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Effect of solvent volume on the optical properties of SnO$_2$:F films deposited by a simplified spray technique

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Transparent conducting fluorine doped tin oxide (FTO) films are fabricated onto glass substrates using a simplified spray pyrolysis technique at a substrate temperature of 340°C. The optical constants such as refractive index, absorption coefficient, extinction coefficient are estimated using the Swanepoel method and the solvent volume dependence of these optical constants are investigated in detail and reported. The refractive index ($n_f$) of the film is found to be in the range of 1.671-1.675. It is observed that the refractive index increases sharply near the optical absorption edge and the $n_f$ decreases with the increase in the solvent volume which may be mainly attributed to the increase in the carrier concentration. The optical band gap (3.62 – 3.70 eV) and the band edge sharpness of the films are found to be increased with the solvent volume.

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Keywords: Tin oxide thin films, Absorption coefficient, Extinction coefficient and Refractive index

1. Introduction

Tin oxide is the first transparent conductor to have received significant commercialization [1- 3] due to its wide range of applications such as touch panels [4], electroluminescent display [5] and protective coatings [6]. Among the various transparent conductive oxides, SnO$_2$ films doped with fluorine seem to be the most appropriate for use in solar cells, due to its low electrical resistivity and good optical transmittance. Being a wide band gap semiconductor ($E_g = 3.6$ eV), these films are attractive for many optoelectronic device [7] applications.

The knowledge of the optical constants such as refractive index, absorption coefficient, along with dielectric constant, is of great interest in the design and analysis of materials to be used in optoelectronics. In addition to that, optical measurements are extensively used for the characterization of composition and quality of the materials. Refractive index is one of the key properties of an optical material, owing to its close relationship with the electronic polarizibility of ions and the local field inside the materials. The estimation of refractive indices of optical materials for different wavelength ranges is important for the applications in integrated optic devices, such as switches, filters and modulator etc. [8]. Keeping the above mentioned observations in mind, in the present study, the effect of solvent volume on the optical properties of fluorine doped tin oxide films are investigated in detail.

The optical properties along with the thickness of the films can be determined by classical oscillator fit procedure, the Kramers-Kronig analysis and Swanepoel method [9, 10]. Of these methods, Swanepoel method is widely used because it enables the determination of the refractive index and other optical constants from the normal incident optical transmittance spectrum only [11]. In the present work, Swanepoel method is employed for the determination of the above said optical constants of fluorine doped tin oxide films.

In the form of a thin film, SnO$_2$:F has been prepared by various techniques such as electron beam evaporation (EBE) [12], chemical vapour deposition (CVD) [13], sol gel [14], pulsed laser deposition (PLD) [15, 16], sputtering [17] and spray pyrolysis [18-22] etc. Of these techniques, spray pyrolysis is well-suited for the preparation of doped tin oxide thin films because of its high growth rate, ease of adding various doping materials, reproducibility and mass production capability for uniform large area coatings and most importantly its simple and inexpensive experimental arrangement which are desirable for industrial applications [23, 24]. In the present study, fluorine doped tin oxide (FTO) films are fabricated by employing a further simplified spray technique using perfume atomizer [25], generally used for cosmetic purpose.

2. Experimental method

Fluorine doped tin oxide films are deposited by a low cost and simplified spray pyrolysis method using perfume atomizer. The experimental set up and other process details are reported elsewhere [25]. SnCl$_2$.2H$_2$O is used as the host precursor and fluorine doping was achieved by adding NH$_4$F (10 wt. %) with the precursor solution. Five sets of starting solutions are prepared by dissolving 1 g of SnCl$_2$.2H$_2$O with different volumes of (10, 20, 30, 40, and...
50 ml) doubly deionized water. This solution was magnetically stirred for 1 h which is followed by an ultrasonic agitation for 20 min. The precursor solution thus obtained is sprayed manually by means of a perfume atomizer on pre-heated glass substrates of dimensions 75 x 25 x 1.35 mm\(^2\). The temperature of the substrates is maintained at 340 ±5°C using a temperature controller with chromel–alumel thermocouple. The intermittent spray cycle followed in this study consists of two steps viz.: a spray of 1 s and an interval of 5 s. Several sets of films with same deposition conditions are fabricated to confirm the reproducibility. The optical transmission spectra are obtained using UV–Vis-NIR double beam spectrophotometer (Perkin Elmer LAMBDA-35). Veeco-di CP-II atomic force microscopy is employed to investigate the surface morphology of the films.

3. Results and discussion

3.1 Determination of optical constants

The optical transmission spectra of the SnO\(_2\):F films prepared from starting solutions having different solvent volumes are shown in Fig.1. The volume of the solvent in the starting solution influences the film structure remarkably which in turn affects the optical properties as seen in Fig.1.

![Fig.1. Transmission spectra of FTO films.](image)

The optical transmittance in the visible and near infrared range decreases markedly as the solvent volume in the starting solutions increases. This decrease in transmittance can be understood on the basis of the fact that the transmittance generally decreases when the carrier concentration of the heavily doped semiconductor increases [26]. For example, Muiva et al. [27], in their study on aluminium doped zinc oxide films, observed that there is a doping level dependent reduction in the transmittance which is attributed to the strong scattering of absorption of photons by the increased number of carrier concentration resulted from the defects created in the ZnO lattice. In the present study, when the solvent volume increases, the spray flux density decreases which makes the growth rate slow and thereby enhances the probability of substitutional incorporation of fluoride ions in the oxygen sites. Consequently, the carrier concentration increases as reported in our previous study [22]. This variation in the carrier concentration as a function of solvent volume is confirmed by the obtained optical band gap values as discussed in the section 3.2.

The interference fringes appeared in the spectra clearly showed that the thickness of the films is uniform. These interference fringes can be used to estimate the refractive index of the films by employing the envelope method proposed by Swanepoel [10, 28] using the following equations,

\[ n_f = \left[ M + \left( 2n_f^2 - n_e^2 \right) \frac{\lambda^2}{4M} \right]^{1/2} \]  
\[ M = 2n_e^2 \frac{T_m - T_e}{T_e - T_m} + \frac{kM}{t} \]  

where \( T_m \) and \( T_e \) are the transmittance for maxima and minima and \( n_e \) is the refractive index of the substrate. By interpolating the envelopes corresponding to \( T_m \) and \( T_e \), the refractive indices of the films for different wavelength values are determined. The refractive index \( n_f \) of the film is found to be in the range of 1.671-1.675. The variation in the refractive index as a function of wavelength of the incident radiation (\( \lambda \)) is shown in Fig 2. The plots clearly showed that the variation in \( n_f \) with respect to the wavelength is very minimal in the visible range for all the films irrespective of the solvent volume. The decrease in \( n_e \) with the increase in the solvent volume may be mainly attributed to the increase in the carrier concentration as reported by Caglar et al. for Al doped zinc oxide films [8]. Even though the refractive index in the visible region changes a little, it varies sharply at the absorption edge especially in the case of higher solvent volume.

