Chapter VI

EFFECT OF DOPING LEVEL ON PHYSICAL PROPERTIES
OF ANTIMONY DOPED NANOCRYSTALLINE TIN OXIDE
FILMS FABRICATED USING LOW COST SPRAY
TECHNIQUE

6.1. INTRODUCTION

As discussed in detail in Chapter I, doped tin oxide films have a wide range of applications due to their high electrical conductivity and high transparency in visible and near infrared region of solar radiation [1]. There are several deposition such as precursor concentration, substrate temperature, spray rate, doping level etc. that can be varied suitably to tailor the properties of tin oxide films. Of these parameters, doping level is one of the important process parameters which determine the characteristics of transparent conducting oxide films. In the present study, the effect of antimony doping level on the properties of tin oxide films fabricated by employing the simplified spray technique using perfume atomiser is studied and reported. The precursor solution was prepared by dissolving high pure $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.8 M) with a very small amount of $\text{HCl}$ (0.1 mol L$^{-1}$) and then diluting it by doubly deionised water. Antimony doping was achieved by adding suitable proportion of $\text{SbCl}_3$ (0.5 – 3.0 at.% in steps of 0.5 at.%) in the starting solution. This aqueous solution was magnetically stirred for 45 min,
which was followed by an ultrasonic agitation for 45 min, to get a clear solution.

6.2. EXPERIMENTAL DETAILS

The precursor solution thus obtained was sprayed intermittently by means of a perfume atomiser [2, 3] on preheated glass substrates of dimensions 75×25×1.35 mm. The substrates were maintained at a temperature 340 ± 5 °C using a temperature controller and a chromel–alumel thermocouple. The intermittent spray deposition followed in this study is a two-step procedure: a spray and a 10 s interval. The spray interval enables the substrates to attain the required temperature before the start of the next spray. The substrates were precleaned ultrasonically [4, 5] with organic solvents and doubly deionised water for degreasing and to remove the contaminations if any on the substrate surface [6]. The experiment was repeated several times to confirm the reproducibility of the films.

6.2.1. CHARACTERIZATION DETAILS

X-ray diffraction patterns were recorded using X-ray diffractometer (PANalytical – PW 340/60 X’ pert PRO) which was operated at 40 kV and 30 mA with X-ray source of Cu Kα radiation having wavelength 1.5406 Å. AFM and SEM images were obtained by employing atomic force microscope (Veeco-di CP II) and scanning electron microscope (HITACHI S-3000 H) respectively. UV-vis-NIR
double beam spectrophotometer (LAMBDA-35) is used to record transmission spectra in the range of 300 – 1100 nm. The sheet resistance values are estimated with the use of four-point probe with van der Paw configuration.

6. 3. RESULTS AND DISCUSSION

6.3.1. Film formation

In conventional spray pyrolysis technique, in general, the substrate temperature is maintained at 400 °C or above. However, in the case of simplified spray technique using perfume atomiser, a comparatively lesser temperature (340 ± 5 °C) is employed without compromising for the quality of the films. The formation of good quality thin films at a lesser temperature in this simplified spray technique than the conventional technique can be explained as follows. In the growth kinetics of sprayed films, it was showed that the sprayed liquid droplets tend to flatten as discs on the substrate surface due to their momentum \([7]\). The disc geometry depends on the momentum and volume of the droplet and the substrate temperature \(T_s\) \([7]\). Thus, the deposition process is the net result of spreading of a drop into a disc and pyrolytic reaction between the decomposed reactants. In the present study, as the droplets are finer than that of the conventional spray method, the discs of the droplets only require lesser temperature than that of the conventional spray method for the decomposition and film formation.
6.3.2. Structural studies

