Chapter III

Studies on SnO₂ Thin Films

III.1. Introduction

Thin film technology is of great interest for a variety of applications. The simultaneous occurrence of high optical transparency and electrical conductivity in thin solid films has been the subject of investigation since last century [1-6]. Owing to its low resistivity and high transmittance, SnO₂ thin films are used as window layers and heat reflectors in solar cells [7,8], various gas sensors [9], LCDs etc. Now the SnO₂ transparent semi-conducting films have become an integral part of modern electronic technology.

Doped or undoped SnO₂ films can be prepared by many methods such as Spray Pyrolysis, Electron Beam Evaporation, Chemical Vapour Deposition, Magnetron Sputtering and Pechini method [10]. The SnO₂ films are n-type semiconductors with a direct optical band gap of about 3.87 – 4.3 eV [11,12]. The structure of the material in its bulk form is tetragonal rutile with lattice parameters of a = b = 4.737Å and c = 3.816 Å [13]. However in thin film form, depending on the deposition technique its structure can be polycrystalline or amorphous [14]. The grain size is typically 200-400 Å, which is highly depended on deposition technique, temperature, doping level etc [11,12]. The SnO₂ films close to stochiometric condition have low free carrier concentration and high resistivity, but non-stochiometric SnO₂ films have high carrier concentration, high conductivity and high transparency. In other words, there is an oxygen vacancy in the structure so that the formula
for the thin film of the material is SnO$_{2-x}$, where $x$ is the deviation from stoichiometry [11].

SnO$_2$ thin films with electrical resistivity of $2.7 \times 10^{-4}$ $\Omega$m at a deposition temperature of 500°C [15] and SnO$_2$: Sb thin films with electrical resistivity of $7.74 \times 10^{-6}$ $\Omega$m at 350°C [10] have been prepared by spray pyrolysis technique. SnO$_2$ thin films of electrical resistivity of $4.8 \times 10^{-4}$ $\Omega$m with an average optical transmission of 85% have been prepared in presence of oxygen by thermal evaporation method [16]. Spray deposited SnO$_2$: Sb thin films with electrical resistivity of $1.69 \times 10^{-4}$ $\Omega$m have been prepared at 370°C [10]. Conventional n-type Transparent Conducting Oxide (TCO) thin films are In$_2$O$_3$: Sn (ITO), SnO$_2$:F (FTO) and ZnO: Al (AZO) [17]. CuAlO$_2$ and SrCu$_2$O$_2$ thin films are found to be true p-type TCOs. [18-20]. Transparent p-n junctions can be fabricated by use of n-type and p-type TCOs [21, 22]. P-type conducting transparent thin films of SnO$_2$: Al [14] with resistivity in the range of $2.7 \times 10^{-4}$ $\Omega$m to $90 \times 10^{-4}$ $\Omega$m and band gap in the range of 4.105-3.604 eV and SnO$_2$: Li [23] with resistivity in the range of $2.7 \times 10^{-4}$ $\Omega$m to $1890 \times 10^{-4}$ $\Omega$m and band gap in the range of 4.11 – 3.61 eV have been prepared recently by spray pyrolysis technique.

This chapter illustrates the role of deposition parameters on SnO$_2$ thin film formation and doping effect of rare earths (Nd, Dy and La) and metals (Fe, Cu and Mn) on the structural, photo-electronic, optical and electrical properties of SnO$_2$ films, prepared by a Cost Effective Vapour Deposition Technique (CEVDT). We have chosen this technique because of the ease of selectivity of resistivity and transmittance by controlling deposition parameters. The deposition parameters play an important role in the film formation. The deposition parameters like substrate temperature, time of
vapour deposition, flow rate, amount of reactant and the substrate to spray source distance are optimized for good conducting transparent SnO2 films. Doped SnO2 films are prepared by changing the concentration of rare earths Nd (NO3) 3.6H2O / DyCl3.6H2O / La (NO3) 3.6H2O and metals Cu (NO3) 2.3H2O / Fe (NO3)3.9H2O / MnCl2.4H2O from 1wt % to 4wt % in SnCl2.2H2O. Moreover, the SnO2 films produced possess large area and uniform coverage of the substrate. Like most other techniques, this demonstrates an apparent trade-off between the conductivity and transmittance of the films.

III.2. Results and Discussion

III.2.1 Structural Studies

Structure of the doped and undoped SnO2 films are studied by taking XRD using Cu Kα (λ=0.154056nm) radiation and are compared with JCPDS data card. The XRD pattern of SnO2 films prepared at various temperatures

Fig. 3.1. XRD pattern for SnO2 thin films at different temperatures.
is shown in Fig. 3.1. The film coated at 575 °C is found to be better (see also section III.2.3 and III.2.4) and shows a polycrystalline nature oriented along the (101), (211) and (301) planes at $2\theta = 34.281^\circ$, $52.156^\circ$ and $66.285^\circ$ respectively with single phase SnO$_2$. The peak intensity position and (hkl) values are found in good agreement with that reported by K.S. Shamala et.al; [10] and M.M.B. Mohaghery et.al; [14]. The presence of other orientations such as (110), (200), (220), (310) is also detected with lower intensities. The hkl values of SnO$_2$ films are given in Table 3.1. Fig. 3.2 gives the surface morphology photograph of SnO$_2$ thin film taken with Olympus Trinocular Microscope CX – 31, Japan.