The extinction coefficient is calculated using the equation

\[ k = \frac{\alpha}{t} \]

where \( \alpha \) is the absorption coefficient. The absorption coefficient is given by the relation [29,30]

\[ \alpha = \frac{2}{t} \ln(\frac{T}{T_e}) \]

where \( t \) is the thickness of the film and \( T \) is the transmittance. The wavelength dependence of absorption coefficient and extinction coefficient are shown in Fig.3 and 4 respectively. The \( \alpha \) and \( k \) values are found to oscillate in the visible region monotonically for all solvent volumes and increase suddenly at the absorption edge. The thickness of the films can be obtained by knowing the values of the refractive indices \( n_1 \) and \( n_2 \) at two
consecutive maxima or minima corresponding to the wavelength $\lambda_1$ and $\lambda_2$ using the following equation

$$n = \frac{\Delta \lambda}{2B_2 n_2 - B_1 n_1}$$

(5)

Step 1: By interpolating the successive maxima and minima of the transmission spectra, envelops are drawn.

Step 2: The refractive indices corresponding to the various wavelength values are estimated using the relation (1) and (2).

Step 3: A plot for $n$ as a function of $\lambda$ is drawn (Fig.2).

Step 4: The average value of the $t_{pre}$ obtained from each two adjacent maxima (or minima) appeared in the $n$ vs $\lambda$ plot is found out.

Step 5: Using equation

$$2m_{est} = n t_{pre}$$

(5)

the order number ($m_{est}$) for each extreme from the average value of $t_{pre}$ and $n_{pre}$ is estimated.

Step 6: Each of the resulting $m_{est}$ is rounded off to the closest integer for maxima and half integer for minima. (these rounded off value of $m_{est}$ will be considered as the exact order number $m_{exact}$).

Step 7: Using $m_{exact}$ and $n_{pre}$, the accurate thickness $t_{accurate}$ is calculated.

Step 8: Finally, from $m_{exact}$ and $t_{accurate}$, the accurate refractive index $n_{accurate}$ is evaluated for each maximum and minimum using equation

$$2m_{est} = n t_{accurate}$$

(6)

Table 1. Thickness and optical parameters of FTO films.

<table>
<thead>
<tr>
<th>Solvent volume (ml)</th>
<th>Thickness (nm)</th>
<th>$B_0 \times 10^{14}$ (eV m²)</th>
<th>$n_f$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>787</td>
<td>0.7653</td>
<td>1.7768</td>
<td>3.62</td>
</tr>
<tr>
<td>20</td>
<td>734</td>
<td>4.8645</td>
<td>1.7972</td>
<td>3.64</td>
</tr>
<tr>
<td>30</td>
<td>770</td>
<td>6.038</td>
<td>1.8106</td>
<td>3.66</td>
</tr>
<tr>
<td>40</td>
<td>812</td>
<td>7.454</td>
<td>1.8311</td>
<td>3.67</td>
</tr>
<tr>
<td>50</td>
<td>682</td>
<td>7.418</td>
<td>1.8252</td>
<td>3.70</td>
</tr>
</tbody>
</table>

$B_0$ - Band edge sharpness, $n_f$ – Refractive index of the film, $E_g$ – Optical band gap.
3.2 Optical band gap study

Fig. 5 shows the Tauc’s plots [31] drawn between \((αhν)^2\) and \(hν\). The optical band gap (\(E_g\)) is estimated by extrapolating the linear portion of the Tauc’s plot to the energy axis. The \(E_g\) values of the films are also determined from the plots (Fig.6) drawn between the first derivative of the transmittance \((dT/dλ)\) with respect to wavelength and the average wavelength \(λ_{average}\).

The corresponding values obtained from the two methods are comparable with each other and the average values are presented in Table 1. The obtained values of \(E_g\) are plotted as a function of solvent volume in the starting solution (Fig.7). The plot clearly shows that optical band gap progressively increases with the solvent volume. This increase in the band gap is associated with the Moss-Burstein effect [22]. According to the Moss-Burstein theory, donor electrons occupy the conduction band states at the bottom in heavily doped n-type semiconductor films. The valance electrons, therefore, require an additional energy to be excited to a higher energy state in the conduction band indicating an increase in the optical band gap. In other words, we can say that the increase in the solvent volume causes an increase in the carrier concentration. This results is a strong supporting evidence for the discussion (section 3.1) on the effect of solvent volume on the refractive index.

![Fig. 5 Plot of \((αhν)^2\) vs \(hν\)](image)

![Fig. 7 Variation in \(E_g\) with respect to solvent volume](image)

![Fig. 8. Band edge sharpness as a function of solvent volume](image)

![Fig. 6 Plot of dT/dλ vs \(λ_{average}\)](image)

![Fig. 9 AFM image of FTO film (30 ml).](image)

![Fig. 9 AFM image of FTO film (30 ml).](image)

The band edge sharpness value (\(B_s\)) was estimated from the slope of the Tauc’s plot in the range of band-to-band absorption. The lowest value of \(B_s\) is obtained for the film prepared from the lowest solvent volume (10 ml) which indicates the presence of a large number of crystal defects. The \(B_s\) increases gradually with the solvent volume and attains a maximum value for 40 ml which shows the progressive enhancement in the degree of crystallinity of the films. Beyond 40 ml, the \(B_s\) appears to be saturated (Fig 8).
One of the atomic force micrographs (AFM) of the FTO films (30 ml) is presented as a representative image in Fig. 9. The image depicts that the surface of the films have closely packed, nearly uniform sized grains.

4. Conclusion

The optical constants such as refractive index, absorption coefficient and extinction coefficient along with the thickness of the FTO films prepared from starting solutions having different solvent volumes are determined by employing the Swanepoel method. The refractive index is found to be in the range of 1.671 - 1.675. The slight decrease in the refractive index with the increase in the solvent volume may be mainly attributed to the increase in the carrier concentration. The absorption coefficient and extinction coefficient values increased sharply at the absorption edge for all the films irrespective of the solvent volume. The optical band gap progressively increases with the solvent volume. This increase in the band gap is associated with the Moss-Burstein effect.

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References


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Effect of solvent volume on the physical properties of sprayed fluorine-doped zinc oxide thin films

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Key words spray pyrolysis, optoelectronic devices, optical and electrical properties, structural properties.

