CHAPTER III

ELECTRICAL STUDIES ON 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 are discussed. Many techniques\(^1\)\(^-\)\(^4\) are used for the preparation and characterization 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 Hoffman \textit{et al.}\(^5\)\(^,\) Habibi and Talebian\(^6\), Shamala \textit{et al.}\(^7\) and Ishibashi \textit{et al.}\(^8\) 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 electrical conductivity in the presence of electrons and holes is given by

\[ \sigma = \sigma_n + \sigma_p \]

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

\[ n_i = N_c \exp \left( \frac{(E_F - E_c)}{k_B T} \right) \]

\[ p_i = N_v \exp \left( \frac{(E_v - E_F)}{k_B T} \right) \]
where \( N_C \) and \( N_V \) are the density of states in the conduction band and valence band respectively. \( E_C \) is the bottom of the conduction band and \( E_V \) the top of the valence band. \( E_F \) is the Fermi level, \( k_B \) is the Boltzmanns constant and \( T \) is the absolute temperature. \((E_C - E_V)\) is the forbidden energy gap \((E_g)\).

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

\[
\sigma = \sigma_0 \exp \left( -\frac{\Delta E}{2k_B T} \right)
\]

(3.4)

(for single level) where \( \sigma_0 \) is a constant, \( \Delta E \) is the activation energy, \( k_B \) is the Boltzmanns constant and \( T \) is the temperature in absolute scale. But

\[
\sigma = Ne\mu
\]

(3.5)

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

The conductivity \( \sigma \) of a thin film of resistance \( R \), length \( L \), breadth \( b \) and thickness \( d \) is given by

\[
\sigma = \frac{L}{Rbd}
\]

(3.6)

3.3. **Indium oxide**

3.3.1 **Experiment**

Thin films of Indium oxide are prepared using thermal evaporation described in chapter 2 (Section 2.14). Spectroscopically pure (99.9%)
Indium procured from Nuclear Fuel Complex, Hyderabad is used as the source material. Initially the vacuum chamber is evacuated 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 is rapidly reached by adjusting the needle valve of the plant. Glass slides have been used as substrates onto which a calibrated chromel-alumel thermocouple is attached. The substrates are cleaned using the procedure described in Chapter 2 (Section 2.15). Inside the bell jar the substrates are subjected to ionic bombardment for 5 minutes as final cleaning 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. 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 films.
3.3.2 Results and Discussion

Figure 3.1 shows the variation of \(\ln(R_{sh})\) with thickness of the indium oxide films deposited at substrate temperatures (Ts) 100, 125, 175 and 225\(^\circ\)C. For the film of Ts = 100\(^\circ\)C, a sheet resistance \(R_{sh}\) of 3169 \(\Omega/\square\) is obtained for a thickness 80nm. Sheet resistances for substrate temperatures 125\(^\circ\)C, 175\(^\circ\)C and 225\(^\circ\)C are 2468\(\Omega/\square\), 659 \(\Omega/\square\), and 782 \(\Omega/\square\) respectively, for films of thickness 80nm. Lowest sheet resistance for as-deposited films obtained for the substrate temperature 175\(^\circ\)C.

The variation of sheet resistance of the samples with substrate temperature is plotted in Figure 3.2. Films of thickness 80 nm are used for the study. A minimum sheet resistance of 659 \(\Omega/\square\) is obtained at a substrate temperature 175\(^\circ\)C. Above this substrate temperature the sheet resistance shows an increase. The highest sheet resistance 3169 \(\Omega/\square\) is obtained at the substrate temperature 100\(^\circ\)C. The dc electrical conductivity is calculated from resistance measurements and by knowing the area and thickness of the film. The temperature dependence of conductivity is given by Arrhenius relation given in equation (3.4), Chapter 3 (Section 3.2).