Figure 6.1. shows the diffraction patterns of the ATO films. The diffraction peaks reveal that the films are highly crystalline with the preferential orientation along the (110) plane. The other prominent peaks in the pattern are (101), (200), (211), (220), (310), (301) and (400). The preferred orientation remains predominant irrespective of the doping concentration of antimony in the starting solution and at the same time, the degree of preferred orientation increases with increasing doping ratio as indicated by the intensity of the peak. However, the intensities of the second and third stronger peaks (211) and (200) decrease gradually with increasing doping concentration. The variation in intensities of the (110) and (211) peaks as a function of antimony doping level in the starting solution are shown in Fig.6.2. These results reveal that the growth along the (110) plane enhances progressively as the Sb doping level increases. The matching of observed and standard interplanar distance d values confirm that the deposited films are of SnO$_2$ with tetragonal structure. The lattice parameters $a$ and $c$ are calculated from the equation (3.1) given in Chapter III [8, 9] and the values are listed in Table 6.1. It is observed that the lattice parameter value first decreases as the doping level increases up to 2.5 at-% and begins to increase for further doping. This variation can be explained as follows. Initially, for lower doping levels, $Sn^{4+}$ ions are replaced by $Sb^{5+}$ ions. As the ionic radius of $Sb^{5+}$ ions is lesser (62 pm) than that (71 pm) of the $Sn^{4+}$ ions, the lattice parameter values decrease gradually
up to the doping level 2.5 at.%. However, beyond that, according to Kojima et al., [10] Sn$^{4+}$ ions are replaced by Sb$^{3+}$ ions which have higher ionic radius (76 pm), resulting in an increase in the lattice parameters $a$ and $c$ increase. The average grain size $D$ of the films is determined using equation (2.3) given in Chapter II [11-13]. The sizes of the grains in all the cases are found to be in the nano range (70.2 – 79.2 nm). The grain size is found to increase as the Sb doping level increases which confirms the enhancement in the crystallinity of the films due to doping. These results are supported by the AFM images of the films. The number of grains per unit area $N$ [14, 15] of the films was calculated from the equation (2.4) given in Chapter II. The calculated structural parameters are summarised in Table 6.2.

<table>
<thead>
<tr>
<th>Doping Sb/Sn ratio (at.%)</th>
<th>Observed values* Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
</tr>
<tr>
<td>0.5</td>
<td>4.750</td>
</tr>
<tr>
<td>1.0</td>
<td>4.749</td>
</tr>
<tr>
<td>1.5</td>
<td>4.745</td>
</tr>
<tr>
<td>2.0</td>
<td>4.739</td>
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<tr>
<td>2.5</td>
<td>4.734</td>
</tr>
<tr>
<td>3.0</td>
<td>4.751</td>
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</table>

*Standard values of $a = 4.737$ Å and $c = 3.187$ Å, JCPDS Card No.41-1445.
Fig. 6.1. Patterns (XRD) of ATO films deposited from starting solutions having Sb/Sn ratios of (a) 0 at.% (undoped), (b) 0.5 at.%, (c) 1.0 at.%, (d) 1.5 at.%, (e) 2.0 at.%, (f) 2.5 at. % and (g) 3.0 at.%
6.3.3. Elemental analysis

![Elemental analysis diagram](image)

**Fig. 6.3.** Spectrum (EDX) of doped SnO$_2$: Sb (2.5 at.%) film
Table 6.2.

Structural parameters grain size ($D$) and number of grains/unit area ($N$) of ATO films

<table>
<thead>
<tr>
<th>Doping $Sb/ Sn$ ratio (at.%</th>
<th>$D$ (nm)</th>
<th>$N \times 10^{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>70.2</td>
<td>2.983</td>
</tr>
<tr>
<td>1.0</td>
<td>71.1</td>
<td>2.963</td>
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<td>1.5</td>
<td>76.8</td>
<td>2.435</td>
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<tr>
<td>2.0</td>
<td>78.1</td>
<td>2.278</td>
</tr>
<tr>
<td>2.5</td>
<td>79.2</td>
<td>2.075</td>
</tr>
<tr>
<td>3.0</td>
<td>78.6</td>
<td>2.166</td>
</tr>
</tbody>
</table>

