CHAPTER IV
PREPARATION OF TIN OXIDE THIN FILMS
AND THEIR CHARACTERIZATION

4.1. Introduction

Transparent conducting Tin Oxide (TO; SnO$_2$) thin films have been attracting increasing interest as they present many important applications such as liquid crystal displays, opto electronic devices, solar cells, gas sensors, protective coatings, resistors and coating for energy saving windows /1&2/. A number of methods such as chemical vapour deposition /3&4/, sputtering /5-8/, electron beam and reactive evaporation /9-12/, spray pyrolysis /3-16/ and sol-gel spin coating /2&17/ have been used by several investigators to develop tin oxide thin films. The film properties are strongly depended on the crystal structure and the stoichiometry of oxygen and hence the film properties depend strongly on the preparation process and therefore on the process parameters involved /1 & 21/.

Of the various methods, the sol-gel spin coating technique is capable of giving films of good uniformity and better-controlled composition and doping level and does not require any expensive and sophisticated equipment /2,17&19/. So in the present work an attempt has been made to use the spin coating technique through the sol-gel route to prepare tin oxide thin
films for device applications using as minimum a concentration of tin precursor as possible.

The spin coating technique using sol-gel form of processing of the coating solution involves several process parameters. The precursor solute concentration, gelation stage of the sol-gel, the turn table spin rate and time and the heat treatment temperature, time and atmosphere are the process parameters that are to be considered in the spin coating technique.

Investigation of the influence of the process parameters on the film characteristics is essential to obtain definite control of the opto electronic properties of the films. This procedure helps in developing quality conducting oxide films for device applications/2/. In the present work such investigations to study the influence of the spin coating parameters on the quality of the TO films have been carried out and the process parameters are optimized to obtain device quality tin oxide thin films. The investigations made and the results obtained are presented in this chapter.

4.2. Preparation and Cleaning of the Substrate

The substrates used should be chemically and mechanically stable when spun and when subjected to thermal cycling. In the present study clear microscope glass slides (Blue Star make), cut into 2.5X2.5 cm square plates have been used
as substrates. Prior to deposition the substrates are subjected to the following cleaning process to remove the unwanted impurities normally present on the surfaces of the glass plates exposed to the atmosphere.

1. The glass substrates are washed in soap solution by scrubbing the surfaces with a cotton swab dipped in liquid soap till they pass the breathe figure test to remove oil, grease etc.

2. The glass slides are then rinsed thoroughly in deionized water to remove any trace of the soap solution left on the surface followed by acetone rinsing.

3. Then the slides are soaked in chromic acid kept at a temperature of 90°C for about two hours to dissolve the fine silica layers possibly formed on the surface and to make a new surface for the deposition of the film.

4. Finally, the substrates are rinsed thoroughly in deionized water and dried at 100°C for one hour in an oven.

4.3. Preparation Of **Sol-Gel** and Spin Coating of Tin Oxide films

The various steps involved in obtaining Tin Oxide thin films using the spin coating technique through the sol-gel route are depicted sequentially in the flow chart (Fig.4.1). The precursor solution has been prepared by dissolving the desired quantity of stannic chloride (SnCU,5H20) in a certain volume of ethanol adding a small quantity of Hydrochloric acid (to serve as a
Fig. 4.1
Flow chart showing the steps involved for the preparation of Tin Oxide films using spin coating technique.
catalyst). This solution is refluxed at 60°C for a specified time of one hour, kept in an open beaker to gelate and after allowing sufficient number of days for gelation; the sol-gel obtained is used for preparing coatings.

A cleaned substrate is arranged on the turntable of the spin coating unit symmetrically with respect to the central hole in the turntable, which is connected to a rotary vacuum pump. The vacuum pump is switched on. Since vacuum is created underneath the substrate, it gets firmly and uniformly attached to the top surface of the turntable and does not come off the turntable even when the turntable spin rate is as high as 6000 rpm. The selected turntable spin rate and time are fed into the spin coating unit. A few drops (5 to 6 drops) of sol-gel are placed at the centre of the substrate. The unit is switched on. The turntable spins at the pre-determined rate fed into the instrument and automatically stops revolving at the end of the predetermined time fed into the unit. During the high spin speed centrifugal forces drive the liquid radially outwards. Excess material is driven off the edges (rim) of the substrate but the remainder is retained on the substrate as a very thin layer by the viscous and surface tension forces/22/.

The vacuum pump is switched off. The substrate is carefully removed from the turntable holding at the edges and its back side (un coated side) is wiped with a cloth to remove
unwanted material, if any on this side. The substrate is then allowed to air dry.