Figure 3.3 shows the temperature dependence of dc electrical conductivity of Indium oxide thin films of thickness 60, 80, 100, 120 nm deposited at 125\(^\circ\)C. The plot of \(\ln \sigma\) vs 1000/T exhibits a straight region of activation energy \(\Delta E\) in the temperature region 300-500 K. The values of activation energies are shown in Table 3.1.
Fig. 3.1  Plot of $\ln R_{sh}$ vs thickness for indium oxide films deposited at substrate temperatures 100, 125, 175 and 225 °C.
Fig. 3.2 Plot of sheet resistance vs substrate temperature for indium oxide thin films of thickness 80nm
Fig. 3.3 Plot of lnσ vs 1000/T for indium oxide thin films of various thickness.
It is seen that activation energy $\Delta E$ varies considerably with film thickness. The activation energy $\Delta E$ is found to decrease with increase in film thickness. Figure 3.4 shows the temperature dependence of dc electrical conductivity of indium oxide thin films deposited at a substrate temperature $175^\circ C$ and annealed at $250^\circ C$ for 30 minutes. The plot of $\ln \sigma$ vs $(1000/T)$ gives the activation energy $\Delta E$. The activation energies corresponding to each sample have been calculated and are shown in Table 3.2.

**Table 3.1 Variation of activation energy with thickness for indium oxide films**

<table>
<thead>
<tr>
<th>Thickness $d$ (nm)</th>
<th>Activation energy $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.029</td>
</tr>
<tr>
<td>80</td>
<td>0.027</td>
</tr>
<tr>
<td>100</td>
<td>0.024</td>
</tr>
<tr>
<td>120</td>
<td>0.017</td>
</tr>
</tbody>
</table>

**Table 3.2 Variation of activation energy with thickness for indium oxide films**

<table>
<thead>
<tr>
<th>Thickness $d$ (nm)</th>
<th>Activation Energy $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.037</td>
</tr>
<tr>
<td>100</td>
<td>0.035</td>
</tr>
<tr>
<td>150</td>
<td>0.034</td>
</tr>
<tr>
<td>180</td>
<td>0.028</td>
</tr>
</tbody>
</table>
Fig. 3.4 Plot of $\ln \sigma$ vs 1000/T for indium oxide thin films of thickness 60, 100, 150 and 180 nm
Fig. 3.5 gives the plot of $\ln \sigma$ vs $1000/T$ for indium oxide thin films deposited at oxygen partial pressures of $3 \times 10^{-4}$, $4 \times 10^{-4}$, $6 \times 10^{-4}$ and $8 \times 10^{-4}$ mbar. The activation energies corresponding to each sample have been calculated and are shown in Table 3.3.

### Table 3.3 Variation of activation energy with oxygen partial pressure for indium oxide thin films

<table>
<thead>
<tr>
<th>Oxygen partial Pressure ($\times 10^{-4}$ mbar)</th>
<th>Activation energy $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.039</td>
</tr>
<tr>
<td>4</td>
<td>0.040</td>
</tr>
<tr>
<td>6</td>
<td>0.037</td>
</tr>
<tr>
<td>8</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Variation of $\ln \sigma$ vs $1000/T$ for indium oxide thin film deposited at substrate temperatures 100, 125, 175 and 225°C are given in Fig 3.6. The activation energies corresponding to each sample is given in Table 3.4.

### Table 3.4 Variation of activation energy with substrate temperature.

<table>
<thead>
<tr>
<th>Substrate temperature $T_s$ (°C)</th>
<th>Activation energy $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.316</td>
</tr>
<tr>
<td>125</td>
<td>0.310</td>
</tr>
<tr>
<td>175</td>
<td>0.304</td>
</tr>
<tr>
<td>225</td>
<td>0.340</td>
</tr>
</tbody>
</table>
Fig. 3.5  Plot of $\ln \sigma$ vs $1000/T$ for indium oxide thin films deposited at $200^\circ\text{C}$ and at different oxygen partial pressures.
Fig. 3.6 Plot of $\ln \sigma$ vs $1000/T$ for indium oxide thin films deposited at various substrate temperatures.
For highly conducting transparent films, thickness is an important parameter. The as-deposited films of indium oxide show a decrease in sheet resistance with thickness. Mirzapour et al.\textsuperscript{9} and Jeong et al.\textsuperscript{10} have reported that for indium oxide thin films sheet resistance decreases with increase in thickness.