Fluorine-doped zinc oxide (FZO) films were deposited from aged starting solutions having different solvent volumes (10, 20, 30, 40 and 50 ml) using a simplified spray pyrolysis technique. The electrical studies showed that the resistivity is minimum (4.68 × 10⁻² Ω cm) for lowest solvent volume (10 ml) and the value progressively increased with the increase in the solvent volume indicating that the fluorine incorporation increases with solvent volume. The systematic study clearly showed that the spray flux rate plays a crucial role in determining the electrical, optical, surface and structural properties of the FZO films. The optical transparency is found to be gradually increased (from 85 to 95%) as the volume of the solvent increases. The scanning electron microscope images depicted that the decrease in the spray flux rate caused an enhancement in the grain size. The X-ray diffraction profile clearly showed that all the films have preferential orientation along the (002) plane with hexagonal wurtzite structure.

1 Introduction

Recently, there is a worldwide interest in developing low cost and good quality transparent conducting oxides (TCO) for the development of transparent electronics and photonic devices, transparent conducting electrodes for photovoltaic cells, flat panel displays, green LEDs, piezoelectrical devices [1-3], ultraviolet laser diodes, acousto-optical devices, gas sensing devices [4-7], etc. Many kinds of TCO materials have been developed until now, but only a limited number of materials such as zinc oxide (ZnO), indium oxide (In₂O₃), cadmium oxide (CdO) and tin oxide (SnO₂) based TCO are in practical use for conventional transparent electrode applications [8].

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 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 [9,10]. 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 solar cell technology. Fluorine contributes one free electron to the ZnO lattice making the resistivity lesser when it enters in a substitutional form into the ZnO matrix [11].

The ZnO thin films can be prepared by a variety of methods such as chemical vapour deposition (CVD) [10], dc reactive magnetron sputtering [13], rf magnetron sputtering [14], metal organic chemical vapour
deposition (MOCVD), molecular beam epitaxy (MBE) [15], sol–gel process [16], pulsed laser deposition [17], chemical bath deposition [3], etc. Of these methods, the spray pyrolysis technique has several advantages over the others such as low cost, safety, easy handling and large area deposition [11]. This technique does not require vacuum conditions, and by employing different deposition parameters, one can control the microstructure and surface features of the films [18,19]. In the present work, FZO films are fabricated by employing a further simplified spray pyrolysis technique using perfume atomizer which has several additional advantages [20] over the conventional spray technique. Many researchers studied and reported the effect of concentration of precursor on the physical properties of FZO films. But the increase in the concentration of the starting solution with the same amount of solvent volume causes an unintentional increase in the thickness of the films which would affect the properties of the films undesirably. Therefore, in the present study, for the first time to the best of our knowledge, the effect of volume of the solvent on the physical properties of FZO films, has been investigated and reported. In this study, the volume of the solvent is varied from 10 ml to 50 ml in steps of 10 ml keeping the amount of precursors (host as well as dopant) constant. This variation in solvent volume determines the spray flux rate impinging on the hot substrate. Hence we can also say that this study is related to the spray flux dependent characteristics of the FZO films.

2 Experimental

Pure and fluorine-doped zinc oxide thin films were deposited onto ultrasonically cleaned corning glass substrates, by a simplified spray pyrolysis method using a perfume atomizer. Details of the simplified spray system have been described elsewhere [21]. Zinc acetate dihydrate [Zn (CH$_3$COO)$_2$ · 2H$_2$O] and ammonium fluoride [NH$_4$F] were used as host and dopant precursors, respectively. Doubly deionized water, methanol and acetic acid were used as solvents with a ratio 7:2:1, respectively. Different sets of starting solutions were prepared by dissolving 2 g of zinc acetate dihydrate and 0.2 g of ammonium fluoride with different volumes (10, 20, ..., 50 ml) of solvent. All sets of solutions are aged four days in order to enhance the fluorine incorporation efficiency into the ZnO lattice. Though different researches reported different aging times for achieving minimum electrical resistivity [22-25], in the present study, this aging time of four days is selected because this value is found to be the optimum for our deposition conditions.

The proportions of solvents, the molar concentration of the starting solutions and the calculated spray flux rate are given in table 1. The precursor solution was sprayed onto the preheated glass substrates kept at optimized substrate temperature of 350±5 °C. The substrate temperature was continuously sensed by a temperature controller with chromel–alumel thermocouple. In the intermittent deposition followed in this study, each cycle consisted of a spray and 10 s interval. After the completion of the each deposition process, the substrate was taken out, washed with doubly deionized water and dried out. Several sets of films were fabricated repeatedly in order to confirm the reproducibility. The structural properties of the as-grown ZnO:F films were investigated by X-ray diffractometer (PANalytical-pw 340/60 X’pert pro) with CuK$_\alpha$ radiation (\(\lambda = 0.1542 \text{ nm}\)). The optical transmission spectra were obtained using the UV-Vis-NIR double beam spectrophotometer (Perkin Elmer (LAMBDA-35)). Scanning electron microscopy (SEM) images were recorded using a scanning electron microscope (HITACHI S-3000H). The electrical sheet resistance (\(R_{sh}\)) of the FZO films is observed using a linear four probe apparatus. Thickness of the films was measured with a profilometer (Surf Test SJ-301) and the obtained values were found to be comparable with that estimated using the weight gain method. The thickness values were in the range of 580–597 nm as given in table 2.

<table>
<thead>
<tr>
<th>Solvent volume (ml)</th>
<th>Proportions of solvents (ml) in the given order (deionized water: methanol: acetic acid)</th>
<th>Molar concentration (M)</th>
<th>Spray flux rate (g/spray)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7:2:1</td>
<td>0.911</td>
<td>0.0227</td>
</tr>
<tr>
<td>20</td>
<td>14:4:2</td>
<td>0.456</td>
<td>0.0116</td>
</tr>
<tr>
<td>30</td>
<td>21:6:3</td>
<td>0.304</td>
<td>0.0075</td>
</tr>
<tr>
<td>40</td>
<td>28:8:4</td>
<td>0.229</td>
<td>0.0060</td>
</tr>
<tr>
<td>50</td>
<td>35:10:5</td>
<td>0.182</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

Table 1 | Control parameters employed in the deposition process.
3 Results and discussion

Electrical properties  The resistivity $\rho$ values are obtained by finding the products of magnitudes of sheet resistance and the thickness of the films ($\rho = R_{sh}t$). The variation in sheet resistance and resistivity of the FZO films as a function of volume of the solvent is shown in figure 1. It is found that the resistivity is minimum for the film prepared from the lowest solvent volume (10 ml). Then the resistivity value increases gradually as the solvent volume increases as shown in figure 1. This interesting phenomenon can be explained on the basis of the following two factors which play crucial roles in creating free charge carriers in the ZnO lattice [26]:

1. The number of oxygen vacancies created in the ZnO lattice, each of which results in a pair of free electrons.
2. The substitutional incorporation of fluorine in an oxygen site of the ZnO lattice, which contributes a free electron to the system.