Five such coated substrates have been carefully arranged side by side on a mild steel plate placed inside the furnace where the desired heat treatment temperature 400°C is maintained and the coated substrate heated for the desired time of 5 minutes. This heat treatment results in the formation of tin oxide films. The heat treated substrates are carefully transferred from the furnace on to an Asbestos strip to avoid sudden temperature drop and the substrates are allowed to cool.

The next coating is made on the coated substrates, they are air dried and subjected to heat treatment in the furnace and then cooled. The whole process is repeated for every one of the coatings and the desired number of successive coatings (say 8 or 9) has been made on the same substrate. It is to be noted that after each cooling, the substrate is dried and subjected to heat treatment separately in order to avoid cracking of the film and building up of desired thickness. The volume of ethanol, volume of HCl, refluxing temperature and time have been taken as 100 ml, 5 ml, 60°C and 1 hour respectively and the process parameters optimized.

4.4. Fixing the Solute Concentration

Initially a concentration of 0.06 mole % of precursor salt i.e. stannic chloride (SnCU.5H₂O) was used and the sol-gel was
prepared. When this was used for coating, the SnCh films prepared with a heat treatment temperature of 400°C had powdery layer formation and the films showed a sheet resistance of infinity. This powdery layer could not be removed fully by gentle wiping. When the concentration of stannic chloride was lowered to 0.055, 0.05 and 0.045 mole % the powdery layer formation was reduced progressively and at 0.040 mole % there was no powder formation at all and Sn₀₂ uniform film with good luster with a resistivity of 0.05 Qcm. could be obtained. When the solute concentration was reduced to 0.035 mole %, uniform good film formation was available and a minimum resistivity of 0.04 Qcm was obtained. Further lowering of the solute concentration resulted in films of progressively higher resistivity only though film uniformity and higher transparency were still retained. The variation of resistivity with precursor solute concentration is shown in Fig.4.2

Tin Oxide (Sn₀₂) in its pure form is fully stoichiometric in oxygen and non-conducting. However electrical conductivity can result in tin oxide (Sn₀₂) films due to the existence of point defects in the atoms which act as donors. This is achieved by the oxygen vacancies in the lattice which can leave two unbound electrons on a tin atom or by a tin atom that may be located in an interstitial site with its valance electrons not particularly bound to any other lattice points/20/. So it is only the
Fig. 4.2
Influence of the solute concentration on the resistivity of TO films
availability of oxygen vacancies that makes SnO₂ films a semiconductor.

When the solute concentration is low, the number of atoms and consequently the number of oxygen vacancies may be small resulting in low conductivity (or high resistivity). When the solute concentration increases, the number of atoms (and therefore the crystallite size) and hence the number of oxygen vacancies may increase (for the same number of heat treatment steps) and hence the conductivity rises and therefore the resistivity falls. This will continue until the solute concentration is such that the number of atoms are optimum for the film and hence the number of oxygen vacancies are optimum at which stage the conductivity will be maximum and the resistivity will be minimum. For SnO₂ films, this happens at a precursor solute concentration of 0.035 mole % where a minimum resistivity occurs.

At still higher solute concentration, there appears to be excess solute, which is deposited as a powdery layer on the surface, giving rise to practically zero conductivity, and hence the resistivity would be infinity for these higher concentrations. This happens beyond 0.040 mole % of solute concentration. So a mole % of 0.035 for the precursor salt Stannic Chloride (12.27gm) in 100 ml of ethanol has been fixed for the present work. After fixing this important process parameter, the other
process parameters such as the gelation stage, the turntable spin rate and time, numbers of coatings and heat treatment temperature have been optimized.

4.5 Optimization Of Gelation Time/ Aging Time:

The variation of viscosity of precursor sol with gelation time/aging time has been studied and the results obtained are shown in Fig.4.3a. After the second day of aging, the viscosity of the sol rises showing that the gelation process has set in and the rise is uniform upto 6th day, between 7 and 10 days aging, the viscosity abruptly rises and after 12 days it tends to a saturation value indicating that gelation stage is complete and thick gel is formed. After 6 days of aging (viscosity of sol-gel >4.5cp) the coating on the glass substrate becomes less uniform and at higher viscosities streaks of coatings are obtained which progressively becomes more and more irregular and after 12 days of aging the material has been completely thrown off the substrate without any coating.

Uniform coating could be obtained using the sol-gel of 2-6 days of aging, i.e. with viscosities 2.5 to 4.5 cp. Below 2 days, the coating is ultra thin. Lin and Wu, (1996) from their TEM studies, have established that the particle size grows with the gelation time/aging time. So perhaps very heavy particles corresponding to near complete gelation stage are unable to adhere to the substrate and perhaps only when the viscosity is
Fig 4.3

Variation of Viscosity and density of Tin Chloride solution with number of days of gelation
between 2.5 to 4.5 cp (corresponding to 2-6 days of aging) the particle size is optimum for developing good uniform films.