The low sheet resistance of the as-deposited film is due to the presence of indium and other sub oxides of indium. Many workers have reported\textsuperscript{11,12} the formation of indium oxide during reactive evaporation as InO and In\textsubscript{2}O\textsubscript{3}. 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\textsubscript{2}O\textsubscript{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.\textsuperscript{13} Since higher substrate temperature accelerates oxidation in vacuum, grain size in the film becomes larger as the substrate temperature is higher. In Fig 3.2, the decrease in resistivity up to 175\textdegree{}C of the substrate temperature means the existence of structural imperfection in the film, oxygen vacancies and excess of atoms acting as charged donor centers\textsuperscript{14}. There may be a high density of ionized impurity centres in the film caused by oxygen vacancies and excess indium atoms.
Sundaram and Bhagavat\textsuperscript{15} reported the activation energy of 0.007 eV for indium oxide. Arvin\textsuperscript{16} has reported activation energy of 0.87 eV. The value of activation energy obtained in the present study is 0.017 eV for a film of thickness 120 nm deposited at a substrate temperature of 125\textdegree{}C.

3.4 Tin Oxide

3.4.1 Experiment

Thin films of tin oxide are prepared by using the thermal evaporation technique described in chapter 2 (Section 2.14). Spectroscopically pure (99.9\% of purity) tin powder produced from Nuclear Fuel Complex, Hyderabad, is used as the source material. 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 attached to the substrates. The rate of evaporation is 7-8 nm/min. 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 are carried out in a muffle furnace at a temperature 300\textdegree{}C for 30 minutes. The electrical conductivity is measured using the Keithley Electrometer (Model No.617) and the conductivity cell, in vacuum.

3.4.2 Results and Discussion

The variation of sheet resistance with thickness for tin oxide films deposited at 225\textdegree{}C and 275\textdegree{}C are plotted in Figure 3.7. For the film
Fig 3.7 Plot of $\ln R_{sh}$ vs thickness for tin oxide thin films deposited at substrate temperatures 225 and 275°C
deposited at 225°C, the sheet resistance is greater than that of the films of substrate temperature 275°C. The films deposited at a temperature <200°C are found to be amorphous and are having very high resistivity. Figure 3.8 is the plot of $\ln(R_{sh})$ vs substrate temperature for tin oxide films having thickness 100 nm. At a substrate temperature 225°C, the sheet resistance is 28.3K ohm/□ and resistivity $\rho = 0.28 \times 10^{-2} \Omega$m. Figure 3.9 shows the temperature dependence of the electrical conductivity of tin oxide thin films deposited at temperature 50, 125, 225 and 275°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 deposited at different substrate temperatures is shown in Table 3.5.

**Table 3.5 Variation of activation energy with substrate temperature**

<table>
<thead>
<tr>
<th>Substrate temperature $T_s$ (°C)</th>
<th>Activation energy $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.569</td>
</tr>
<tr>
<td>125</td>
<td>0.375</td>
</tr>
<tr>
<td>225</td>
<td>0.299</td>
</tr>
<tr>
<td>275</td>
<td>0.268</td>
</tr>
</tbody>
</table>