The elemental analysis of the deposited films is carried out using the energy dispersive spectroscopy (EDS). Figure 6.3. shows the EDS spectrum of the film deposited from the starting solution having 2.5 at.% $Sb$. The spectrum confirms the presence of expected elements $Sn$, $O$ and $Sb$ in the films. The quantitative results given in the table reveal that the atomic percent of oxygen (66.13 at.%) is nearly two times that of the sum of the atomic percent of $Sn$ and $Sb$ ($30.64 + 2.43 = 33.07$ at.%). The ratio between the atomic percent values of $O$ and ($Sn + Sb$) is 1.999. Even though the ratio is almost 2, it does not confirm that the $SnO_2$ lattice is in perfect stoichiometric condition. There may be some oxygen vacancies and some interstitial incorporation of $Sn$ or $Sb$ ions in the lattice.
Although the proportion of Sb atoms with respect to the Sn atoms is only 3% in the starting solution, it is 7.3 % in the deposited film as estimated by EDS, indicating that the incorporation of Sb\(^{5+}\) ions in the SnO\(_2\) lattice has more chances than Sn\(^{4+}\), as the ionic radius of Sb\(^{5+}\) is lesser (62 pm) than that of the Sn\(^{4+}\) (71 pm). This interpretation is strongly supported by the enhancement in the intensity of the (110) plane due to doping. The increasing intensity of (110) plane with increasing Sb doping level in the starting solution suggests that the substitutional incorporation of Sn\(^{4+}\) by Sb\(^{5+}\) is predominant and the interstitial incorporation is negligible. From the structure factor calculations for (110) and (200) planes with different occupation probabilities of interstitial tin at sites (1/2, 0, 1/2) and (0, 1/2, 1/2), Agashe et al.,\(^{16}\) established that the structure factor value \(|F(110)|^2\) and the intensity of (110) plane are maximum when interstitial incorporation of Sn is negligible for undoped SnO\(_2\) film. On the basis of these observations, we can conclude that the increase in intensity of (110) plane in the SnO\(_2\):Sb films in the present study clearly shows that the Sb incorporation in the SnO\(_2\) lattice is mostly substitutional up to doping level 2.5 at.%. The decrease in sheet resistance up to this doping level also supports this conclusion. As the increase in grain size up to 2.5 at.% doping is an evidence for the enhancement in crystallinity, the increase in grain size can also be considered as another support to the above discussion, since proper incorporation in the lattice generally increases the degree of crystallinity.
6.3.4. Surface morphology

**Fig. 6.4.** Images (AFM) of ATO films deposited from starting solutions having Sb/Sn ratios of (a) 0.5 at.%, (b) 1.5 at.% and (c) 2.5 at.%
**Fig. 6.5.** Images (SEM) of ATO films deposited from starting solutions having $Sb/Sn = 2.5$ at.%
The surface morphology of the films is examined using the AFM and SEM images of the films. The AFM images of the films deposited from the starting solution having doping ratio $\text{Sb}/\text{Sn} = 0.5, 1.5$ and $2.5$ at.% are presented in Fig. 6.4. The AFM images clearly depict that the deposited ATO films are uniform, homogeneous and pin hole free with well developed and finely visible grains. The grain size value observed from the SEM image (Fig. 6.5) is in good agreement with the values obtained from the XRD results. The SEM image shows that the films have uniform closely packed petal shaped well defined grains.

6.3.5. Optical studies

The optical properties of the ATO films were investigated using the transmission and absorption spectra observed in the wavelength range 300 – 1100 nm. The transmission spectra recorded for different doping levels of antimony in tin oxide films are shown in Fig. 6.6. which depicts that the transmittance in the visible range is greater than $80\%$ for ATO films grown by this simplified technique, making them suitable for solar cell applications [17]. The transmittance in the near infrared range decreases considerably indicating the increase in reflectivity. The transmittance of the films found to decrease remarkably in the infrared range when the doping level increases. This may be due to the increase in carrier concentration in the ATO films at higher doping levels and
the calculated values are given in Table 6.3. The fundamental absorption which clearly shows itself by a rapid rise in absorption can be used to determine the band gap of materials. The absorption coefficient \( \alpha \) can be calculated from the transmittance \( T \) values [18, 19] at the absorption edge from the Lambert law \( \alpha = \ln \left( \frac{1}{T} \right)/t \). The variation of absorption coefficient against photon energy \( (hv) \) [20, 21] has the form of \( \alpha = A(hv-E_g)^{n/2} \), where \( E_g \) is the band gap, \( A \) is a constant related to the effective masses [using equation (3.2) and (3.3) given in
Chapter III] associated with the bands and \( n \) is a constant which is equal to one for a direct gap material and four for an indirect gap material.

