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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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]. $SnCl_2.2H_2O$ is used as the host precursor and fluorine doping was achieved by adding NH_4F (10 wt. %) with the precursor solution. Five sets of starting solutions are prepared by dissolving 1 g of $SnCl_2.2H_2O$ 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^3. 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.

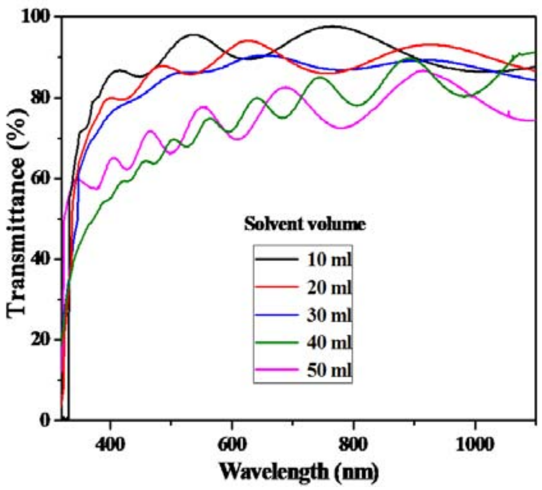

Fig.1. Transmission spectra of FTO films.

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 or 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,

$$n_f = [M + (M^2 - n_s^2)^{1/2}]^{1/2} \qquad (1)$$

where

$$M = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \qquad (2)$$

where T_M and T_m are the transmittance for maxima and minima and n_s is the refractive index of the substrate. By interpolating the envelopes corresponding to T_M and T_m, 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 (λ) 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_f 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]**. Eventhough, 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

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

where α is the absorption coefficient. The absorption coefficient is given by the relation [29,30]

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \qquad (4)$$

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 α 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 λ_1 and λ_2 using the following equation

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \tag{5}$$

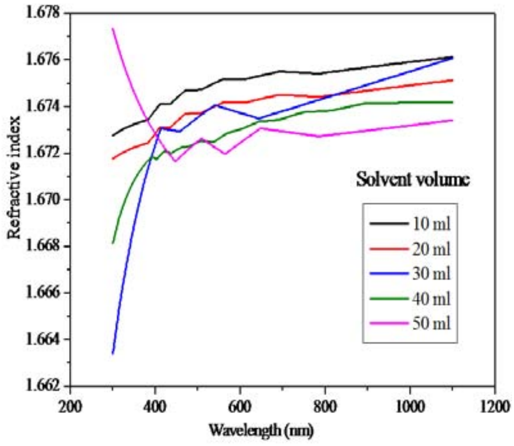

Fig.2 Refractive index vs wavelength

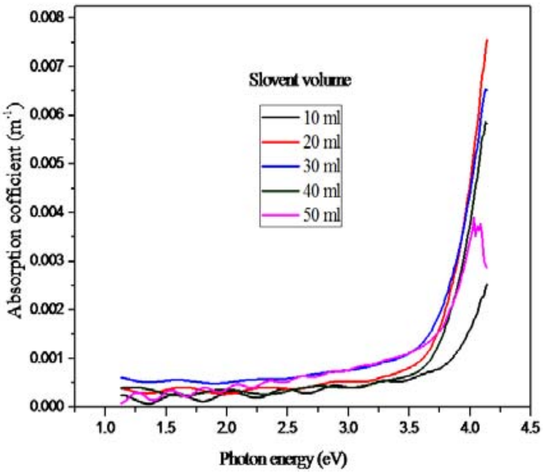

Fig.3 Plots for absorption coefficient vs photon Energy.

The thickness of the films lies in the range of 682-812 nm and the values are presented in Table 1. These values of thickness obtained by the Swanepoel method are found to be comparable with that estimated by the weight gain method as well as with profilometer. Practically, there will be errors in the determination of extreme positions in the transmittance curve and the corresponding values of the interpolated envelopes. Hence, the preliminary values of the refractive index and thickness calculated from equations (1) and (5) are inaccurate and are denoted as n_{pre} and t_{pre}, respectively in this paper. The more accurate values of refractive index and thickness can be obtained by performing the steps- given below.

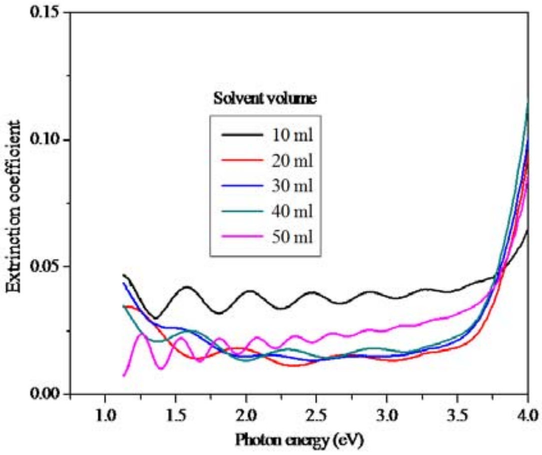

Fig. 4 Variation in extinction coefficient as a function of photon energy.