Temperature dependence of dc electrical conductivity of thin films of tin oxide evaporated at a substrate temperature 225°C and having different thickness is shown in Figure 3.10. The plot of $\ln \sigma$ vs 1000/T gives a straight line. The activation energies calculated from the straight-line region are listed in Table 3.6.
Fig. 3.8 Plot of $\ln R_{sh}$ vs substrate temperature for tin oxide thin films.
Figure 3.9 Plot of $\ln \sigma$ vs $1000/T$ for tin oxide thin films deposited at various substrate temperatures.
Figure 3.10 Plot of $\ln \sigma$ vs $1000/T$ for tin oxide thin films of various thickness deposited at 225°C
Table 3.6 Variation of activation energy with thickness for tin oxide films deposited at 225°C

<table>
<thead>
<tr>
<th>Thickness d (nm)</th>
<th>Activation energy ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.292</td>
</tr>
<tr>
<td>100</td>
<td>0.276</td>
</tr>
<tr>
<td>120</td>
<td>0.242</td>
</tr>
<tr>
<td>140</td>
<td>0.203</td>
</tr>
</tbody>
</table>

The dc electrical conductivity of thin films of tin oxide evaporated at a substrate temperature 225°C and annealed at 300°C for one hour is shown in Figure 3.11. The activation energy is given in Table 3.7.

Table 3.7. Variation of activation energy with thickness for tin oxide thin films deposited at a substrate temperature 225°C and annealed at 300°C for one hour

<table>
<thead>
<tr>
<th>Thickness d (nm)</th>
<th>Activation energy ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.052</td>
</tr>
<tr>
<td>80</td>
<td>0.037</td>
</tr>
<tr>
<td>100</td>
<td>0.035</td>
</tr>
<tr>
<td>120</td>
<td>0.028</td>
</tr>
<tr>
<td>150</td>
<td>0.021</td>
</tr>
</tbody>
</table>

The variation of sheet resistance ($R_{sh}$) of the tin oxide samples deposited at various oxygen partial pressures is plotted in Figure 3.12. A
Figure 3.11 Plot of $\ln \sigma$ vs $1000/T$ for tin oxide thin films of various thickness, deposited at $225^\circ$C and annealed at $300^\circ$C for one hour.
Fig 3.12  Variation of $R_{sh}$ with oxygen partial pressure for tin oxide thin films
A drastic change in sheet resistance is obtained, as the partial pressure was increased to $2 \times 10^{-4}$ mbar. The corresponding sheet resistance obtained is $485 \, \text{ohm/} \square$. The sheet resistance is not much affected with the increase of oxygen partial pressure up to $6 \times 10^{-4}$ mbar. A further increase in oxygen partial pressure causes an increase in sheet resistance. So, an oxygen partial pressure of $2 \times 10^{-4}$ to $6 \times 10^{-4}$ mbar is found to be the optimised partial pressure of oxygen for a low sheet resistance.

The as deposited tin oxide thin films are annealed in a muffle furnace for different intervals of time and the corresponding sheet resistances are recorded.

Figure 3.13 represents the variation of sheet resistance of tin oxide thin films deposited at various partial pressures of oxygen. All samples show an increase in sheet resistance with annealing. It was observed that the variation of sheet resistance with annealing time is more for samples deposited at an oxygen partial pressure of $10^{-4}$ and $8 \times 10^{-4}$ mbar. Samples deposited within the oxygen partial pressure range of $2-6 \times 10^{-4}$ mbar showed less variation in $R_{\text{sh}}$ with respect to other samples.

Changes in sheet resistance with the annealing time for films deposited at various substrate temperatures is shown in Figure 3.14. Tin oxide samples deposited at substrate temperature varying from $50^\circ \text{C}$-$275^\circ \text{C}$ is annealed for 150 minutes and the sheet resistance at different intervals of time is recorded. The samples deposited at substrate...
Fig. 3.13 Plot of $R_{sh}$ vs annealing time for tin oxide thin films deposited at various oxygen partial pressures.
Fig 3.14 Variation of sheet resistance with annealing time for tin oxide thin films
temperature 50°C shows a variation of 16.8KΩ to 46.25KΩ in 20 minutes time. It shows a decrease in $R_{sh}$ on further annealing. It also shows an irregular behaviour on annealing.