The XRD pattern of SnO$_2$ films doped at different concentrations of rare earths is given in Figs. (3.3 - 3.5). On rare earth (Nd, Dy and La) doping no peaks corresponding to them or their compounds are detected but the intensity of SnO$_2$ peaks are decreased. On increasing the concentration of the dopants, the intensity of the peaks is further decreased.
The decrease in peak intensities is basically due to the replacement of Sn$^{4+}$ with Dy and Sn$^{4+}$ with Nd and O$^{2-}$ ions with La ions in the lattice, which is reported in [23] similar to the reported works of M.M.B. Mohagheri et.al; [14,24]. This process leads to the movement of Sn$^{4+}$ or O$^{2-}$ ions to the interstitial sites and also increases the amorphous phase.
Fig. 3.4. XRD pattern for Dy doped SnO$_2$ thin films for different concentrations of Dy.

The XRD pattern of SnO$_2$ films doped at different concentrations of Cu, Fe, and Mn are given in Figs. (3.6 - 3.8) respectively. Similarly on doping Cu, Fe, and Mn, no peaks corresponding to them or their compounds were detected. The intensity of the peak corresponding to the planes (310) and (200) is increased on Cu doping and (301) plane on Fe doping which shows better atomic arrangement and lower scattering in these planes. On Mn doping the intensity of all peaks were decreased. On increasing the concentration of Cu, Fe, and Mn, the intensity of SnO$_2$ peaks are further decreased due to the decrease in the atomic density in these planes. Here also the decrease in peak intensities is basically due to the replacement of Sn$^{4+}$ ions with Cu, Fe, and Mn ions in the lattice of SnO$_2$ film similar to the works of M.M.B. Mohagheri et.al; [14,24] and reported in [25].
Fig. 3.5. XRD pattern for La doped $\text{SnO}_2$ thin films for different concentrations of La.

Fig. 3.6. XRD pattern for Fe doped $\text{SnO}_2$ films for different concentrations of Cu.
Fig. 3.7. XRD pattern for Fe doped SnO$_2$ films for different concentrations of Fe.

Fig. 3.8. XRD pattern for Mn doped SnO$_2$ films for different concentrations of Mn.
The average grain size is calculated by using Scherrer formula [26]. The average crystalline size is found to be ~ 100 Å. The effect of substrate temperature on grain size of the obtained phase was also investigated using XRD pattern. It is observed that the grain size increases with increase in substrate temperature as in [27], which is shown in (Fig.3.9). The increase in substrate temperature may cause decrease of the density of nucleation centers and, under these circumstances, a smaller number of centers start to grow, which results in large grains as reported in [23].

![Graph showing variation of grain size with substrate temperature.](image)

**III.2.2 Photoconductivity and Photovoltaic Studies**

The phenomenon of increase in conductivity due to absorption of light is known as photoconductivity (PC). Photovoltaic (PV) effect is the conversion of optical energy into electrical energy. As the PC/PV system is exposed to excitation source, photocurrent / photovoltage increases and reaches saturated value. (Saturated value of photocurrent/photovoltage of
the film is measured for each case separately). Fig.3.10 and Fig.3.11 shows the variation of saturated value of photocurrents and photovoltages of SnO₂ films with different concentration of the rare earths Nd, Dy and La. (Saturated value of photocurrent and photovoltage of SnO₂ films is measured for each case separately). It is observed that when Nd is doped on the SnO₂ films, the maximum photocurrent occurs at 2 wt % doping and maximum photovoltage occurs at 1 wt% doping. From the Table.3.3 (see electrical properties in section III.2.4) it can be seen that maximum carrier concentration occurs at 1wt% and then decreases with increasing Nd concentration. Maximum PV at 1wt% of Nd may be due to charge separation, which is more in number compared to its other concentrations. In the case of PC, the largest carrier concentration at 1wt% of Nd causes

![Graph showing variation of saturated photocurrents of SnO₂ films with Concentration of dopants.](image-url)

Fig.3.10. Variation of saturated photocurrents of SnO₂ films with Concentration of dopants.
Fig. 3.11. Variation of saturated photovoltages of SnO$_2$ films with concentration of dopants.

Fig. 3.12. Variation of saturated photocurrents of SnO$_2$ films with concentration of the dopants.
more carrier collision probability during charge transport which in turn reduces the photoconductivity. At 2wt% of Nd in the sample, the charge concentration seems to be optimum for better PC. But higher percentage of Nd doping reduces charge concentration and hence PC and PV. Similar explanation can be given for Dy and La doped films which are reported in [23]. Dy doped thin films show maximum photocurrent and photovoltage at 2 wt% concentration. Table 3.4 shows that maximum carrier concentration of Dy doped film occurs at 2wt%. La doped films also show a maximum at 2wt% concentration though the photovoltage is less than that of the undoped. Table 3.5 shows that maximum carrier concentration of La doped film occurs at 2wt%.

