Chapter III

EFFECT OF SOLVENT VOLUME ON THE PHYSICAL PROPERTIES OF UNDOPED AND FLUORINE DOPED TIN OXIDE FILMS DEPOSITED USING A LOW COST SPRAY TECHNIQUE

3.1. INTRODUCTION

Among the currently available transparent conducting oxide (TCO) materials, fluorine doped tin oxide (FTO) is one of the most competing cost effective substitutes for indium doped tin oxide which is widely used as transparent electrode in photovoltaic and other optoelectronic applications. Pure and fluorine doped tin oxide films have been prepared by various techniques such as electron beam evaporation (EBE) [1], chemical vapour deposition [2], pulsed laser deposition [3], sol–gel [4-6], thermal evaporation [7] and spray pyrolysis [8-11], etc. Among these techniques, spray pyrolysis is simple, inexpensive and has many other advantages such as easy doping and scalable processing in industrial productions, etc. [12, 13]. In the present study, undoped and fluorine doped tin oxide films are fabricated by employing a further simplified spray technique using perfume atomizer which has several advantages over conventional spray technique [14, 15] as explained in detail in Chapter II. Many researchers studied and reported the effect of concentration of the precursor solution on the physical properties of
undoped and fluorine doped tin oxide films. But in this study, the effect of solvent volume on the properties of these films have been studied systematically and reported which is not available in the literature to the best of our knowledge.

3.2. DEPOSITION PARAMETERS EMPLOYED

An aqueous solution of high pure $SnCl_2 \cdot 2H_2O$ was used as the starting solution. Fluorine doping was achieved by adding $NH_4F$ (10 wt.%) with the starting solution. Different sets of starting solutions were prepared by dissolving 2 g of $SnCl_2 \cdot 2H_2O$ with different volumes of (10, 20, 30, 40, and 50 ml) the solvent (doubly deionized water). A very small amount of $HCl$ (0.1 mol/l) was used to dissolve $SnCl_2 \cdot 2H_2O$ and $NH_4F$. This solution was magnetically stirred for 1 h and was followed by an ultrasonic agitation for 20 min. The precursor solution thus obtained was sprayed manually by means of a perfume atomizer on pre-heated (340 ± 5° C) glass substrates of dimensions $75 \times 25 \times 1.35$ mm$^3$. The temperature of the substrates was monitored using a temperature controller with chromel–alumel thermo couple. The intermittent spray deposition followed in this study is a two step procedure: a spray and 5 s interval. The schematic diagram of the experimental set up and other details have been already presented in Chapter II.

The substrates were pre-cleaned ultrasonically with organic solvents and doubly deionized water for degreasing and to remove the
contaminations if any, on the surface. The experiment was repeated several times to confirm the reproducibility.

X-ray diffraction patterns were recorded using X-ray diffractometer (PANalytical-PW340/60 X’pert PRO) which was operated at 40 kV and 30 mA with X-ray source of CuKα radiation having wavelength 1.5406 Å. Scanning electron microscopy (SEM) images, atomic force microscopy (AFM) images and optical transmission spectra were obtained using a scanning electron microscope (HITACHI-S-3000H), atomic force microscope (Veeco-di CPII) and the UV–Vis-NIR double beam spectrophotometer (Perkin Elmer LAMBDA-35) respectively. The electrical parameters were measured with the use of a four-point probe and Hall effect apparatus (ECOPIA HMS-3000) with van-der-Paw configuration.

3.3. RESULTS AND DISCUSSION

3.3.1. Structural studies

Fig. 3.1 shows the XRD patterns of the undoped tin oxide films grown from starting solutions having different solvent volumes. All the patterns fit well with the tetragonal structure of SnO₂ and contain the characteristic SnO₂ peaks only. The preferential orientation is along the (211) plane for the films deposited from solutions having lesser volume of solvent viz., 10 and 20 ml, whereas for the other three cases (30, 40 and 50 ml), the film grown along the (110) plane. These results are
strongly supported by the observations reported by Agashe et al., [16] for sprayed tin oxide films. They reported that the intensity of (211) peak is increased with the growth rate. In the present study, the growth rate is higher when the volume of the solvent is 10 and 20 ml, as the concentration of the solution in these two cases is comparatively higher. This result is an expected one, as generally, the growth rate is directly proportional to the impinging flux. Moreover, Chin-Ching Lin et al. [17] reported a (211) preferred orientation for FTO films deposited at lesser substrate temperatures (360° C). In the present work also the temperature of the substrate is kept at a lesser value (340°C). Beyond 30 ml, the degree of preferential orientation of (110) plane progressively increases as the volume of the solvent increases further.