Similar behaviour is also observed for the samples deposited at substrate temperature of 275°C. Samples deposited at substrate temperatures 125°C and 225°C shows an increase in $R_{sh}$, as the annealing time is increased. The samples deposited in this range of the substrate temperature show steady increase in $R_{sh}$ without abrupt changes during annealing.

The activation energy for the film of thickness 120nm deposited at substrate temperature 225°C is determined as 0.242eV. The activation energy of tin oxide film is due to the formation of donor levels below the conduction band. Das and Banerjee\textsuperscript{17} have obtained activation energy 0.26 eV for tin oxide thin films. Sanjines et al.\textsuperscript{18} reports an activation energy of 0.2 eV. Sanjines and Levy\textsuperscript{19} obtained an activation energy for 0.73 eV. Kohnke\textsuperscript{20} obtained activation energy for stannic oxide crystals as 0.72 eV whereas Miloslavskii\textsuperscript{21} calculated activation energy of 0.12 eV in the same temperature region. Nishino and Hamakawa\textsuperscript{22} reports an activation energy of 0.023eV for tin oxide thin films. In the present study the activation energy obtained for films deposited at 225°C and having thickness 80 and 140 nm are 0.292 and 0.203 eV respectively.
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 are described in Chapter 2 (Section 2.13). Spectroscopically pure indium oxide (99.9% pure) and tin oxide (99.9% pure) procured from Nuclear Fuel complex, Hyderabad is used as the source material. The indium powder and tin powder are taken in weight percentage proportion 95:5 and mixed well using a pestle and mortar. The mixture is taken in a quartz tube, evacuated and sealed. It is sintered in a furnace for 24 hours at 500 K. (Melting point of Tin is 505.1K and that of Indium is 429.8K at one atmosphere pressure.) It is cooled very slowly to room temperature. The quartz tube is broken and the alloy formed is taken out. Alloys of different tin concentrations (90:10, 85:15, 80:20) are made as described above.

It is evaporated from the tantalum boat in an oxygen atmosphere. Glass slides have been used as substrates. The substrates are cleaned using the process described in Chapter 2 (Section 2.15). The substrate temperature is varied using the substrate heater and the temperature is measured using a chromel-alumel thermocouple attached to the substrates. The rate of evaporation is controlled within the range 13-15 nm/min. 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 2.19). The deposited films are subjected
to a post-deposition annealing in air for 30 minutes at a temperature
300°C in 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 samples.

3.5.2 Results and Discussion

Figure 3.15 is the plot of sheet resistance vs percentage of tin. The
thickness of the films is 50 nm. It is found that the resistivity is lowest
when the sample is of 95% (indium): 5% (tin) by weight proportion. Here
the resistivity obtained is $9.07 \times 10^{-6}$ Ωm. When the weight proportion of tin
increases or decreases, the sheet resistance increases.

Figure 3.16 is the plot of $\ln \sigma$ vs $1000/T$ for the indium tin oxide thin
film deposited at 200°C with tin concentrations of 0%, 10% and 15%. The
thickness is 100 nm each. The graphs show a straight-line region
indicating the presence of an activation energy $\Delta E$. The activation energy
of the samples is calculated from the slope of the straight lines. The
Fig. 3.15  Plot of $R_{\text{sh}}$ with doping percentage of tin for indium tin oxide thin films
Fig. 3.16  Plot of ln$\sigma$ vs 1000/T for ITO thin films of various tin concentrations
activation energies $\Delta E$ for films of different tin concentration are given in Table 3.8.