Fig.3.12 and Fig.3.13 depict the variation of saturated value of photocurrents and photovoltages of SnO$_2$ films with different...
concentration of the metals Cu, Fe, and Mn respectively. Table 3.6 shows that maximum charge concentration of Cu doped film occur at 2 wt% doping. The largest carrier concentration at 2 wt% causes more carrier collision probability during charge transport which in turn reduces the photoconductivity. Cu doped film shows maximum PC at 3 wt% similar to the case of Nd doped films. PV is decreased on Cu doping but it shows a maximum at 2 wt%. Fe doped SnO₂ films show maximum photocurrent and photovoltage at 3wt% but PV is found to be decreased on Fe doping. It can be seen from the Table 3.7 that maximum carrier concentration for Fe doped film occurs at 3wt%. Mn doped SnO₂ films shows maximum photocurrent and photovoltage at 2 wt%. But PC is decreased on Mn doping. As shown in Table 3.8 the maximum carrier concentration of Mn doped films occur at 2wt% and it decreases with increasing dopant concentration. But higher percentage of doping reduces charge concentration and hence PC and PV. Decrease of PC or PV on doping is attributed to increase in amorphous phase in the film on doping as reported in [25].

**III.2.3 Optical Studies**

The UV-VIS-NIR transmittance spectra of the SnO₂ films prepared at various temperatures is shown in Fig.3.14. Transparency is increased as substrate temperature is increased as in [27] from 400 °C and reaches maximum at 525 °C then starts decreasing as temperature is increased. A compromise between the conductivity (see electrical studies section III.2.4) and transparency of the prepared film is found at substrate temperature 575 °C. The resistance at 575 °C is found to be minimum with moderately good transparency. Hence doped SnO₂ thin films are prepared at 575 °C.
Fig. 3.14. Optical Transmittance (T%) versus wavelength (λ) of SnO$_2$ thin films prepared at different temperature. The transmittance spectra of the SnO$_2$ thin films prepared at different concentrations of the dopants Nd, Dy and La are shown in Fig. 3.15, Fig. 3.16 and Fig. 3.17 respectively and similar observation is found by M.M.B. Mohagheri et.al; [14, 24]. Films prepared at 575°C with 1 wt%...
and 2 wt % of Nd exhibit a transmission of above 75% in the visible region. Films prepared at 575°C and doped with 1, 2 and 3 wt% of Dy also exhibit a transmission of above 75% in the visible region and the transparency is found to be greater than that of undoped film. But films prepared by doping La are less transparent than undoped films. The transmittance of the films is also influenced by a number of minor effects, which include surface roughness and optical inhomogeneity in the direction normal to the film surface [23].

The transmittance spectra of the SnO$_2$ films prepared at different concentrations of Cu, Fe, and Mn doping are shown in Fig. 3.18, Fig. 3.19 and Fig. 3.20 respectively and similar observation is found in the works of M.M.B. Mohagheri et.al; [14, 24]. Films prepared at 575°C with 1 wt% and 2 wt % of Cu, 1wt%, 2wt% and 3wt%Fe and all the Mn doped films exhibit a transmission of greater than 75% in the visible region and is found to be greater than that of undoped film.

Fig.3.16. Optical Transmittance (T%) versus wavelength ($\lambda$) of SnO$_2$ thin films doped at different concentrations of Dy.
From the transmittance/absorption spectra optical parameters like absorption coefficient ($\alpha$), optical band gap ($E_g$) refractive index ($\mu$) and thickness ($t$) are evaluated. The absorption coefficient ($\alpha$) is evaluated from

![Graph showing optical transmittance T% versus wavelength (\(\lambda\)) for SnO\textsubscript{2} thin films doped at different concentrations of La.](image)

**Fig.3.17.** Optical Transmittance (T\%) versus wavelength (\(\lambda\)) of SnO\textsubscript{2} thin films doped at different concentrations of La.

![Graph showing optical transmittance T% versus wavelength (\(\lambda\)) for SnO\textsubscript{2} films doped at different concentrations of Cu.](image)

**Fig.3.18.** Optical Transmittance (T\%) versus wavelength (\(\lambda\)) of SnO\textsubscript{2} films doped at different concentrations of Cu.
Fig. 3.19. Optical Transmittance (T%) versus wavelength (λ) of SnO₂ films doped at different concentrations of Fe.

Fig. 3.20. Optical Transmittance (T%) versus wavelength (λ) of SnO₂ films doped at different concentrations of Mn.
Fig. 3.21. \((\alpha h\nu)^2\) versus \(h\nu\) graph of \(\text{SnO}_2\) thin films prepared at different temperature.