The variation of density of the sol with aging/gelation time is presented in Fig.4.3b along with the viscosity variation curve. When the gelation process sets in after 2 days of aging both density and viscosity start increasing. After 6 days of aging corresponding to less uniform streaky coating the viscosity as also the density rise sharply. After 12 days when the gelation is complete and thick gel is formed; the viscosity saturates and so does the density. Thus the density of the sol also follows the same trend as viscosity of the sol with respect to the aging/gelation time and is complementary to each other. So either the density or viscosity variation of the sol with aging /gelation time could very well be used for gelation stage optimization. Thus 2-6 days of aging time has been taken as optimum for developing tin oxide films.

4.6. Selection Of Turn Table Spin Rates

The variation of the resistivity of the TO films with respect to turntable spin rate is shown in Fig.4.4a. At relatively low spin rates of 2000 rpm, formation of yellowish white islands were seen in the films and the lustre and uniformity of the films were rather poor. When the spin rate was increased better film uniformity due to reduction in island effect and better film lustre were obtained but however the thickness falls. Less island
Spin rate - $\omega$ (rpm)

Fig. 4.4

Variation of Thickness and resistivity of TO films with turn table spin rate ($\omega$)
formation (i.e. better film uniformity) may tend to decrease the sheet resistance whereas thickness reduction will tend to increase the sheet resistance. These contrasting effects will decide whether there is a decrease/increase in the sheet resistance of the film and consequently the decrease/increase of the resistivity of the film. If the first effect contributes more than the second effect, the resistivity of the film may decrease, on the other hand if the second effects contribute more, the resistivity may increase. When the turntable spin rate is increased from 2000 rpm, the contribution from the first effect may be a little dominant resulting in lowering of the resistivity of the film. At 3500 rpm the film uniformity may be optimum without any island formation and at which stage the resistivity is minimum. After this stage even though the film uniformity continues to exist, the thickness falls and the contribution from the second effect may be more than that due to the first effect and hence the resistivity may rise. This may account for the increase in the resistivity of the film beyond 3500 rpm. So, in the present work 3500 rpm has been selected as the turntable spin rate for preparing SnO$_2$ films.

4.7. Fixing The Turn Table Spin Time

In the spin coating method, the turntable spin time is a parameter to be fixed for obtaining uniform good films. To optimize the time of spinning, the spinning speed is fixed at 3500 rpm and the spin time has been varied from 5 seconds to
25 seconds in steps of 5 seconds. 400°C is the heat treatment temperature 5 minutes is the heat treatment time and the number of coatings is 6 coatings. The variation of resistivity of the films with spin time is given in Fig.4.5a.

Initially when 5 seconds was used as the spin time, films of poor lustre and uneven surfaces with islands of whitish yellow patches and a high sheet resistance and a consequent high resistivity were obtained. As the time of spinning was increased to 10 seconds the lustre, the surface smoothness and film uniformity improved and the resistivity of the film decreased. At 15 seconds of spinning time good film with minimum resistivity was obtained. Further increase in the time of spinning resulted in a marginal increase in resistivity. The plot of film thickness shows that initially ie at t = 5 seconds the film thickness is relatively high and it decreases on increasing the time of spinning and this happens upto 15 seconds beyond which the thickness variation is small reflecting the behaviour exhibited by resistivity also. So any turntable spin time between 15 seconds and 25 seconds is suitable and for the present study 15 seconds has been fixed as the turntable spin time.

As mentioned earlier, in the spin coating method when a few drops of the coating solution is placed at the centre of the substrate and the substrate spun at a high speed, the excess solution splashes out leaving a layer of coating on the
Fig. 4.5
Variation of thickness and resistivity of TO film with spinning time (t)
substrate. For splashing out the excess solution a certain time may be needed. When the turntable is allowed to spin only for 5 seconds, perhaps the time may not be sufficient to splash out the entire excess solution and so a sort of uneven coating with poor lustre could be formed. When the turntable spin time is increased, it is quite possible that more and more excess solution may be splashed out of the substrate resulting in a coating with improved uniformity. At 15 seconds turntable spin time; practically the entire excess solution may be splashed out of the substrate resulting in much improved uniform coating with minimum resistivity. Beyond this spin time, there is practically no excess solution available for throwing out and hence the uniformity, film thickness and resistivity may be more or less unchanged.