**Table 3.8 Variation of activation energy with tin concentration for ITO thin films deposited at 200°C**

<table>
<thead>
<tr>
<th>Tin %</th>
<th>Activation energy $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.032</td>
</tr>
<tr>
<td>10</td>
<td>0.020</td>
</tr>
<tr>
<td>15</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Plot of $\ln \sigma$ vs $1000/T$ for the samples deposited at 200°C is given in Figure 3.17. The thickness of the samples are 80, 100, 120 and 140 nm. The graph shows a straight-line region. The activation energies of ITO films deposited at 200°C are shown in Table 3.9. The conductivity of the samples increases with thickness.

**Table 3.9 Variation of activation energy with thickness for ITO films deposited at 200°C**

<table>
<thead>
<tr>
<th>Thickness $d$ (nm)</th>
<th>Activation energy $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.053</td>
</tr>
<tr>
<td>100</td>
<td>0.060</td>
</tr>
<tr>
<td>120</td>
<td>0.075</td>
</tr>
<tr>
<td>140</td>
<td>0.084</td>
</tr>
</tbody>
</table>
Fig. 3.17  Plot of $\ln \sigma$ vs $1000/T$ for ITO thin films with 15% tin concentration.
At this substrate temperature ($200^\circ$C) the conductivity of the films shows a negative slope, indicating semi conducting nature of the samples.

ITO thin films (In: Sn = 95:5, by weight) are deposited at different substrate temperatures. In Figure 3.18 sheet resistance of the sample is plotted as a function of temperature. In the temperature region $150^\circ$C - $200^\circ$C a sudden drop in sheet resistance is obtained.

In the entire cases sheet resistance shows thickness dependence. The carriers liberated from substitutional tin ($Sn^{4+}$) increases carrier density. Increase in thickness improves film crystallinity that results in decrease in donor sites trapped at the dislocation or point defect aggregates. Shigesato and Paine 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.

Variation of sheet resistance on annealing is studied and is given in Fig 3.19. The increase in resistivity on annealing is caused by the decrease in oxygen vacancies due to oxidation. In the case of indium oxide 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
Fig. 3.18  
Plot of $R_{sh}$ with substrate temperature for ITO thin films of 5% tin concentration
Fig. 3.19 Variation of $R_{sh}$ with annealing for ITO thin films
stoichiometric with the disappearance of these carriers with increase in resistivity.

The crystalline nature may reduce the grain boundary scattering mechanism. The carrier density. \[ N = N_0 \exp \left( \frac{-q\phi}{kT} \right) \]

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 temperatures 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 \( \text{Sn}^{4+} \) gives raise 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 proposed a model to explain the physical properties of ITO as shown in Figure 3.20. According to this model the conduction band is mainly from \( \text{In}^{3+} \) 5s electrons and the valence band from \( \text{O}^{2-} \) 2p electrons. The doubly charged oxygen vacancies and the singly charged tin are represented as donor levels with low ionization energies. At high density of the dopants,
Fig. 3.20 Schematic energy band model for ITO
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 may be estimated from the Mott's criterion.\(^{26}\)

The schematic density of states diagram is shown in Figure 3.21. 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 \( k_B T \). Due to the tailing of the Fermi-Dirac distribution function

\[
f_{FD}(E) = \frac{1}{e^{[(E-E_F)/k_B T]} + 1}
\]

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 \( 10^{20} / \text{cm}^3 \) such as those normally present in ITO films, the Fermi level is high up in the conduction band. The function \(-df/dE\) in Figure 3.21 is sharp and the semiconductor is said to be highly
Fig. 3.21 Schematic density of states diagram for a semiconductor doped to various extents.
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. Thus the electrical conductivity mechanism of metals is reasonably valid for indium tin oxide.

Investigations on doped indium films for conductivity by Hoffman et al.\textsuperscript{5} obtained activation energies of conduction in between 0.035 eV and 0.045 eV. The value of activation energy obtained in the present study is 0.053 eV for a film of thickness 80 nm, deposited at 200\degree C.

The films obtained for the three materials –indium oxide, tin oxide and indium tin oxide –are found to be highly conducting.

References