Agashe et al. [18] reported a change in preferred orientation from (110) to (200), as the concentration of tin chloride increases in the starting solution because of the gradual incorporation of Sn at interstitial sites in the SnO₂ lattice. Similarly, Shanthi et al. [19] observed that above the optimum tin chloride concentration (0.1 g ml⁻¹) in the solution, the growth along (200) tends to increase and thereby the electro optical properties of the films degraded to a very large extent. But in the present study, even when the tin chloride concentration in the solution is 0.2 g ml⁻¹ (2 g dissolved in 10 ml of solvent), the films exhibited good electro optical properties (optical transparency and electrical conductivity). Hence, we can conclude that the process
conditions and spraying pattern employed in the present study may be suitable for the fabrication of good quality $SnO_2$ films from highly concentrated precursor solutions.

**Fig. 3.1.** X-ray diffraction patterns of $SnO_2$ films deposited from starting solutions having different solvent volumes.
The crystallite size of all the deposited films are calculated using the well known Scherrer’s formula [20] in equation (2.3) given in Chapter II. The sizes of the crystallites in all the cases are found to be in the nano range (60–98 nm). The size of the crystallites shows (Table 3.1) that the crystallinity of the films increases with the increase in solvent volume. The number of crystallites per unit area ‘N’ of the films is calculated with use of the equation [21] (2.4) given in Chapter II. The obtained values of ‘N’ [21] are presented in Table 3.1. The lattice constants ‘a’ and ‘c’ are estimated using the relation

\[
\frac{1}{d^2} = \left(\frac{h^2+k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \quad ------ (3.1)
\]

where \(d\) is the interplaner distance and \(hkl\) are Miller indices. The obtained values are well agreed with the reported results [22].

3.3. 2. Surface morphology

The SEM micrographs displaying the surface morphology of the undoped tin oxide films are shown in Fig.3.2. The surface of the films are homogeneous (practically no voids) and the well defined grains showed that the films are crystallized well. The films deposited from
solution having lesser solvent volume (10 ml) have grains like metal turnings with uniform size distribution.

The grain size of the film gradually decreases as the solvent amount increases, and the grain size appears saturated as the volume of the solvent reaches 40 ml. For higher solvent volumes, the surface has heavily packed needle shaped grains which is the characteristic feature of $SnO_2$ films. The AFM images (Fig.3.3) also support the above mentioned observations.

The XRD results (Section 3.3.1) showed that the crystallite size increases with the increase in the solvent volume, whereas the SEM images showed that the grain size of the film gradually decreases as the volume of the solvent increases. The results may seem to be contradictory in the first sight. But, actually it is not a contradiction as crystallite size and grain size are not necessarily the same, since a grain may be composed of multiple crystallites [23]. Crystallites are the “coherently diffracting domains” of crystals and grains may contain several of these domains. If we deform a single crystal, several sub grains having different orientations are formed. Then, each and every sub grain will be considered a crystallite. In other words, if a grain contains several sub grains, then each sub grain is a crystallite. As a special case, if a grain is made up of a single crystallite, then only the grain size and crystallite size have the same value.
In the present work, the grain size is the largest for the film deposited from 10 ml (Fig. 3.2a) solvent for which the crystallite size is the smallest (Table 3.1). It may be due to the fact that the grain is composed of two or more number of smaller crystallites i.e., the agglomeration of more crystallites takes place to form a grain in this case. This phenomenon of agglomeration of crystallites which causes an increase in the grain size is discussed by Losurdo et al. [24] for indium tin oxide films. In the case of the film prepared from 20 ml solution, the grain (Fig.3.2b) may be composed of comparatively lesser number of crystallites. Hence, the grain size is lesser, even though the crystallite size is slightly larger when compared with the previous case. This trend continues up to the film prepared from the solution having solvent volume 40 ml. For 40 and 50 ml cases (Fig.3.2d and e), the crystallite size appears to be equal to the grain size suggesting that the grain is composed of a single crystallite.