[28,29] the equation 2.12 in chapter II. The absorption coefficient of the film is found to be of the order of \(10^5 /\text{m}\). The direct optical band gap \((E_g)\) is determined by [30] fitting the absorption data to the equation 2.13. \(E_g\) is found by extrapolating the linear portion in the \(\alpha^2\) versus \(h\nu\) graph at \(\alpha = 0\). It is observed that \(E_g\) increases on increasing the substrate temperature from 3.96 eV to 4.09 eV (Fig. 3.21) as similar to the observations found by P.S.Raghupathy et.al; [27].

The refractive index and thickness of the film are determined by Swanepoel technique [31] (see section II.7.2). The refractive index of the film is found to be \(\sim 1.8\). The value of refractive index seems to be in
good agreement with earlier results [10]. The thickness of the SnO$_2$ films is obtained as 1.5µm (at 575°C) and is confirmed by measuring the thickness using Dektak – 6M Stylus Profiler. $E_g$ of undoped film is found to be 4.08 eV. The variation in $E_g$ on changing the concentration of Nd, Dy and La are given in Figs. (3.22 - 3.24) and that of Cu, Fe, and Mn are depicted in Figs. (3.25 - 3.27). It is found that $E_g$ decreases initially on doping, then increases on increasing the concentration of dopants.

Fig.3.22. $(a\ h\nu)^2$ versus $h\nu$ graph of SnO$_2$ thin films doped at different concentrations of Nd.
Fig. 3.23. \((\alpha h \nu)^2\) versus \(h \nu\) graph of SnO\(_2\) films doped at different concentrations of Dy.

Fig. 3.24. \((\alpha h \nu)^2\) versus \(h \nu\) graph of SnO\(_2\) films doped at different concentrations of La.
Fig. 3.25. \((\alpha h\nu)^2\) versus \(h\nu\) graph of SnO\(_2\) films doped at different concentrations of Cu.

Fig. 3.26. \((\alpha h\nu)^2\) versus \(h\nu\) graph of SnO\(_2\) films doped at different concentrations of Fe.
Fig. 3.27. \((\alpha \cdot h \nu)^2\) versus \(h \nu\) graph of SnO\(_2\) films doped at different concentrations of Mn.

Fig. 3.28. Variation of thickness of SnO\(_2\) thin films with temperature.
Fig. 3.28 shows the variation of thickness on increasing substrate temperature as in [10]. The film thickness decreases on increasing the substrate temperature. The decrease in the film thickness is attributed to a decrease in the deposition rate of initial constituent with increasing substrate temperature as reported in [23].

III.2.4 Electrical Studies

Electrical parameters of the SnO$_2$ films are measured by Four Probe, Van der Pauw and Hall Probe methods. The variations of resistance of SnO$_2$ films with respect to the deposition parameters are given in Figs. (3.29 - 3.33). These figures reveal the optimum deposition parameters for highly conducting transparent films. Resistance of the film is decreased on increasing the substrate temperature from 400°C and obtained a minimum value at 575 °C and then started increasing on increasing the substrate temperature. The change in conductivity is due to both changes in carrier concentration as well as the mobility [32] (see
Table 3.2). The other deposition parameters like time of vapour deposition (3 mins.), flow rate (2 arb. units), amount of SnCl₂·2H₂O (5 gms.) and the substrate to spray source distance (2 mm) are optimized for good conducting thin films. Hence doped SnO₂ thin films are prepared at these optimized deposition parameters.

![Fig.3.30. Variation of resistance with deposition time.](image)

![Fig.3.31. Variation of resistance with flow rate.](image)
Fig. 3.32. Variation of resistance with mass of SnCl₂.