When the solvent volume is minimum (say 10 ml), the spray flux density is maximum in each spray. In other words, the number of Zn and F species reaching the hot substrate in each spray is maximum. Therefore, during the formation of film layers, as the number of available Zn atoms is higher, there is lack of oxygen atoms to form a stoichiometric ZnO matrix and hence oxygen [27] vacancies are created in the lattice, which offer free electrons to the system. These free electrons contributed by the oxygen vacancies, cause an increase in the carrier concentration which in turn causes a decrease in the electrical resistivity. When the solvent volume increases (20, 30 ml and so on), the amount of Zn species reaching the hot substrate in each spray gradually decreases. Hence, the probability of the availability of oxygen atoms, to pair up with the comparatively lesser number of Zn atoms provided by the diluted flux, gradually increases resulting in a decrease in the number of oxygen vacancies which in turn results in an increase in the resistivity.

Optical studies  The optical transmittance spectra of the FZO films prepared from starting solutions having different volumes of the solvents are shown in figure 2. The optical transmittance at the wavelength of 550 nm ranges from 85-95%. Table 2 clearly shows that the transmittance (%) at the wavelength of 550 nm increases progressively, as the volume of the solvent in the starting solution increases. This result agrees well
with the report of Rodriguez-Baez et al. [28]. They observed that at high molar concentrations of the precursor, the FZO films showed a reduction in the optical transmission.

Table 2  Thickness and optical parameters of FZO films.

<table>
<thead>
<tr>
<th>Solvent volume (ml)</th>
<th>Thickness (nm)</th>
<th>$dT/d\lambda$ vs. $\lambda_{average}$ plots (eV)</th>
<th>Tauc’s plot (eV)</th>
<th>Transmittance (%) at 550 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>597</td>
<td>3.31</td>
<td>3.30</td>
<td>85.2</td>
</tr>
<tr>
<td>20</td>
<td>580</td>
<td>3.30</td>
<td>3.28</td>
<td>87.5</td>
</tr>
<tr>
<td>30</td>
<td>583</td>
<td>3.29</td>
<td>3.27</td>
<td>92.0</td>
</tr>
<tr>
<td>40</td>
<td>590</td>
<td>3.28</td>
<td>3.26</td>
<td>93.3</td>
</tr>
<tr>
<td>50</td>
<td>596</td>
<td>3.24</td>
<td>3.25</td>
<td>95.5</td>
</tr>
</tbody>
</table>

In transparent metal oxides, metal to oxygen ratio decides the percentage of optical transmittance and a metal rich film usually exhibits less transparency [29]. In the present work, it is already discussed in the previous section that when the concentration is high (solvent volume is 10 ml), more Zn species impinge on the hot substrate in each spray, with lack of oxygen atoms in the vicinity of the growth centers to form a stoichiometric ZnO matrix. Due to this reason, we can expect the formation of a metal rich film. Hence, the optical transmittance is low (85%) in this case compared to other films, which are deposited from solutions with lower concentration or in other words, higher solvent volume (solvent volume 20, 30, 40 and 50 ml). Another important result which is worth mentioning here is that, the transmittance in the near infrared (IR) region is very low for the lowest solvent volume. This may be attributed to the higher IR reflectivity of the film. Generally, the IR reflectivity $R$ is greater, when the sheet resistance is lesser [30], according to the relation $R = \frac{1}{1 + \frac{1}{\varepsilon_0} C_0 R_{sh}}$, where $1/\varepsilon_0 C_0 = 376 \, \Omega$ which is valid over a wide range of the IR region. This result provides a strong evidence for the discussion, presented in the electrical studies, about the carrier concentration.

All the films have sharp absorption edges indicating the good crystallinity of the films [31]. Eventhough all the films have good band edge sharpness, there is a slight difference in the degree of sharpness as seen in figure 3, which shows the expanded band edge portions of the transmission spectra.

Figure 4 shows the plots of $(\alpha h\nu)^2$ as a function of $h\nu$ (Tauc’s plot) where $\alpha$ is the optical absorption coefficient and $h\nu$ is the energy of incident photons. The absorption coefficient $\alpha$ is calculated from the relation $\alpha = 1/t \ln(1/T)$ where $t$ is the thickness of the film and $T$ is the optical transmittance. The band edge sharpness value ($B_s$) was obtained from the slope of the Tauc’s plot in the range of band-to-band absorption. The band edge sharpness of the films is minimum (Fig. 5) in the case of the film corresponding to the lowest solvent volume (10 ml) indicating the comparatively larger number of crystal defects. The band edge sharpness then increases gradually as the solvent volume increases up to 30 ml which shows the progressive
improvement in the degree of crystallinity of the films. Beyond 30 ml, the band edge sharpness appears to be saturated. These results are compatible with the results observed in the surface morphological studies.

Fig. 4 Tauc’s plots for FZO films.

From Tauc’s plots, we can estimate the optical band gap $E_g$ values by the extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ as shown in figure 4. For calculating $E_g$, the above method is followed because ZnO is a direct transmission semiconductor for which $\alpha$ is related to $E_g$ by the relation: $\alpha = A/h\nu(h\nu-E_g)^{1/2}$, where $A$ is a constant. $E_g$ values are found to be around 3.31 to 3.24 eV. The $E_g$ values are also calculated using the plots (Fig. 6) drawn between the first derivative of transmittance with respect to wavelength ($dT/d\lambda$) and the average wavelength ($\lambda_{average}$). These values are found to be in good agreement with that obtained from the former method, as seen in table 2.

The $E_g$ value is found to be decreased gradually as the volume of the solvent in the starting solution is increased as seen in figures 4 and 6. This shift in $E_g$ towards lower energy is associated with the Moss–Burstein (MB) effect [32,33]. The MB effect is related to the lifting of the Fermi level into the conduction band of degenerate semiconductors which leads to the band energy gap broadening (blue shift). This phenomenon is based on the fact that when the carrier concentration of a semiconductor exceeds a critical value, the electronic states overcome the bottom of the conduction band resulting in an increase in the band gap energy. Consequently, more amount of photon energy is required for optical transition from the top of the valance band to the conduction band. The shift in the $E_g$ associated with the MB effect ($\Delta E_g$) in this study is
70 meV. This enhancement in $E_g$ is another strong supporting evidence for the discussion given in the electrical studies related to the higher value of the carrier concentration observed when the volume of the solvent is less. In the electrical studies, it is observed that the carrier concentration decreases gradually as the volume of the solvent in the starting solution increases.