The change in the electrical resistivity of the tin oxide films as a function of solvent volume (discussed in the Section 3.3.3) can be correlated with the variation in the grain size as follows: when the grain size is larger, the charge transport is predominantly intra-grain resulting a substantial improvement in the electrical conductivity of the films. But in the case of smaller grains, the comparatively higher number of grain boundaries may act as low conductivity blockades making the resistivity higher [25]
**TABLE 3.1.**

Structural parameters of undoped tin oxide films.

<table>
<thead>
<tr>
<th>Volume of the solution (ml)</th>
<th>Lattice constants (Å) *</th>
<th>D (nm)</th>
<th>N (×10^{15})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4.729</td>
<td>3.191</td>
<td>60.66</td>
</tr>
<tr>
<td>20</td>
<td>4.713</td>
<td>3.222</td>
<td>74.94</td>
</tr>
<tr>
<td>30</td>
<td>4.743</td>
<td>3.197</td>
<td>94.93</td>
</tr>
<tr>
<td>40</td>
<td>4.749</td>
<td>3.206</td>
<td>97.11</td>
</tr>
<tr>
<td>50</td>
<td>4.750</td>
<td>3.193</td>
<td>98.09</td>
</tr>
</tbody>
</table>

*Standard lattice constant values \(a = 4.7382\,\text{Å}, c = 3.1871\,\text{Å}\) (JCPDS card no 41-1445)
Fig. 3.2. SEM images of undoped $\text{SnO}_2$ films deposited from solutions having solvent volume (a) 10 ml, (b) 20 ml (c) 30 ml, (d) 40 ml and (e) 50 ml.
Fig. 3.3. AFM images of undoped SnO$_2$ films deposited from solutions having solvent volume (a) 10 ml, (b) 20 ml (c) 30 ml, (d) 40 ml and (e) 50 ml.

3.3.3. Electrical studies

The sheet resistance and resistivity of the undoped and fluorine doped tin oxide films deposited from precursor solutions having varying solvent amount are presented in Table 3.2. For undoped tin oxide films, the $R_{sh}$ is 13.58 k$\Omega$ for 10 ml solution and the value increases sharply to 163.04 k$\Omega$ (by nearly 12 times) for 20 ml solution. Then it increases
gradually for further increase in the solvent amount as shown in the Table 3.2. The number of oxygen vacancies may be the main reason for the above said results. When the amount of solvent in the solution is very low (say 10 ml), the number of oxygen atoms offered by the solvent (water) is insufficient for the formation of stoichiometric SnO$_2$ structure. Hence, a large number of oxygen vacancies are present in the deposited film. The representative EDAX spectrum shown in Fig.3.4a and the quantitative results presented in the inset confirm the presence of oxygen vacancies in the tin oxide films prepared from solution having lesser solvent volume. In a perfect stoichiometric SnO$_2$ lattice, there would be two oxygen atoms for each Sn atom. i.e., for ‘m’ number of Sn atoms, there should be ‘2m’ number of oxygen atoms.

**TABLE 3.2.**

Electrical parameters of undoped and fluorine doped SnO$_2$ films.

<table>
<thead>
<tr>
<th>Volume of the solution (ml)</th>
<th>SnO$_2$</th>
<th>SnO$_2$:F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t$ (nm)</td>
<td>$R_{sh}$ ($\times 10^3 \Omega/\square$)</td>
</tr>
<tr>
<td>10</td>
<td>839</td>
<td>13.58</td>
</tr>
<tr>
<td>20</td>
<td>840</td>
<td>163.04</td>
</tr>
<tr>
<td>30</td>
<td>826</td>
<td>190.21</td>
</tr>
<tr>
<td>40</td>
<td>838</td>
<td>213.50</td>
</tr>
<tr>
<td>50</td>
<td>821</td>
<td>258.15</td>
</tr>
</tbody>
</table>
But, in the present study, the atomic percent of oxygen atoms (59.39) (Fig. 3.4a) is remarkably less than twice (81.22) the value of the existing Sn atomic percent (40.61) suggesting the presence of oxygen vacancies. Each of these oxygen vacancies creates a pair of free electrons in the $SnO_2$ lattice and thereby increases the carrier concentration ($n$). As the value of $R_{sh}$ is inversely proportional to the carrier concentration in the system, the $R_{sh}$ is very low in this case. The reported results of Agashe et al., [26] supported these discussions. They observed that the $SnO_2$ films contained a large proportion of oxygen vacancies as well as excess tin as interstitial incorporation, and consequently a high carrier concentration when the impinging flux (cationic and anionic) was high. It is noteworthy to mention here that, such a high carrier concentration in $SnO_2$ films can be occurred from any one or all of the following factors, [26] viz.,