Fig. 3.33. Variation of resistance with height of the spray source.
Resistivity (\(\rho\)) is calculated from Four Probe and Van der Pauw methods (see section II.5.1 and II.5.2). Sheet resistance (Rs) is calculated by using the equation 2.5. The charge carrier concentration (n (p)) and Hall mobility (\(\mu_H\)) is determined from the equations 2.9 and 2.10. The effect of background (drift) voltage in the absence of magnetic field was taken into account and compensated. The sign of the Hall voltage determines the type of the carriers ((+) for p-type and (-) for n-type). Sn forms an interstitial bond with oxygen and exists either as SnO or SnO\(_2\) – accordingly it has a valency of +2 or +4 respectively. This valency state has a direct bearing on the ultimate conductivity of Tin Oxide. The lower valence state results in a net reduction in carrier concentration since a hole is created which acts as a trap and reduces conductivity. On the other hand, predominance of SnO\(_2\) state means \(\text{Sn}^{4+}\) acts as an n-type donor-releasing electron to the conduction band. The large value of n indicates that Sn forms bond with oxygen and exists as SnO\(_2\). As Hall voltage \(V_H\) is negative, SnO\(_2\) film behaves as n-type semi-conductor. Table 3.2 gives the results of Four Probe, Van der Pauw and Hall Probe measurements for undoped films prepared at different temperatures. The values of \(\rho\) calculated from Four Probe and Van der Pauw methods are found in good agreement with each other. Fig.3.34 shows the variation of \(\rho\) with substrate temperature. It is found that conductivity is greater for unoped SnO\(_2\) films prepared at 575\(^\circ\)C. Resistivity is decreased as substrate temperature is increased as reported by K.S. Shamala et.al; [10] and M.K. Jayaraj et.al; [32]. The decrease in \(\rho\) with substrate temperature is attributed to the growth of grain size and the improvement in film stoichiometry as reported in [23].
Table 3.2. Electrical parameters of SnO$_2$ thin films with substrate temperature.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Rs (Ω)</th>
<th>$\rho$ four probe (10$^{-4}$ Ωm)</th>
<th>$\rho$ van der pauw (10$^{-4}$ Ωm)</th>
<th>B (T)</th>
<th>I (mA)</th>
<th>$V_H$ (mV)</th>
<th>$\mu_H$ (m$^2$/V/s)</th>
<th>n (p) (N/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>161K</td>
<td>112</td>
<td>112</td>
<td>0.2</td>
<td>1</td>
<td>-56.1</td>
<td>0.0174</td>
<td>3.89 x 10$^{22}$</td>
</tr>
<tr>
<td>450</td>
<td>4.8K</td>
<td>28.6</td>
<td>91.9</td>
<td>0.2</td>
<td>1</td>
<td>-31.4</td>
<td>0.0327</td>
<td>6.57 x 10$^{22}$</td>
</tr>
<tr>
<td>500</td>
<td>920</td>
<td>7.96</td>
<td>8.02</td>
<td>0.2</td>
<td>1</td>
<td>-12.2</td>
<td>0.0663</td>
<td>1.17 x 10$^{23}$</td>
</tr>
<tr>
<td>525</td>
<td>166.56</td>
<td>1.865</td>
<td>1.935</td>
<td>0.2</td>
<td>1</td>
<td>-2.8</td>
<td>0.081</td>
<td>3.98 x 10$^{23}$</td>
</tr>
<tr>
<td>550</td>
<td>78.29</td>
<td>1.21</td>
<td>1.093</td>
<td>0.2</td>
<td>1</td>
<td>-1.3</td>
<td>0.083</td>
<td>6.88 x 10$^{23}$</td>
</tr>
<tr>
<td>575</td>
<td>71.27</td>
<td>1.16</td>
<td>1.073</td>
<td>0.2</td>
<td>1</td>
<td>-1.2</td>
<td>0.0842</td>
<td>6.91 x 10$^{23}$</td>
</tr>
<tr>
<td>600</td>
<td>585.4</td>
<td>12.6</td>
<td>10.25</td>
<td>0.2</td>
<td>1</td>
<td>-5</td>
<td>0.0427</td>
<td>1.42 x 10$^{23}$</td>
</tr>
</tbody>
</table>

Fig. 3.34. Variation of resistivity of SnO$_2$ thin films with temperature.
Fig. 3.35. Variation of carrier concentration of SnO$_2$ thin films with temperature.

Fig. 3.36. Sheet resistances of SnO$_2$ films with substrate temperature.
Fig. 3.37. Mobility Variation of SnO\textsubscript{2} films with substrate temperature.

Fig. 3.35 shows the variation of n (p) with respect to the deposition temperature of SnO\textsubscript{2} thin films. Carrier concentration is increased as substrate temperature is increased as reported in [10]. Fig. 3.36 gives the variation of Rs with growth temperature of SnO\textsubscript{2} films. Sheet resistance is decreased as substrate temperature is increased as in [10,14,24]. The decrease in Rs with substrate temperature is due to the increase in the crystalline nature as temperature increases which is reported in [25]. Fig. 3.37 gives the variation of $\mu_H$ with substrate temperature. Hall mobility is increased as substrate temperature is increased as in [10]. It is seen that the $\mu_H$ increases with substrate temperature and attains a maximum value at 575 °C. It is because of the
increase in crystalline nature and decrease in Rs and $\rho$ as temperature is increased [25].

Tables. (3.3 - 3.5) gives the results of Four Probe, Van der Pauw and Hall Probe measurements for Nd, Dy and La doped films. On doping (1 wt% of Nd) carrier concentration increases from $6.91 \times 10^{23}$ N/m$^3$ to $3.33 \times 10^{25}$ N/m$^3$ with a reduction in Rs from 71.27 Ω/□ to 37.05 (Ω/□) and $\rho$ from 1.073 x10^{-4} Ωm to 0.556 x10^{-4} Ωm. As seen in the tables, Rs and $\rho$ of the films doped with Dy and La is found to be greater than that of

Table 3.3. Electrical parameters of Nd doped SnO$_2$ thin films.