**Table 6.3.**

Electrical and optical parameters of ATO films

<table>
<thead>
<tr>
<th>Doping Sb/Sn ratio (at.%)</th>
<th>Thickness (nm)</th>
<th>Sheet resistance (( \Omega /\square ))</th>
<th>Transmittance (%)</th>
<th>Figure of merit ( \times 10^{-2} ) (( \Omega^{-1} ))</th>
<th>Reflectivity (%) (in infrared range)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1032</td>
<td>6.90</td>
<td>88</td>
<td>4.04</td>
<td>93.04</td>
<td>3.26</td>
</tr>
<tr>
<td>1.0</td>
<td>1065</td>
<td>6.79</td>
<td>87</td>
<td>3.65</td>
<td>93.15</td>
<td>3.30</td>
</tr>
<tr>
<td>1.5</td>
<td>1103</td>
<td>6.73</td>
<td>85</td>
<td>2.92</td>
<td>93.21</td>
<td>3.44</td>
</tr>
<tr>
<td>2.0</td>
<td>1085</td>
<td>6.51</td>
<td>95</td>
<td>9.19</td>
<td>93.41</td>
<td>3.45</td>
</tr>
<tr>
<td>2.5</td>
<td>1031</td>
<td>6.34</td>
<td>90</td>
<td>5.56</td>
<td>93.58</td>
<td>3.59</td>
</tr>
<tr>
<td>3.0</td>
<td>1052</td>
<td>7.69</td>
<td>88</td>
<td>3.62</td>
<td>93.29</td>
<td>3.55</td>
</tr>
</tbody>
</table>

To determine whether the ATO films deposited using perfume atomiser have direct or indirect band gap, \((ah_v)^2\) versus \(h_v\) and \((ah_v)^{1/2}\) versus \(h_v\) plots were drawn. Since better linearity was obtained in the \((ah_v)^2\) versus \(h_v\) plots, the direct band gap values were determined by extrapolating the linear portion of these plots to the energy axis. The average optical transmittance and the estimated \( E_g \) values are presented
in Table 6.3. The values are found to be comparable with the earlier reports [22]. The increase in values of $E_g$ for higher doping may be attributed to the Moss–Burstein effect [23].

### 6.3.6. Electro-optical studies

![Graph showing the variation in sheet resistance as a function of antimony doping ratio in tin oxide films.](image)

**Fig. 6.7.** Variation in sheet resistance as a function of antimony doping ratio in tin oxide films

Sheet resistance $R_{sh}$ is a useful parameter in comparing thin films, particularly, those of the same material deposited under similar conditions. The plot of sheet resistance as a function of $Sb$ dopant concentration in the spray solution of ATO film is shown in Fig. 6.7. $R_{sh}$ is found to decrease as the antimony doping level increases and reach...
the minimum at the concentration $Sb/\text{Sn}$ $52.5$ at.%. The $R_{sh}$ value begins to increase for further doping. The reason for this trend is analysed in detail by Ravichandran and Philominathan [2]. The figure of merit ($\phi$) [24, 25] is calculated from the equation (1.1) given in Chapter I. The figure of merit is a good criterion to define the quality of highly transparent and conductive thin films [26]. The reflectivity $R$ [27] of the ATO films is calculated using the relation (4.1) and (4.2) given in Chapter IV, which is valid over a wide range in the infrared region.

The obtained $R$ values are lying between $92.29$ and $93.58$ %. These high values of $R$ of the ATO samples along with the good transmittance values make these films desirable for photothermal conversion also [28]. The ATO films prepared in this study were found to have desirable $\phi$ values [28] suitable for solar cell applications. The calculated $R_{sh}$, $\phi$ and $R$ values are given in Table 6.3.

6.4. REFERENCES