1. presence of oxygen vacancies,

2. $Sn$ incorporation at interstitial sites and

3. inclusion of residual chlorine through the precursor 

\[(SnCl_2 \cdot 2H_2O).\]

It is clearly established that at high precursor concentration, the expected $Sn$ incorporation at interstitial sites provided conduction electrons due to an overlap of outer orbital when they can easily occupy the most spacious combination of interstitial lattice sites (1/2,0,1/2) and (0,1/2,1/2) [27, 19]. In addition, Agashe et al., [26] recorded that
for high precursor concentration, the interstitial Sn atoms play a major
role like oxygen vacancies in assigning a high carrier concentration.

But when the solvent (water) amount increases, the availability of oxygen atoms from the $H_2O$ molecules increases correspondingly, resulting a decrease in the number of oxygen vacancies which is obvious from the quantitative EDAX results of the film prepared from staring solution having solvent volume 20 ml (inset of Fig.3.4b). The EDAX results reveal that there are lesser oxygen vacancies in the system as the solvent volume increases (The EDAX results of 30, 40 and 50 ml solution are not shown). This reduction in oxygen vacancies causes a decrease in carrier concentration and consequently an increase in the $R_{sh}$ as shown in the Table 3.2. The carrier concentration values obtained for the samples are found to be strong supporting evidences for the above mentioned discussions.

The carrier concentration is $4.029 \times 10^{20}$ cm$^{-3}$ for the 10 ml film and the value of ‘$n$’ decreases as the volume of the solvent increases as shown in Fig.3.5. The carrier mobility ($I$) has an opposite trend as that of ‘$n$’ as expected which is also plotted in the same figure (Fig.3.5) as a function of volume of the solvent in the starting solution.
**Fig.3.4.** EDAX spectrum of undoped $SnO_2$ film deposited from solution having solvent volume (a) 10 ml and (b) 20 ml.

But when fluorine is doped with tin oxide films, the value of $R_{sh}$ decreases by three orders due to the substitutional incorporation of fluorine atoms in the oxygen sites. For 10 ml solution, the $R_{sh}$ is only 63.40 $\Omega/\square$ and the value decreases sharply to 15.39 $\Omega/\square$ (nearly four
times) for 20 ml film and then decreases gradually for further increase in the solvent volume as shown in the Table 3.2. Thus the variation in the $R_{sh}$ of FTO film has an exactly opposite trend as that of undoped tin oxide film. This decrease in $R_{sh}$ may be attributed to the progressive enhancement in the $F$ substitution caused by the reducing growth rate which in turn is due to the lesser value of impinging flux. Bilgin et al., [28] observed that the increasing $F$ incorporation reduces the growth rate of $SnO_2:F$ films. In the present study, as the impinging flux becomes lesser, the $F$ incorporation improves progressively. When the volume of the solvent in the starting solution increases, the total spray time also increases correspondingly which facilitates the increasing incorporation of fluorine in the $SnO_2$ lattice. Consequently, the carrier concentration increases, resulting in a decrease in the $R_{sh}$.

### 3.3.4. Optical studies

The transmission spectra of the $SnO_2$ films deposited from starting solutions having different solvent volumes are shown in Fig. 3.6a. The variations in the solvent volume affect markedly the optical properties. For film prepared from 10 ml solvent, a high transmittance (93%) is obtained for wavelength $\lambda = 550$ nm. However, as the solvent volume increases, the transmittance decreases gradually as shown in the Fig.3.6a which may be attributed to the decrease in the grain size. Roman et al. [29] observed similar grain size dependent optical transmittance results for the sprayed $SnO_2$ films. It is also
observed that the optical absorption edge slightly shifts towards the red, as the solvent amount increases, indicating a gradual decrease in the optical band gap ($E_g$). In FTO films, an opposite trend is observed which is shown in Fig. 3.6b. The sharp absorption edges obtained for all cases clearly show the good crystallinity of the films. The interference patterns (crests and troughs) observed for the spectra confirm the uniformity in the thickness of the films. The fundamental absorption which clearly shows itself by a rapid fall in the transmission can be used to determine the band gap of materials.