**Surface morphology and X-ray diffraction studies** The SEM images of FZO films prepared from starting solutions having solvent volume 10 ml, 30 ml and 50 ml are shown in figure 7. The deposits appear to be composed of uniformly distributed small spherical grains. The grain size is found to be 150 nm (Fig. 7a) for the film deposited from starting solution having solvent volume 10 ml and the grain size is 185 nm and 200 nm for solvent volumes 30 ml and 50 ml, respectively (Fig. 7b,c). i.e the size of the grains increases progressively as the volume of the solvent increases suggesting a slight increase in the degree of crystallinity of the films. This result is an evidence for the gradual decrease in the fluorine incorporation into the ZnO lattice, with the increase in the solvent volume and this result agrees well with the observations of Yakuphanoglu et al. [34]. They reported that the crystallinity of the sprayed FZO films enhances and the crystallite size becomes larger with the decrease in the fluorine content. In other words, eventhough the surface morphology of the films does not influence directly the resistivity of the films to a notable extent, the slight increase in the grain size may be due to the lesser incorporation of fluorine atoms which in turn causes an increase in the resistivity.

![Fig. 7](image_url) SEM images of FZO films prepared from starting solutions having solvent volume (a) 10 ml (b) 30 ml and (c) 50 ml.

![Fig. 8](image_url) X-ray diffraction patterns of FZO films.

The XRD spectra of the FZO films prepared from the starting solutions, having solvent volumes 10 ml, 30 ml and 50 ml are shown in figure 8. The peaks of the XRD patterns are corresponding to those of the ZnO patterns from the JCPDS data file [35] (card no: 36-1451), with a hexagonal wurtzite structure. Even though all the films have a preferential orientation along the (002) plane irrespective of the solvent volume, the peak corresponding to lowest solvent volume (10 ml) is comparatively shorter and broader (Fig. 8a), indicating the lower degree of crystallinity. But when the solvent volume increases, the intensity and sharpness of the peak
are found to increase gradually, as shown in figure 8b, c. This increase in the crystalline quality of the film is ascribed to the gradual decrease in the fluorine incorporation. Yakuphanoglu et al. [34] reported similar results for sprayed FZO films. These results agree well with electrical and surface morphological studies. As this study mainly focuses on the electrical and optical properties of FZO films, a detailed investigation on the structural properties is out of the scope of this study and hence only three XRD patterns are presented here as representative patterns, just in order to exhibit the structure of the film.

4 Conclusions

Highly transparent and conductive fluorine doped zinc oxide films were fabricated using a simplified spray technique that employs a perfume atomizer. The effect of solvent volume on the physical properties of FZO films was studied. From the structural studies, it is observed that all the films were grown along the (002) plane with c-axis perpendicular to the substrate irrespective of the solvent volume. The electrical sheet resistance and resistivity were found to be minimum ($7.839 \times 10^2 \Omega$ and $4.68 \times 10^{-2} \Omega \text{cm}$ respectively) when the solvent volume is minimum and the value increases as the solvent volume increases. The optical band gap was maximum (3.31 eV) for the film corresponding to the lowest solvent volume. Eventhough the optical transmittance at 550 nm is the highest (95.5%) for the films prepared from starting solution having highest solvent volume, generally the films prepared from starting solution with the lowest solvent volume were found to have good optoelectronic properties suitable for low cost thin film solar cell applications.

Acknowledgements Financial support from the University Grants Commission of India through the Major Research Project (F. No. 40-28/2011 (SR)) is gratefully acknowledged. The authors are also thankful to Dr. C. Sanjeeviraja, Professor and Head, Department of physics, Alagappa University, Karaikudi, for XRD characterizations.

References


Effect of solvent volume on the physical properties of undoped and fluorine doped tin oxide films deposited using a low-cost spray technique

G. Muruganantham, K. Ravichandran, K. Saravanakumar, A.T. Ravichandran, B. Sakthivel

Transparent conducting oxides (TCO) such as SnO₂, In₂O₃, CdSnO₄, CdO and ZnO have been widely used in the optoelectronic devices, coating for energy conversion windows, detection of oxidizing and reducing gases. However, the use of TCOs is still limited due to high cost, complicated processing, and the lack of flexibility. In this study, we investigate the effect of solvent volume on the physical properties of undoped and fluorine doped SnO₂ films deposited using a low-cost and simplified spray technique using perfume atomizer.

X-ray diffraction studies showed that there was a change in the preferential orientation from (211) plane to (110) plane as the volume of the solvent was increased. The sheet resistance ($R_{sh}$) of undoped SnO₂ film was found to be minimum (13.58 KΩ/□) when the solvent volume was lesser (10 ml) and there was a sharp increase in $R_{sh}$ for higher values of solvent volume. Interestingly, it was observed that while the $R_{sh}$ increases sharply with the increase in solvent volume for undoped SnO₂ films, it decreases gradually in the case of fluorine doped SnO₂ films. The quantitative analysis of EDAX confirmed that the electrical resistivity of the sprayed tin oxide film was mainly governed by the number of oxygen vacancies and the interstitial incorporation of Sn atoms which in turn was governed by the impinging flux on the hot substrate. The films were found to have good optical characteristics suitable for opto-electronic devices.

1. Introduction

Transparent conducting oxides (TCO) such as SnO₂, In₂O₃, CdSnO₄, CdO and ZnO have been widely used in the optoelectronic devices, coating for energy conversion windows, detection of oxidizing and reducing gases. However, the use of TCOs is still limited due to high cost, complicated processing, and the lack of flexibility. In this study, we investigate the effect of solvent volume on the physical properties of undoped and fluorine doped SnO₂ films deposited using a low-cost and simplified spray technique using perfume atomizer.

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reducing gases [1], solid state gas sensor devices [2], heat reflecting mirrors, solar cells, defrost windows, anti static materials, touch panels and photo conductors [3–5] because of their wide range of band gap values (2.8–4.2 eV) which allow visible and reflect IR radiation, high electrical conductivity, excellent chemical stability and other useful characteristics [6,7]. Amongst them, tin oxide (SnO$_2$) is one of the prominent low cost conducting materials as well as window layers in these devices. Pure SnO$_2$ is either an insulator or an intrinsic semiconductor. In order to use it as a conducting layer, the resistivity of SnO$_2$ has to be reduced. To reduce the resistivity, dopants such as F, Cl, Sb, Br, Ni and Cu can be employed. In undoped SnO$_2$ also, the resistivity can be reduced by creating oxygen vacancies in the SnO$_2$ lattice.

Among the currently available TCO materials, fluorine doped tin oxide (FTO) is one of the most competing substitutes for indium doped tin oxide. Pure and fluorine doped tin oxide films have been prepared by various techniques such as electron beam evaporation (EBE) [8], chemical vapour deposition [9], pulsed laser deposition [10], sol–gel [11–13], thermal evaporation [14] and spray pyrolysis [15–18], 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. [19,20]. In the present study, pure and FTO films are fabricated by employing a further simplified spray technique using perfume atomizer which has several advantages over conventional spray technique [21,22]. 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.

