activation energies of conduction in between 0.015 and 0.027 eV. Similar to our results they observed a decrease in conductivity with temperature, for films deposited at substrate temperature 350\(^{\circ}\)C and above.

The values of activation energy obtained in the present study is 0.007 and 0.032 eV at lower and upper temperature region respectively, for a film of thickness 91.4 nm, deposited at room temperature.
References

11. A. Goswami and A. P. Goswami, Pramana, 8 (1977) 335.