The variation of the film thickness ‘h’ with spin time t is shown in Fig.4.5b and the data are furnished in Table 4.1. The ratio $h_1/h_2$, $t_2/t_1$ and $\sqrt{t_2/t_1}$ have been found for various combinations of values and the results obtained are shown in the Table 4.2. From the table, it can be seen that the film thickness (or thickness/coat) is more or less inversely proportional to the square root of the spin time t,

i.e. \[ h \propto 1/\sqrt{t}. \]

A plot of \[ h - 1/\sqrt{t} \] (fig.4.6) is more or less a straight line indicating again \[ h \propto 1/\sqrt{t}. \]
Table 4.1
Variation of thickness and Resistivity with time of spinning in the preparation of TO films

<table>
<thead>
<tr>
<th>SNo.</th>
<th>Spin Time - $t$ (sec)</th>
<th>Thickness - $h$ (nm)</th>
<th>Resistivity (Ωcm)</th>
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<tr>
<td>1</td>
<td>5</td>
<td>253</td>
<td>0.130</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>184</td>
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<td>3</td>
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<td>161</td>
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<td>138</td>
<td>0.041</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>138</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Table 4.2
Relation between film thickness ($h$) and time of spinning ($t$) for Tin Oxide

<table>
<thead>
<tr>
<th>S.No</th>
<th>$h_1$ (nm)</th>
<th>$h_2$ (nm)</th>
<th>$t_1$ (sec)</th>
<th>$t_2$ (sec)</th>
<th>$l_1/l_2$</th>
<th>$t_2/t_1$</th>
<th>$h/U$</th>
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<td>184</td>
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<td>2</td>
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<td>161</td>
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<td>15</td>
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<td>1.732</td>
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<td>20</td>
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<td>1.833</td>
<td>5</td>
<td>2.236</td>
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<td>161</td>
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<td>15</td>
<td>1.143</td>
<td>1.5</td>
<td>1.225</td>
</tr>
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<td>6</td>
<td>184</td>
<td>138</td>
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<td>20</td>
<td>1.333</td>
<td>2</td>
<td>1.414</td>
</tr>
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<td>25</td>
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<td>161</td>
<td>138</td>
<td>15</td>
<td>20</td>
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<td>1.333</td>
<td>1.155</td>
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<td>9</td>
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<td>25</td>
<td>1.167</td>
<td>1.667</td>
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<tr>
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<td>138</td>
<td>138</td>
<td>20</td>
<td>25</td>
<td>1</td>
<td>1.256</td>
<td>1.118</td>
</tr>
</tbody>
</table>
Fig. 4.6
Variation of thickness with inverse of sq.rt of spin time of TO films
A simple theoretical model for the spin coating of thin films has been proposed by Doughton and Given (1985) and Hirasawa et al. (1997) /23&24/. When a drop of liquid/solution is placed at the centre of the substrate and the substrate spun at a high speed, the liquid/solution spreads into a thin layer under the influence of three forces:  

i) Centrifugal force,  
ii) viscous force and iii) surface tension force. In the simple model, it is assumed that the presence of the boundary at the periphery of the substrate has no effect on the spreading process; further the surface tension is neglected because the centrifugal force is dominant. In such a case, for spreading process,

The viscous drag at a point $z$ above the substrate = The centrifugal force per m the radial direction $r$ J unit volume at the point.

Using Newton’s law for viscous drag, the relation becomes

$$r \frac{|(3 \cdot v/dz^2)|}{2} = p \omega^2 r \text{------------------------ (3.1)}$$

where $r$ and $p$ are the viscosity and density of the liquid and $\omega$ the angular speed of rotation of the turn table.

Taking $dv/dz = 0$ at the film surface ie at $z= h$, where $h$ is the film thickness and $v = 0$ at $z=0$ ie at the substrate/liquid interface, using the equation of continuity and taking the experimental results that $h$ is independent of $r$

$$dh/dt = p \omega h^2 / 3 r$$
\[ h_0 \]

and

\[ h = \frac{h_0}{[1 + \frac{(4pcot^2)}{r}]} \]  

where \( h_0 \) is the thickness when \( t=0, r=0 \)

If \( \frac{(4pcot^2)}{r} \) \( \leq 1 \)

\[ h = \frac{r}{\sqrt{4pcot^2}^{1/2}} \]

This equation shows that

\[ h \sim \frac{1}{\omega t} \]  

Following Peurrung and Graves (1993), if it is assumed that drying/heat treatment has no significant effect on the shape of the film profile, then

\[ h \sim \frac{1}{\omega t} \]

may be taken to be reasonably valid for dried/heat treated films also. Thus this theoretical prediction more or less agrees with the experimental results.