2. Experimental method

Pure and fluorine doped tin oxide films have been produced by an easy, low cost and simplified spray pyrolysis method using perfume atomizer. The schematic diagram of the experimental set up and other details have been reported elsewhere [23]. An aqueous solution of high pure SnCl$_2$·2H$_2$O was used as the deposition solution. Fluorine doping was achieved by adding NH$_4$F (10 wt.%) with the starting solution. Different sets of starting solutions were prepared by dissolving 2 g of SnCl$_2$·2H$_2$O with different volumes of (10, 20, 30, 40, and 50 ml) doubly deionized water. A very small amount of HCl (0.1 mol/l) was used to dissolve SnCl$_2$·2H$_2$O and NH$_4$F. This solution was magnetically stirred for 1 h and it 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 × 25 × 1.35 mm$^3$. The temperature of the substrates was monitored using a temper-ature 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 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–PW 340/60 X’pert PRO) which was operated at 40 kV and 30 mA with X-ray source of CuK$_\alpha$ 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. Results and discussion

3.1. Structural studies

Fig. 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 SnO$_2$ and contain the characteristic SnO$_2$ 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., for sprayed tin oxide films [24]. 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. Chin-Ching Lin et al. [25] also 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. [26] 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. [27] 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 resistivity). 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 SnO2 films from highly concentrated precursor solutions.

The crystallite size of all the deposited films are calculated using the well known Scherrer’s formula, $D = \frac{0.94 \lambda}{\beta \cos \theta}$ [28] where $\lambda$ is the wavelength of the X-ray used (1.5406 Å), $\beta$ is the full-width at half maximum of the peak which has maximum intensity and $\theta$ is the Bragg angle. The sizes of the crystallites in all the cases are found to be in the nano range (60–98 nm). The size of crystallites shows (Table 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 following relation \( N = \frac{t}{D^3} \) [29] where \( t \) is the thickness of the film and the obtained values are presented in Table 1. The lattice constants 'a' and 'c' are estimated using the relation \( \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \) [29] where \( d \) is the interplaner distance and \((hkl)\) are Miller indices. The obtained values are well agreed with the reported results [30].

3.2. Surface morphology

The SEM micrographs displaying the surface morphology of the undoped tin oxide films are shown in Fig. 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 volumes, the surface has heavily packed needle shaped grains which is the characteristic feature of SnO₂ films. The AFM images (Fig. 3) also support the above mentioned observations.

The XRD results (Section 3.1) showed that the crystallite size increases with the increase in 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 [31]. 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. Now 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 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. 2a) solvent while the crystallite size is the smallest (Table 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 in this case. This phenomenon of agglomeration of crystallites which causes an increase in the grain size is discussed by Losurdo et al. [32] for indium tin oxide films. In the case of the film prepared from 20 ml solution, the grain (Fig. 2b) is composed of comparatively lesser number of crystallites. Hence, the grain size is lesser eventhough 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. 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) 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

<table>
<thead>
<tr>
<th>Volume of the solution (ml)</th>
<th>Lattice constants (Å)</th>
<th>( D ) (nm)</th>
<th>( N ) (( \times 10^{15} ))</th>
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<tr>
<td></td>
<td>( a )</td>
<td>( c )</td>
<td></td>
</tr>
<tr>
<td>10</td>
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<td>60.66</td>
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<td>3.197</td>
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</tr>
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<td>4.749</td>
<td>3.206</td>
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<td>50</td>
<td>4.750</td>
<td>3.193</td>
<td>98.09</td>
</tr>
</tbody>
</table>

*a Standard lattice constant values \( a = 4.7382 \text{ Å} \) \( c = 3.1871 \text{ Å} \) (JCPDS card no 41–1445).
A comparatively higher number of grain boundaries may act as low conductivity blockades making the resistivity higher [33].

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 2. For undoped tin oxide films, the $R_{sh}$ is 13.58 kΩ for 10 ml solution and the value increases sharply to 163.04 kΩ (by nearly 12 times) for 20 ml solution. Then it increases gradually for further increase in the solvent amount as shown in the Table 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. 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

![SEM 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.](image-url)
of Sn atoms, there should be ‘2 m’ number of oxygen atoms. But, in the present study, the atomic percent of oxygen atoms (59.39) (Fig. 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 SnO₂ 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. [34] supported these discussions. They observed

![Fig. 3. AFM images of undoped SnO₂ films deposited from solutions having solvent volume (a) 10 ml, (b) 20 ml (c) 30 ml, (d) 40 ml and (e) 50 ml.](image)

<table>
<thead>
<tr>
<th>Volume of the solution (ml)</th>
<th>SnO₂</th>
<th>$t$ (nm)</th>
<th>$R_{sh}$ ($\times 10^3$ Ω/□)</th>
<th>$\rho$ (Ω cm)</th>
<th>SnO₂:F</th>
<th>$t$ (nm)</th>
<th>$R_{sh}$ (Ω/□)</th>
<th>$\rho$ ($\times 10^{-3}$ Ω cm)</th>
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<td>10</td>
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<tr>
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<td>820</td>
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</tr>
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<td>10.41</td>
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</tr>
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</table>
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 arise from any one or all of the following factors, [34] viz., (1) presence of oxygen vacancies, (2) Sn incorporation at interstitial sites and (3) inclusion of residual chlorine through the precursor. 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) [35,27]. Agashe

Fig. 4. EDAX spectrum of undoped SnO$_2$ film deposited from solution having solvent volume (a) 10 ml and (b) 20 ml.
et al. [34] also recorded that for high precursor concentration, the interstitial Sn atoms also play a major role as oxygen vacancies in assigning a high carrier concentration.

But when the solvent (water) amount increases, the availability of oxygen atoms from the H$_2$O 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. 4b). The EDAX results reveal lesser oxygen vacancies 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 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. 5. The carrier mobility ($\mu$) has an opposite trend as that of ‘$n$’ as expected which is also plotted in the same figure (Fig. 5) as a function of volume of the solvent in the starting solution.

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 63.4$\Omega \square$ and the value decreases sharply to 15.39$\Omega$ (nearly four times) for 20 ml film and then decreases gradually for further increase in the solvent volume as shown in the Table 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. [36] observed that the increasing F incorporation reduces the growth rate of SnO$_2$:F films. In the present

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{carrier_concentration_mobility.png}
\caption{Variation in carrier concentration and mobility as a function of volume of solvent in the starting solution.}
\end{figure}
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 $R_{sh}$.