<table>
<thead>
<tr>
<th>Concentration of Nd (wt%)</th>
<th>Rs (Ω)</th>
<th>$\rho_{\text{four probe}}$ (10$^{-4}$ Ωm)</th>
<th>$\rho_{\text{van der pauw}}$ (10$^{-4}$ Ωm)</th>
<th>B (T)</th>
<th>I (mA)</th>
<th>$V_H$ (mV)</th>
<th>$\mu_H$ (m$^2$/V/s)</th>
<th>$n$ (p) (N/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.27</td>
<td>1.16</td>
<td>1.073</td>
<td>0.2</td>
<td>1</td>
<td>-1.2</td>
<td>0.0842</td>
<td>6.91 x 10$^{23}$</td>
</tr>
<tr>
<td>1</td>
<td>37.05</td>
<td>0.62</td>
<td>0.556</td>
<td>0.2</td>
<td>4</td>
<td>+0.1</td>
<td>0.00337</td>
<td>3.33 x 10$^{25}$</td>
</tr>
<tr>
<td>2</td>
<td>49.85</td>
<td>0.81</td>
<td>0.748</td>
<td>0.2</td>
<td>3</td>
<td>+0.1</td>
<td>0.00334</td>
<td>2.49 x 10$^{25}$</td>
</tr>
<tr>
<td>3</td>
<td>62.54</td>
<td>1.1</td>
<td>0.938</td>
<td>0.2</td>
<td>2</td>
<td>+0.1</td>
<td>0.0039</td>
<td>1.66 x 10$^{25}$</td>
</tr>
<tr>
<td>4</td>
<td>121.9</td>
<td>2.3</td>
<td>1.82</td>
<td>0.2</td>
<td>3</td>
<td>+0.2</td>
<td>0.0027</td>
<td>1.25 x 10$^{25}$</td>
</tr>
</tbody>
</table>
Table 3.4. Electrical parameters of Dy doped SnO₂ thin films.

<table>
<thead>
<tr>
<th>Concentration of Dy (wt%)</th>
<th>$R_s$ (Ω)</th>
<th>$\rho_{\text{four probe}}$ ($10^{-4}$ Ωm)</th>
<th>$\rho_{\text{van der pauw}}$ ($10^{-4}$ Ωm)</th>
<th>B (T)</th>
<th>I (mA)</th>
<th>$V_H$ (mV)</th>
<th>$\mu_H$ (m²/v/s)</th>
<th>n (p) (N/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.27</td>
<td>1.16</td>
<td>1.073</td>
<td>0.2</td>
<td>1</td>
<td>-1.2</td>
<td>0.0842</td>
<td>$6.91 \times 10^{23}$</td>
</tr>
<tr>
<td>1</td>
<td>249.5</td>
<td>3.6</td>
<td>3.74</td>
<td>0.2</td>
<td>1</td>
<td>+0.4</td>
<td>0.0081</td>
<td>$2.08 \times 10^{24}$</td>
</tr>
<tr>
<td>2</td>
<td>90.365</td>
<td>1.9</td>
<td>1.355</td>
<td>0.2</td>
<td>1</td>
<td>+0.2</td>
<td>0.01106</td>
<td>$4.161 \times 10^{24}$</td>
</tr>
<tr>
<td>3</td>
<td>171.56</td>
<td>2.7</td>
<td>2.573</td>
<td>0.2</td>
<td>1</td>
<td>+0.3</td>
<td>0.00874</td>
<td>$2.774 \times 10^{24}$</td>
</tr>
<tr>
<td>4</td>
<td>657.19</td>
<td>11</td>
<td>9.85</td>
<td>0.2</td>
<td>1</td>
<td>+0.8</td>
<td>0.0061</td>
<td>$1.04 \times 10^{24}$</td>
</tr>
</tbody>
</table>

Table 3.5. Electrical parameters of La doped SnO₂ thin films.

<table>
<thead>
<tr>
<th>Concentration of La (wt%)</th>
<th>$R_s$ (Ω)</th>
<th>$\rho_{\text{four probe}}$ ($10^{-4}$ Ωm)</th>
<th>$\rho_{\text{van der pauw}}$ ($10^{-4}$ Ωm)</th>
<th>B (T)</th>
<th>I (mA)</th>
<th>$V_H$ (mV)</th>
<th>$\mu_H$ (m²/v/s)</th>
<th>n (p) (N/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.27</td>
<td>1.16</td>
<td>1.073</td>
<td>0.2</td>
<td>1</td>
<td>-1.2</td>
<td>0.0842</td>
<td>$6.91 \times 10^{23}$</td>
</tr>
<tr>
<td>1</td>
<td>139.48</td>
<td>2.2</td>
<td>2.092</td>
<td>0.2</td>
<td>2</td>
<td>-0.3</td>
<td>0.00537</td>
<td>$5.54 \times 10^{24}$</td>
</tr>
<tr>
<td>2</td>
<td>70.93</td>
<td>1.3</td>
<td>1.064</td>
<td>0.2</td>
<td>3</td>
<td>-0.2</td>
<td>0.00705</td>
<td>$8.322 \times 10^{24}$</td>
</tr>
<tr>
<td>3</td>
<td>212.8</td>
<td>3.9</td>
<td>3.192</td>
<td>0.2</td>
<td>2</td>
<td>-0.4</td>
<td>0.00469</td>
<td>$4.161 \times 10^{24}$</td>
</tr>
<tr>
<td>4</td>
<td>667.27</td>
<td>9.8</td>
<td>10.01</td>
<td>0.2</td>
<td>1</td>
<td>-0.8</td>
<td>0.00299</td>
<td>$2.081 \times 10^{24}$</td>
</tr>
</tbody>
</table>
Table 3.6. Electrical parameters of Cu doped SnO$_2$ films.