The variation of film thickness with turn table spin rate is shown in Fig.4.4b. The ratio of \( h_1/h_2 \) and \( \omega_2/\omega_1 \) for various combinations of values have been found and the results obtained are presented in Table 4.3. It is seen that the film thickness \(*h'\) is more or less inversely proportional to the turntable spin rate ‘\( \omega \)’. A near straight line \( h \) vs \( 1/\omega \) plot (Fig.4.7)
### Table 4.3
Relation between film thickness ($h$) and spin rate ($\omega$) for Tin Oxide

<table>
<thead>
<tr>
<th>S.No</th>
<th>$h_1$ nm</th>
<th>$h_2$ nm</th>
<th>$h_1/h_2$</th>
<th>$\omega_1$ rpm</th>
<th>$\omega_2$ rpm</th>
<th>$\omega_2/\omega_1$</th>
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<tbody>
<tr>
<td>1</td>
<td>216</td>
<td>184</td>
<td>1.17</td>
<td>2500</td>
<td>3000</td>
<td>1.20</td>
</tr>
<tr>
<td>2</td>
<td>216</td>
<td>158</td>
<td>1.37</td>
<td>2500</td>
<td>3500</td>
<td>1.40</td>
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<td>216</td>
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<td>1.59</td>
<td>2500</td>
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<td>3000</td>
<td>3500</td>
<td>1.17</td>
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<td>3000</td>
<td>4000</td>
<td>1.32</td>
</tr>
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<td>136</td>
<td>1.16</td>
<td>3500</td>
<td>4000</td>
<td>1.14</td>
</tr>
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</table>

### Table 4.4
Optical properties of Tin Oxide films at different Number of coatings when heat treatment temperature is 400°C

<table>
<thead>
<tr>
<th>No. of coatings</th>
<th>Thickness nm</th>
<th>Absorption Edge (nm)</th>
<th>Transmittance At 550°C (%)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>69</td>
<td>311</td>
<td>97.0</td>
<td>3.43</td>
</tr>
<tr>
<td>4</td>
<td>115</td>
<td>300</td>
<td>91.2</td>
<td>3.46</td>
</tr>
<tr>
<td>6</td>
<td>161</td>
<td>300</td>
<td>93.6</td>
<td>3.46^</td>
</tr>
<tr>
<td>8</td>
<td>207</td>
<td>311</td>
<td>91.5</td>
<td>3.44</td>
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</table>
Fig. 4.7

Variation of thickness with inverse of spin rate of TO films
obtained also confirms it. Thus indicating that the experimental results and the theoretical predictions more or less agree with each other.

4.8. Film Thickness studies

The variation of the thickness of sol-gel spin coated SnC\textsubscript{2} films on the number of coatings is shown in Fig.4.8. The variation is found to be more or less linear and practically no detectable change in film thickness has been observed in the heat treatment temperature range of 375-425°C. This conclusion is consistent with the conclusion arrived at by Lee et al. /22/ while studying the thickness variation with sol-gel derived SnC\textsubscript{2} films on the number of coatings. The average film thickness/coat is found to be 25 nm which is nearly the same as that reported by Cobianu et al. /17/.

4.9. Optimisation. Of Number Of Coatings:

Keeping the heat treatment temperature at 400°C, the number of coatings has been varied and the variation of resistivity of tin oxide film with number of coatings is shown in Fig.4.9. The number of coatings decides the thickness of the film - greater the number of coatings, higher the thickness of the film. From the Fig.4.9, it is seen that as the number of coatings increases from a low value (i.e. as the film thickness increases), the resistivity of TO film decreases, reaches a minimum value at 6 coatings and then increases. This result is rather intriguing.
Fig. 4.8
Variation of thickness of the TO films with number of coatings
Fig. 4.9
Variation of resistivity of TO films with number of coatings
But this can be qualitatively understood if the factors contributing to the conductivity of the film are considered. The factors to be considered are: the crystallite structure and size, surface scattering and oxygen vacancies. Small crystallite size may lead to high grain boundary scattering tending to adversely affect the conductivity and increase the resistivity of the film. Lower crystallinity will also adversely affect the conductivity. The surface scattering may also tend to increase the resistivity of the film. Thus small crystallite size, lack of crystallinity and surface scattering may lead to high resistivity. If the crystallinity and size of the crystallites increases and if the surface scattering decreases, the conductivity will increase and resistivity will decrease.