Fig. 6. Transmission spectra of (a) undoped and (b) fluorine doped SnO$_2$ films deposited from starting solutions having different solvent volumes.
3.4. Optical studies

The transmission spectra of the SnO$_2$ films deposited from starting solutions having different solvent volumes are shown in Fig. 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. 6a which may be attributed to the decrease in the grain size. Roman et al. [37] observed similar grain size dependent optical transmittance results for the sprayed SnO$_2$ films. It is

![Graph showing transmission spectra for different solvent volumes.](image)

Fig. 7. Plots of $(\alpha h v)^2$ vs. $h v$ for (a) undoped and (b) fluorine doped SnO$_2$ films.

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The transmission spectra of the SnO$_2$ films deposited from starting solutions having different solvent volumes are shown in Fig. 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. 6a which may be attributed to the decrease in the grain size. Roman et al. [37] 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. 6b. The sharp absorption edge obtained for all cases clearly show the good crystallinity of the films. The interference patterns (crests and troughs) observed for all 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. The absorption coefficient ($\alpha$) can be calculated from the transmittance ($T$) values at the absorption edge from the Lambert law $\alpha = \ln(1/T)/t$. The variation of absorption coefficient against photon energy ($h\nu$) has the form of $\alpha = A (h\nu - E_g)^n/2$ [33], 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.

To determine whether the undoped tin oxide and FTO films deposited using the simplified spray technique have direct or indirect band gap, $(\alpha h\nu)^2$ vs. ($h\nu$) and $(\alpha h\nu)^{1/2}$ vs. ($h\nu$) plots are drawn. Since better linearity is obtained in the $(\alpha h\nu)^2$ vs. ($h\nu$) plots, the direct band gap values are determined by extrapolating the linear portion of these plots to the energy axis (Fig. 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. 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 SnO$_2$ lattice [38]. 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.

### 4. Conclusion

The undoped and fluorine doped tin oxide films fabricated using the simplified spray technique by employing perfume atomizer are found to have good physical properties. The electrical studies revealed that a low resistivity can be achieved for pure SnO$_2$ films by using precursor solutions prepared from lesser volume of solvent, as it causes large number of oxygen vacancies in the SnO$_2$ lattice. For undoped SnO$_2$ films, the resistivity is found to increase with the increase in solvent volume. But in the case of FTO, an opposite trend is observed which may be due to the enhancement in the fluorine incorporation caused by the increase in the solvent volume. It is found that the increase in the volume of the solvent causes a transition in the preferential orientation from (2 1 1) to (1 1 0) plane. In undoped tin oxide films, the optical band gap is estimated to be high (3.98 eV) for films prepared from lesser volume (10 ml) of the solvent, but for FTO films the band gap is highest (3.95 eV) for films corresponding to the larger volume of the solvent. From the results, we conclude that the process parameters and the spray pattern employed in the present study are found to be suitable for the fabrication of good quality undoped and fluorine doped SnO$_2$ films.

### Acknowledgements

One of the authors, K. Ravichandran, gratefully acknowledges the financial support from the Tamil Nadu State Council for Science and Technology (TNSCST/S&T Projects/PS/AR/2009-2010. 1016). The

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**Table 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>
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<tr>
<td></td>
<td>SnO$_2$</td>
</tr>
<tr>
<td>10</td>
<td>3.98</td>
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<tr>
<td>20</td>
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<tr>
<td>30</td>
<td>3.88</td>
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<tr>
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</tr>
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<td>50</td>
<td>3.83</td>
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</table>
authors are also thankful to Dr. C. Sanjeeviraja, Professor and Head, Department of physics, Alagappa University, Karaikudi for XRD characterizations.

References

Effect of doping level on physical properties of antimony doped nanocrystalline tin oxide films fabricated using low cost spray technique

G. Muruganantham*, K. Ravichandran, K. Saravanakumar, P. Philominathan and B. Sakthivel

Antimony doped nanocrystalline tin oxide (SnO$_2$ : Sb) films have been fabricated using a low cost and simple fabrication technique using a perfume atomiser. The X-ray diffraction patterns of the antimony doped tin oxide (ATO) films show that the films are polycrystalline with tetragonal cassiterite structure having (110) plane parallel to the surface of the substrate. The preferred orientation remains constant for all the doping levels (0–5–3–0 at-%) and the degree of preferred orientation increases with increasing doping concentration in the starting solution. The intensity of the (110) plane steadily increases as the doping concentration of antimony increases. The fine quality of AFM images show that the films have homogeneous and uniform surface. The sheet resistance is found to decrease with increasing antimony doping level, attain a minimum value (6·34 Ω sq$^{-1}$) when the doping concentration is 2·5 at-% and then increase for further doping.

Keywords: Solar cells, Spray pyrolysis, Tin oxide, Structural properties, Electrical properties, EDS

Introduction

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. Such films are essential as substrates for the deposition of solar cell layers such as Si, TiO$_2$, Cu(In,Ga)Se$_2$ and CdS/CdTe. Since the international oil crisis of 1973–74, there has been a phenomenal rise in the researches on low cost solar cell materials. In the present study, a low cost and simplified spray pyrolysis technique is employed for the deposition of highly transparent and conducting antimony doped tin oxide (ATO) films.

Tin oxide films have been prepared by several methods such as chemical vapour deposition, electron beam evaporation, sputtering, thermal evaporation, sol–gel and spray pyrolysis. Among the various deposition techniques, the conventional spray pyrolysis is well suited for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement. In this study, a further simplified technique using a perfume atomiser is employed to fabricate SnO$_2$ : Sb films. Perfume atomiser can collectively perform the functions of spray gun, compressor and solution reservoir. This technique requires simple equipments, which are low in cost but high in throughput, which is the prerequisite for the commercial production of solar cells. Along with low cost, perfume atomisers have several other advantages: lesser substrate temperature is enough when compared with conventional spray technique; atomisation is based on hydraulic pressure without using any carrier gas, intermittent spraying and fine atomisation. Perfume atomisers avoid deposition of annoying large droplets, which often takes place in conventional spray pyrolysis depositions. By employing laser diffraction technique, Fukano and Motohiro observed that the average diameter of the sprayed droplets at 15–25 cm from the nozzle of the perfume atomiser was 62 μm. The size was found to be comparatively smaller than that of the conventional spray method.

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 ATO films fabricated by employing the simplified spray technique using perfume atomiser is studied and reported.

Materials and methods

The precursor solution was prepared by dissolving high pure SnCl$_2$·2H$_2$O (0·8M) with a very small amount of HCl (0·1 mol L$^{-1}$) and then diluting it by doubly deionised water. Antimony doping was achieved by adding suitable proportion of 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.