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 λ 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 λ plot is found out.

Step 5: Using equation

$$2nd = n\lambda \tag{5}$$

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

$$2nt = m\lambda \tag{6}$$

Table 1. Thickness and optical parameters of FTO films.

Solvent volume (ml)	Thickness (nm)	B_s $\times 10^{14}$ (eV m^{-2})	n_f	E_g (eV)
10	787	0.7653	1.7768	3.62
20	734	4.8645	1.7972	3.64
30	770	6.038	1.8106	3.66
40	812	7.454	1.8311	3.67
50	682	7.418	1.8252	3.70

B_s - 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 $(\alpha h\nu)^2$ 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 $(dt/d\lambda)$ with respect to wavelength and the average wavelength (λ_{avg}).

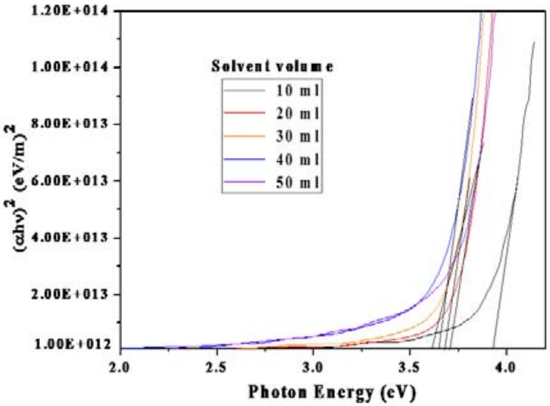

Fig. 5 Plot of $(\alpha h\nu)^2$ vs hν

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.

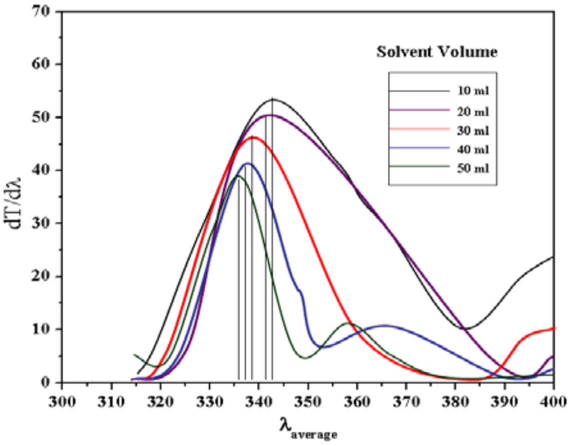

Fig.6 Plot of dT/dλ vs $\lambda_{average}$

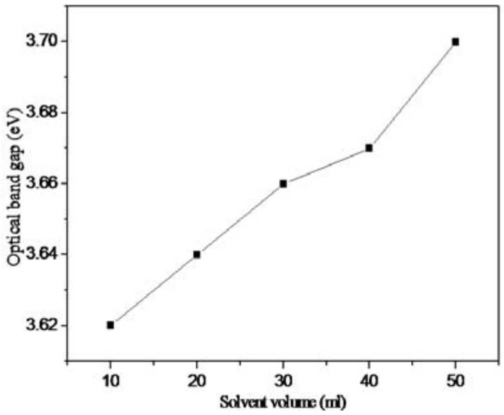

Fig.7 Variation in E_g with respect to solvent volume

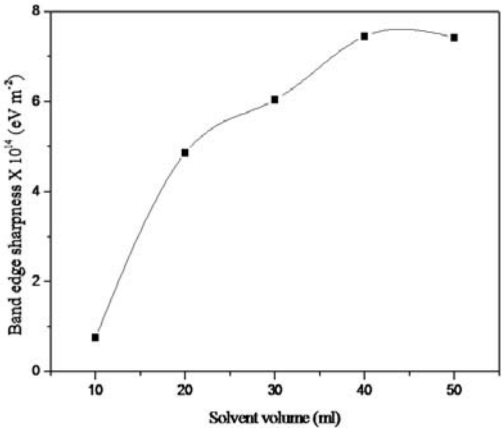

Fig. 8. Band edge sharpness as a function of solvent volume

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).

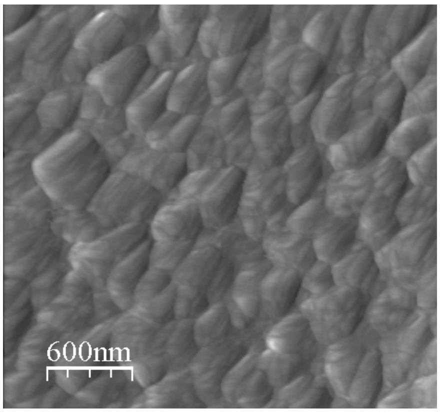

Fig. 9 AFM image of FTO film (30 ml).

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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