As has already been pointed out the conductivity in TO is due to the existence of oxygen vacancies. If the film is formed with a small number of heat treatment steps (so that the total heat treatment duration is small), adequate oxygen vacancies may exist contributing to the conductivity of the film; on the other hand if the number of heat treatment steps increases, the number of oxygen vacancies may fall which may result in lowering the conductivity (and consequently rising the resistivity) of the film. When the total heat treatment time increases, the crystallinity of the film improve.
When the number of coatings is small, crystallinity and size of crystallites may be low and the surface scattering may be considerable due to small mean free path, giving rise to large grain boundary scattering and these would be contributing to high resistivity. At the same time, since the number of heat treatment steps is small, the oxygen vacancies contribute to the conductivity tending to lower the resistivity. Since the former factor may be dominant over the latter factor the film would show high resistivity only. When the number of coatings increases the film thickness increases, the surface scattering may be reduced due to increased mean free path and the crystallinity and size of the crystallites may improve tending to improve the conductivity. But as the numbers of heat treatment steps are to be consequently increased, the number of oxygen vacancies may be lowered tending to rise the resistivity. Under the influence of these two, the resistivity of the film falls because of the dominance of the first factor. This fall will continue to occur as long as the first effect dominates. After a number of coatings and consequent number of heat treatment steps, the oxygen vacancies may become very low resulting in further increase in resistivity and this may become dominant over the reduction in resistivity due to the first factor mentioned above. Therefore the resistivity of the films may increase. The minimum resistivity occurs at the 6th coating. Thus the optimum number of coatings is taken as 6 for the tin oxide films.
The transmittance spectra of these films are shown in Fig. 4.10 and the optical data are presented in Table 4.4. It is seen that as the number of coatings increases, the absorption edge shifts to the lower wavelength side and is comparatively low when the number of coatings is 4-6. The transmittance at 550 nm is high when the number of coatings is small and gets lowered and becomes more or less constant when the number of coatings is between 4 and 8. The film porosity, surface and structural homogeneity and crystallinity are factors that have positive influence on the transmittance of TCO films /27&28/. When the number of coatings is small (say 2), the film thickness is low and there may be less uniformity (i.e. greater porosity) which may tend to increase the transmittance. The surface and structural homogeneity may be less and the crystallinity and size of the crystallites may be low which may tend to decrease the transmittance. The former effect may be dominant when the film thickness is low and this may result in relatively higher transmittance. This is consistent with the contention of Kim et al. (1999) that low film thickness leads to high transmittance. When the number of coatings increases (i.e. when the film thickness increases), the porosity would decrease (i.e. film uniformity will improve) tending to decrease the transmittance; the surface and structural homogeneity and crystallinity and size of crystallites may improve tending to increase the transmittance. Under these effects, the transmittance may fall and may become more or less constant beyond a thickness (i.e.
Fig. 4.10
Transmittance spectra of TO thin films developed at various number of coatings (T=400 deg.C)
beyond a certain number of coatings). Such near constancy of transmittance, at higher film thickness has been reported by Ping and Keran (1992) for sputtered ITO films and Binoy (2001) for Activated Reactive Evaporated ITO films. The gap values from the $a^2$ vs $hv$ plot (Fig.4.11) show that the band gap energy is 3.46eV and does not vary much with the number of coatings i.e. with the film thickness.

4- 10. Optimization Of Heat **Treatment** Temperature

Heat treatment temperature is one of the parameters, which may influence the stochiometry, and structural properties of the films. The Fig.4.12 shows the XRD of TO films prepared at different heat treatment temperatures varying from 350 to 425°C. From the figure, it is seen that the films are polycrystalline in nature with preferred growth direction along [110]. Other peaks corresponding to the directions [101], [200] and [211] are also seen. All the diffraction patterns shown in the Fig.4.12. are characteristic of TO structure (Tetragonal rutile structure). It is observed from the figure that as the heat treatment temperature increases the intensity of the preferred orientation [110] also increases, indicating an improved crystallinity and crystallite size with temperature. This is reflected by the other peaks too for example, at 350°C the [200] peak is very weak, but it shows up as a well marked peak at 400°C and 425°C. The intensity of the [211] peak increases with temperature. Shanon et al /3/ have also observed that the [200]
\( \alpha^2 \text{ (m}^{-1}\text{)}^2 \)

Fig. 4.11

\( \alpha^2 \text{ vs } h\nu \text{ plots for different number of coatings of the TO films} \)
XRD patterns of Tin Oxide films at 350, 375, 400 and 425 deg.C
peak gets intensified at higher temperatures, while analyzing their TO films developed by CVD technique. However no phase change at elevated temperatures as reported /2/ to occur in TO films has been noticed in the spin coated films with heat treatment temperatures of 350-425°C.

Thus it can be seen that the intensity of the peaks obtained increases with increase in heat treatment temperature indicating an improved crystallinity and crystallite size with temperature. This result is consistent with the conclusion arrived at by Vasu and Subrahmanyam/13/ and Shanon et al/3/ using other film preparation techniques.