<table>
<thead>
<tr>
<th>Concentration of Cu [wt%]</th>
<th>Rs [Ω]</th>
<th>$\rho$ four probe $10^4$[Ωm]</th>
<th>$\rho$ van der pauw $10^4$[Ωm]</th>
<th>B [T]</th>
<th>I [mA]</th>
<th>$V_H$ [mV]</th>
<th>$\mu_H$ [m²/v/s]</th>
<th>n (p) [N/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.27</td>
<td>1.16</td>
<td>1.073</td>
<td>0.2</td>
<td>1</td>
<td>-1.2</td>
<td>0.0842</td>
<td>6.91 x 10$^{23}$</td>
</tr>
<tr>
<td>1</td>
<td>121.3</td>
<td>1.6</td>
<td>1.819</td>
<td>0.2</td>
<td>1</td>
<td>-0.4</td>
<td>0.0165</td>
<td>2.083 x 10$^{24}$</td>
</tr>
<tr>
<td>2</td>
<td>34.5</td>
<td>.43</td>
<td>.5175</td>
<td>0.2</td>
<td>1</td>
<td>-0.2</td>
<td>0.0284</td>
<td>4.16 x 10$^{24}$</td>
</tr>
<tr>
<td>3</td>
<td>260.15</td>
<td>4.2</td>
<td>3.902</td>
<td>0.2</td>
<td>1</td>
<td>-0.4</td>
<td>0.00768</td>
<td>2.081 x 10$^{24}$</td>
</tr>
<tr>
<td>4</td>
<td>282</td>
<td>4.62</td>
<td>4.23</td>
<td>0.2</td>
<td>1</td>
<td>-0.5</td>
<td>0.00865</td>
<td>1.66 x 10$^{24}$</td>
</tr>
</tbody>
</table>

Table 3.7. Electrical parameters of Fe doped SnO$_2$ films.

<table>
<thead>
<tr>
<th>Concentration of Fe [wt%]</th>
<th>Rs [Ω]</th>
<th>$\rho$ four probe $10^4$[Ωm]</th>
<th>$\rho$ van der pauw $10^4$[Ωm]</th>
<th>B [T]</th>
<th>I [mA]</th>
<th>$V_H$ [mV]</th>
<th>$\mu_H$ [m²/v/s]</th>
<th>n (p) [N/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.27</td>
<td>1.16</td>
<td>1.073</td>
<td>0.2</td>
<td>1</td>
<td>-1.2</td>
<td>0.0842</td>
<td>6.91 x 10$^{23}$</td>
</tr>
<tr>
<td>1</td>
<td>285.3</td>
<td>4.62</td>
<td>4.279</td>
<td>0.2</td>
<td>2</td>
<td>-0.3</td>
<td>0.00263</td>
<td>5.54 x 10$^{24}$</td>
</tr>
<tr>
<td>2</td>
<td>49.96</td>
<td>.7731</td>
<td>0.749</td>
<td>0.2</td>
<td>3</td>
<td>-0.2</td>
<td>0.00673</td>
<td>1.248 x 10$^{25}$</td>
</tr>
<tr>
<td>3</td>
<td>25.38</td>
<td>.39</td>
<td>0.381</td>
<td>0.2</td>
<td>2</td>
<td>-0.1</td>
<td>0.00985</td>
<td>1.665 x 10$^{25}$</td>
</tr>
<tr>
<td>4</td>
<td>509.9</td>
<td>78.2</td>
<td>76.5</td>
<td>0.2</td>
<td>1</td>
<td>-0.6</td>
<td>0.00585</td>
<td>1.3875 x 10$^{24}$</td>
</tr>
</tbody>
</table>
Table. 3.8. Electrical parameters of Mn doped SnO₂ films.

<table>
<thead>
<tr>
<th>Concentration Of Mn [wt%]</th>
<th>Rs [Ω]</th>
<th>ρ four probe $10^{-4}$ [Ωm]</th>
<th>ρ van der pauw $10^{-4}$ [Ωm]</th>
<th>B [T]</th>
<th>I [mA]</th>
<th>$V_H$ [mV]</th>
<th>$\mu_H$ [m²/v/s]</th>
<th>n (p) [N/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.27</td>
<td>1.16</td>
<td>1.073</td>
<td>0.2</td>
<td>1</td>
<td>-1.2</td>
<td>0.0842</td>
<td>6.91 x 10²³</td>
</tr>
<tr>
<td>1</td>
<td>405.98</td>
<td>5.9</td>
<td>6.089</td>
<td>0.2</td>
<td>2</td>
<td>-0.6</td>
<td>0.00367</td>
<td>3.32 x 10²⁴</td>
</tr>
<tr>
<td>2</td>
<td>125.54</td>
<td>1.7</td>
<td>1.88</td>
<td>0.2</td>
<td>2</td>
<td>-0.3</td>
<td>0.00597</td>
<td>5.54 x 10²⁴</td>
</tr>
<tr>
<td>3</td>
<td>280.3</td>
<td>4.4</td>
<td>4.204</td>
<td>0.2</td>
<td>2</td>
<td>-0.4</td>
<td>0.00356</td>
<td>4.16 x 10²⁴</td>
</tr>
<tr>
<td>4</td>
<td>404.7</td>
<td>6.3</td>
<td>6.07</td>
<td>0.2</td>
<td>2</td>
<td>-0.7</td>
<td>0.00432</td>
<td>2.37 x 10²⁴</td>
</tr>
</tbody>
</table>