The precursor solution thus obtained was sprayed intermittently by means of a perfume atomiser on preheated glass substrates of dimensions 75 \times 25 \times 1.35 mm. The substrates were maintained at a temperature 340 \pm 5^\circ 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 with organic solvents and doubly deionised water for degreasing and to remove the contaminations if any on the substrate surface. The experiment was repeated several times to confirm the reproducibility of the films.

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.

Results and discussion

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 \pm 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. The disc geometry depends on the momentum and volume of the droplet and the substrate temperature $T_s$. Thus, the

Table 1 Lattice constants of ATO films

<table>
<thead>
<tr>
<th>Doping Sb/Sn ratio, at-%</th>
<th>Observed values*, Å</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.750</td>
<td>3.196</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4.749</td>
<td>3.195</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>4.745</td>
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<tr>
<td>2.0</td>
<td>4.730</td>
<td>3.194</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>4.734</td>
<td>3.193</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>4.751</td>
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</tbody>
</table>

*Standard values a=4.737 Å, b=3.187 Å. JCPDS Card No. 41-1445.

Table 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>
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<tbody>
<tr>
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<tr>
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<tr>
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<td>2.435</td>
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<td>78.1</td>
<td>2.278</td>
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<tr>
<td>3.0</td>
<td>78.6</td>
<td>2.166</td>
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</table>
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.

Structural studies

Figure 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. 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 confirms that the deposited films are of $\text{SnO}_2$ with tetragonal structure. The lattice parameters $a$ and $c$ are calculated from the equation

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} + \frac{l^2}{c^2}
\]

and the values are listed in Table 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, $\text{Sn}^{4+}$ ions are replaced by $\text{Sb}^{5+}$ ions. As the ionic radius of $\text{Sb}^{5+}$ ions is lesser (62 pm) than that (71 pm) of the $\text{Sn}^{4+}$ ions, the lattice parameter values decrease gradually up to the doping level 2.5 at-%. However, beyond that, according to Kojima et al., $\text{Sn}^{4+}$ ions are replaced by $\text{Sb}^{3+}$ 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 the Scherrer’s formula

\[
D = \frac{0.94\lambda}{\beta \cos \theta}
\]

where $\lambda$ is the wavelength of the X-ray used (1.5406 Å), $\beta$ is the full-width at half-maximum of the peak which has maximum intensity and $\theta$ is the Bragg angle. 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 $N$ of the films was calculated with the use of the following formula

\[
N = \frac{t}{D^3}
\]

where $t$ is the thickness of the film. The calculated structural parameters are summarised in Table 2.

Elemental analysis

The elemental analysis of the deposited films is carried out using the energy dispersive spectroscopy (EDS). Figure 3 shows the EDS spectrum of the film deposited from the starting solution having 2.5 at-% Sn. 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 per cent of oxygen.

![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-%](image-url)
(66-13 at-%) is nearly two times that of the sum of the atomic per cent 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 SnO₂ 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 Sb³⁺ ions in the SnO₂ lattice has more chances than Sn⁴⁺, as the ionic radius of Sb³⁺ is lesser (62 pm) than that of the Sn⁴⁺ (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 Sn⁴⁺ by Sb⁵⁺ 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 (½,0,½) and (0,½,½), Agashe et al. 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 SnO₂ film. On the basis of these observations, we can conclude that the increase in intensity of (110) plane in the SnO₂ : Sb films in the present study clearly shows that the Sb incorporation in the SnO₂ 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.

<table>
<thead>
<tr>
<th>Doping Sb/Sn ratio, at-%</th>
<th>Thickness, t, nm</th>
<th>Sheet resistance, Rₛₚ, Ω sq⁻¹</th>
<th>Transmittance, T, %</th>
<th>Figure of merit, ϕ, x 10⁻² Ω⁻¹</th>
<th>Reflectivity R, in infrared range, %</th>
<th>Optical band gap, Eₑ, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1032</td>
<td>690</td>
<td>88</td>
<td>4.04</td>
<td>93.04</td>
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<td>3.62</td>
<td>92.29</td>
<td>3.55</td>
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</table>

Table 3: Electrical and optical parameters of ATO films
Surface morphology
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 Sb/Sn=0.5, 1.5 and 2.5 at.-% are presented in Fig. 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. 5) is in good agreement with the values obtained from the XRD results. The SEM image shows that the films have uniformly closely packed petal shaped well defined grains.

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 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.

The transmittance in the near infrared range decreases exponentially from the starting 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 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 α can be calculated from the transmittance T values at the absorption edge from the Lambert law α=ln (1/T)/t. The variation of absorption coefficient against photon energy (hν) has the form of α=4(hν–Eg)2/3, where Eg 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.21

To determine whether the ATO films deposited using perfume atomiser have direct or indirect band gap, (zhν)n versus (hν) and (zhν)(1/n) versus (hν) plots were drawn. Since better linearity was obtained in the (zhν)n versus (hν) 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 Eg values presented in Table 3. The values are found to be comparable with the earlier reports.22 The increase in values of Eg for higher doping may be attributed to the Moss–Burstein effect.

Electro-optical studies
Sheet resistance Rs 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. 7. Rs is found to decrease as the antimony doping level increases and reach the minimum at the concentration Sb/Sn=2.5 at.-%. The Rs value begins to increase for further doping. The reason for this trend is analysed in detail by Ravichandran and Philominathan.23

The figure of merit is \( R = \frac{1}{2} \frac{\alpha}{n} \). A good criterion to define the quality of highly transparent and conductive thin films. The reflectivity R of the ATO films is calculated using the relation \( R = \frac{(1 + 2\alpha C_0 R_s)^2 - 1}{(1 + 2\alpha C_0 R_s)^2} \) where \( C_0 = 376 \Omega \) (the free space impedance) which is valid over a wide range in the infrared region.

The obtained Rs values are lying between 92-29 and 93-58%. These high values of Rs of the ATO samples along with the good transmittance values make these films desirable for photothermal conversion also. The ATO films prepared in this study were found to have desirable \( R_s \) values suitable for solar cell applications.

Conclusion
Antimony doped nanocrystalline tin oxide films are fabricated using a low cost spray technique. Good optical transmittance (>80%), wide optical band gap (3.26–3.59 eV) and the desirable figure of merit (2.92–9.19 Ω−1) observed for the antimony doped tin oxide thin films in this investigation make this technique an economic alternative to conventional spray technique. The sheet resistance is found to be minimum for SnO2: Sb film prepared from starting solution having Sb/Sn=2.5 at.-%.

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The authors are grateful to the Secretary and Correspondent, Principal, Department of Physics, AVVM Sri Pushpam College (Autonomous), Poondi, India, for their excellent encouragement and support. One of the authors, K. Ravichandran, gratefully acknowledges the financial support from the Tamil Nadu State Council for Science and Technology (TNSCST/S&T Projects/PSAR/2009–2010).

References