Regular, strong and sharp crystalline peaks are found even at a relatively low temperature of 350°C. Vasu and Subrahmanyam/13/ have obtained good crystalline peaks for their TO films prepared by spray pyrolysis method at substrate temperature of 300-440°C. Using the CVD technique, Shanon et al/3/ have reported good crystalline TO peaks at temperature of 300-370°C. The results of present study indicates that the spin coating method provides much intense regular crystalline TO films at a heat treatment temperature of even 350°C itself; contrastingly, Lin and Wu/2/ who have grown TO films with gel suspension on glass substrates could not get distinguishable crystalline peaks at 300°C and only at a much higher temperature of 500°C, they could obtain crystalline peaks.
The XRD data for the TO films developed at various heat treatment temperature are presented in Table 4.5. The data agree fairly well with the values given in JCPDS Tables. The calculated values of lattice parameters \( a = 4.73 \, \text{Å} \), \( c = 3.19 \, \text{Å} \) in very good agreement with the values of \( a = 4.737 \, \text{Å} \), \( c=3.185 \, \text{Å} \) reported by Binoy (2001)/26/.

The grain size (D) has been calculated from the Full Width Half Maximum (FWHM) \( \beta \) of the prominent XRD peaks using the Scherrer-Bragg relation

\[
D = K \frac{\lambda}{\beta' \cos \theta}
\]

Where \( K \) is a shape factor taken as 0.94 for spherical particles,

\[
\beta' = (\beta^2 - \delta^2)^{1/2}
\]

\( \delta \) being the resolution of the X-ray spectrometer, \( \lambda \) is the wavelength of X-ray used and \( \theta \) is the Bragg angle. Although this technique does not give any proper idea about the size distribution, nevertheless it gives the average grain size/29/. It is found that the average grain size varies from 1.92 nm to 4.80 nm as the heat treatment temperature varied from 350 to 425° C.

The variation of resistivity of TO films with respect to the heat treatment temperature is shown in Fig.4.13. The plot shows that as the temperature increases from 350° C the
### Table 4.5

XRD data for the Tin Oxide films with different heat treatment temperature

<table>
<thead>
<tr>
<th>Standard data</th>
<th>JCPDS FILE No.6-416</th>
<th>350</th>
<th>375</th>
<th>400</th>
<th>425</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl</td>
<td>d (Å)</td>
<td>i/lo</td>
<td>d (Å)</td>
<td>Peak counts</td>
<td>d (Å)</td>
</tr>
<tr>
<td>110</td>
<td>3.347</td>
<td>100</td>
<td>26.5</td>
<td>3.351</td>
<td>1395</td>
</tr>
<tr>
<td>101</td>
<td>2.643</td>
<td>75</td>
<td>33.7</td>
<td>2.651</td>
<td>1044</td>
</tr>
<tr>
<td>200</td>
<td>2.369</td>
<td>21</td>
<td>37.4</td>
<td>2.387</td>
<td>604</td>
</tr>
<tr>
<td>211</td>
<td>1.764</td>
<td>57</td>
<td>51.8</td>
<td>1.767</td>
<td>697</td>
</tr>
</tbody>
</table>
Fig. 4.13
Variation of resistivity with heat treatment temperature of TO films
resistivity falls and is minimum at 400°C and then rises. As the heat treatment temperature rises, the crystallinity and size of the crystallites may improve, the boundary and surface scattering may be reduced all tending to improve the film conductivity; but the number of oxygen vacancies will decrease tending to decrease the conductivity. If the first factor dominates, the conductivity will be high (and the resistivity will be low). This seems to happen at and below 400°C for sol gel spin coated Sn02 films. However if the second influence dominates over the first, the conductivity will decrease and the resistivity increase. This happens in the present case at 425°C. A minimum resistivity of 3.0x10^{-2} \, \Omega \, \text{cm} (\text{sheet resistance } 528 \, \Omega/\Box) has been obtained. Contrastingly Lin and Wu /1/ obtained an optimized sheet resistance of 5x10^{7} \, \Omega/\Box for their sol gel suspension deposited TO films at 500°C. The present study shows that good quality, TO films at a relatively low heat treatment temperature of 400°C and low heat treatment time of 10 minutes can be obtained using the spin coating technique.