undoped, except in the case of films doped with 2wt% of La. On Nd, Dy and La doping, Hall mobility decreases and carrier concentration increases. On Nd and Dy doping majority carriers converts from electrons to holes and become p-type semi-conductor ($V_H$ becomes positive) similar to the observation found in [14,24]. It may be due to substitution of Sn⁴⁺ ions by Nd³⁺ and Dy³⁺ ions respectively which act as acceptors in the sites of Sn⁴⁺. But in the case of La, the substitution may be by La¹⁺ ions which act as donors in the O²⁻ sites and there by increasing the n conductivity.

Tables. (3.6 - 3.8) gives the results of four probe, Van der Pauw and Hall probe measurements for undoped and that of Cu, Fe, and Mn doped films. It can be observed from the tables that on Cu, Fe, and Mn doping, carrier concentration increases. The increase in carrier concentration is due to substitution of Sn⁴⁺ with dopants at higher oxidation state [25]. No carrier conversion takes place on metal doping.
Rs and ρ of SnO₂ films doped with 2 wt% of Cu and 2 and 3 wt% of Fe are found to be less than that of undoped SnO₂ films. But Rs and ρ of Mn doped SnO₂ films are greater than that of undoped SnO₂ films. It is due to the increase in the amorphous nature on Mn doping [25].

**III.3 Conclusion**

Transparent conducting SnO₂ thin films are prepared by a cost effective vapour deposition technique. The structural property, electrical conductivity and optical transmittance of SnO₂ films depend on the deposition parameters and the concentration of the dopants (rare earths (Nd, Dy and La) and metals (Cu, Fe, and Mn), which are optimized in the present work. XRD analysis shows that the films coated are SnO₂. Undoped SnO₂ films are found to be n-type semiconductors. The undoped SnO₂ films at 575°C give high conductivity (ρ = 1.073 x 10⁻⁴ Ω·m) and good optical transmission above 70% with sheet resistance 71.27 Ω and Eg = 4.08 eV. A compromise between the conductivity and transparency is obtained at 575°C. Hence doped SnO₂ thin films were prepared at 575°C. The refractive index of the film is ~ 1.8 and these films can be of much use in requiring low index multi layer optical films. The thickness of the SnO₂ films was obtained as 1.5µm. The absorption coefficient is of the order of 10⁵ /m which is also a suitable criteria for making a transparent conducting film.

XRD pattern of doped SnO₂ films shows a decrease in the intensity at all the planes which is due to the replacement of Sn⁴⁺ ions with the Dy³⁺ and Nd³⁺, O₂⁻ ions with La¹⁻ and metal ions in the SnO₂ film and also due to the increase in the amorphous background. Doped and undoped SnO₂ thin films show PC and PV effects. Optical
transmission is increased on Nd, Dy, Cu, Fe and Mn doping but decreased on La doping. $E_g$ of SnO$_2$ films is found to vary from 3.96 - 4.09 eV when the substrate temperature changes from 400 °C to 600 °C, 4.08 - 4.11 eV on Nd doping, 4.02 - 4.09 eV on Dy doping, 4.03 - 4.09 eV on La doping, 4 - 4.07 eV on Cu doping, 4.01 – 4.08 eV on Fe doping and 4.05 – 4.11 eV on Mn doping (concentration of all the dopants varied from 1 wt% - 4 wt%). Only on Dy and Nd doping, carrier conversion takes place from n-type to p-type. Conductivity enhances remarkably for Nd, Cu and Fe doping. The increase in conductivity is primarily due to the increase in carrier concentration. On rare earth doping, the best transparent film (above 75%) giving relatively good conductivity is found to be that doped with Dy (at 1 wt % and 2 wt %). The best conducting film ($\rho = 5.56 \times 10^{-5} \ \Omega\text{-m}$) giving relatively good transparency is found to be that doped at 1wt % of Nd. A well-suited compromise between transmittance and conductivity is achieved in the case of SnO$_2$ thin films doped with Nd at 1 wt%. On metal doping the best transparent film (above 80%) giving relatively good conductivity is found to be that doped with Mn. The best conducting film ($\rho = 3.81 \times 10^{-5} \ \Omega\text{-m}$) giving relatively good transparency (above 75%) is found to be that doped at 3 wt % Fe.
References