**Fig. 3.5.** Variation in carrier concentration and mobility as a function of volume of solvent in the starting solution.
Fig. 3. 6. Transmission spectra of (a) undoped and (b) fluorine doped SnO$_2$ films deposited from starting solutions having different solvent volumes.

Fig. 3. 7. Plots of $(ahv)^2$ vs $h\nu$ for (a) undoped and (b) fluorine doped SnO$_2$ films.
The absorption coefficient ($\alpha$) can be calculated from the transmittance ($T$) values at the absorption edge from the Lambert law

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{t} \quad ----- \quad (3.2)$$

The variation of absorption coefficient [25] against photon energy ($h\nu$) has the form of

$$\alpha = A(h\nu - E_g)^{n/2} \quad ----- \quad (3.3)$$

where $E_g$ is the band gap, ‘$A$’ is a constant related to the effective masses 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 3.3.**

Optical band gap of undoped and fluorine doped SnO$_2$ films.

<table>
<thead>
<tr>
<th>Volume of the solution (ml)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{SnO}_2$</td>
</tr>
<tr>
<td>10</td>
<td>3.98</td>
</tr>
<tr>
<td>20</td>
<td>3.90</td>
</tr>
<tr>
<td>30</td>
<td>3.88</td>
</tr>
<tr>
<td>40</td>
<td>3.85</td>
</tr>
<tr>
<td>50</td>
<td>3.83</td>
</tr>
</tbody>
</table>
To determine whether the undoped tin oxide and FTO films deposited using the simplified spray technique have direct or indirect band gap, \((ahv)^2\) vs \((hv)\) and \((ahv)^{1/2}\) vs \((hv)\) plots are drawn. Since better linearity is obtained in the \((ahv)^2\) vs \((hv)\) plots, the direct band gap values are determined by extrapolating the linear portion of these plots to the energy axis (Fig. 3.7a and b). The optical band gap \((E_g)\) is estimated to be in the range of 3.98–3.83 eV and 3.77–3.95 eV for undoped tin oxide and FTO films respectively and the values are presented in Table 3.3. The presence of higher band gap observed can be understood on the basis of the knowledge of Moss–Burstein effect. In FTO films, the decrease in the optical transmittance with the increase in the solvent volume may be caused by the increasing incorporation of fluorine atoms in the \(\text{SnO}_2\) lattice [30]. The results conveyed that the films prepared from starting solutions having lesser solvent volume have better optical properties than their higher solvent volume counterparts for undoped tin oxide films whereas in the case of FTO films higher solvent volume films have good optical characteristics.

3.5. REFERENCES


Chapter IV

EFFECT OF SOLVENT VOLUME ON THE PHYSICAL PROPERTIES OF SPRAYED FLUORINE-DOPED ZINC OXIDE THIN FILMS

4.1. INTRODUCTION

Many kinds of TCO materials have been developed until now, but only a limited number of materials such as zinc oxide (ZnO), indium oxide (In$_2$O$_3$), cadmium oxide (CdO) and tin oxide (SnO$_2$) based TCO are in practical use for conventional transparent electrode applications [1].

Of the above mentioned TCOs, zinc oxide based films have attracted more attention due to the various advantages they have over others. The multifunctional ZnO material is one of the most promising candidates for the fabrication of the next generation of opto electronic devices. Besides being a wide band gap semiconductor with a band gap energy of 3.37 eV, ZnO has several desirable characteristics such as high transmittance in the visible region, low electrical resistivity and non toxicity [2, 3]. More interest has been shown on TCOs based on doped ZnO films with cationic dopants such as Al, Ga, or B. In recent days, several investigations in which fluorine was used as anionic dopant can be found in the literature, due to the stability of fluorine doped ZnO films (FZO) which makes them a potential candidate for