The transmittance spectra of the TO films developed at 350, 375, 400 and 425°C are shown in Fig.4.14 and the spectral data in Table 4.6. The transmittance marginally increases from 350 to 375°C and becomes more or less constant with a value around 93.6%. Such a trend has been observed by Lin and Wu/2/ also for their colloidal gel suspension derived Sn02 films. The absorption edge shifts to lower wavelength side as the heat
Fig. 4.14
Transmittance spectra of the TO films developed at 350, 375, 400 and 424 deg.C
Table 4.6
Optical properties of Tin Oxide films at different heat treatment temperature when number of coatings is 6

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Thickness (nm)</th>
<th>Absorption Edge (nm)</th>
<th>Transmittance At 550 nm(%)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>161</td>
<td>318</td>
<td>89.9</td>
<td>3.39</td>
</tr>
<tr>
<td>375</td>
<td>161</td>
<td>314</td>
<td>94.5</td>
<td>3.41</td>
</tr>
<tr>
<td>400</td>
<td>161</td>
<td>300</td>
<td>93.6</td>
<td>3.46</td>
</tr>
<tr>
<td>425</td>
<td>161</td>
<td>318</td>
<td>93.2</td>
<td>3.42</td>
</tr>
</tbody>
</table>
treatment temperature increases and is minimum (300nm) at 400°C at which stage the band edge is 3.46 eV (Fig.4.15). The linearity of the $(\alpha h\nu)^2$ vs $h\nu$ plot (Fig.4.16) for the SnO2 films indicates that the absorption near the fundamental edge is due to direct allowed transition. Further the value of $\alpha$ is of the order of $10^4$cm$^{-1}$ which is characteristics of direct allowed transition Smith (1978). At the optimum heat treatment temperature of 400°C with 6 coatings, the transmittance is 93.6% with band gap of 3.46 eV. and at this stage the resistivity is also minimum at $3.0 \times 10^{-2}$ Ωcm. This resistivity value is in the range of values reported for TO films grown under optimized conditions by Uen et al./8/ ($\rho=7.2 \times 10^{-2}$ to $2.0 \times 10^{-2}$ Ωcm.) at $T_{\text{sub}} = 400^\circ C$ using reactive evaporation method (with a dc glow discharge of oxygen), Madhusudhana Reddy et al./18/ ($\rho=9.0 \times 10^{-2}$ Ωcm at an annealing temperature of 500°C) using electron beam deposition technique, Vasu and Subrahmanyan/13/ ($\rho=2.1 \times 10^{-3}$ to $1.4 \times 10^{-2}$ Ωcm. $T_{\text{sub}} = 280$ to 440°C, $E_g$ 3.76- 3.86 eV) using spray pyrolysis method, Shanon et al. /3/ ($\rho=4.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$ Ωcm., $T_{\text{sub}} = 300$ to 370°C) using the Chemical Vapour Deposition (CVD) technique.

4.11. Surface morphological studies

Analysis of the surface morphology by SEM studies of the spin coated SnO2 films and heated at temperatures 375, 400, 425°C have been conducted and the micrographs are shown in
Fig. 4.15.

$\alpha^2 - h\nu$ plots for various heat treatment temperature TO films
Fig. 4.16

$h \nu$ vs $(\alpha h \nu)^2$ plot for Tin Oxide film
Fig.4.17(a), (b) and (c) respectively. SnO$_2$ films prepared at 375°C show a uniform surface but with some pin holes and patches. At 425°C, (Fig.4.17 (c)) there are more agglomerations seen all over the surfaces. Fig.4.17 (b) shows a uniform surface morphology for the Sn$_2$O$_3$ film prepared under the optimized conditions at 400°C. Below and above this optimum temperature the surface morphology is not as good as that of the film prepared at 400°C.

The Atomic Force Microscopy (AFM) photographs are shown in Fig.4.18 (a), (b) and (c) for the SnC$_{2}$ films prepared at 375°C, 400°C and 425°C. This study also reveals the uniformity of surface with grain size of about 0.5 μm. This is in support of the SEM surface morphology observed for these films. SnC$_{2}$ film prepared at 375°C shows some non-uniform surface morphology. As heat treatment temperature is increased to 400°C the surface morphology becomes smooth and more uniform. But, when the temperature of heating the film is 425°C the surface morphology one again becomes less uniform. These surface morphology studies show that the spin coating technique can be used for the preparation of large area tin oxide films at a temperature of 400°C for solar cells and other device applications.
Fig. 4.17: SEM micrographs of TO films prepared at (a) 350 (b) 375 and (c) 400°C.
Fig. 4.18 AFM pictures of TO films prepared at (a) 350, (b) 375 and (c) 400°C.
4.12. Conclusion

The study clearly demonstrate that device quality smooth uniform SnO$_2$ films with good luster with a resistivity of $3.0 \times 10^{-2}$ Qcm and band gap of 3.46 eV have been developed by the spin coating method at a relatively low heat treatment temperature of 400°C and relatively small heat treatment time of 5 mt/coat.
References
3. S.G. Shanon, Rajrup and A. Manansingh, Thin solid films, 190 (1990) 287