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Opto-Electronic Properties of Fluorine Doped Tin Oxide Films Deposited by Nebulized Spray Pyrolysis Method

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ABSTRACT

Transparent and conductive fluorine doped tin oxide thin films (FTO) were deposited on to thoroughly cleaned glass substrates by nebulized spray pyrolysis technique using di-hydrated tin (II) chloride ($SnCl_2.2H_2O$) and ammonium fluoride (NH_4F) as the source of tin (Sn) and fluorine (F), respectively. The fluorine concentration was varied from 0.005-0.04 M in the steps of 0.05. The substrate temperature was constantly maintained at 350°C for all depositions. The influence of dopant concentration on the optoelectronic properties of FTO thin films was investigated using X-Ray Diffraction (XRD) analysis, Scanning Electron Micrographs (SEM), Energy Dispersive Analysis of X-rays (EDAX) spectra, optical analysis and electrical measurements.

Key words: Nebulized spray pyrolysis, fluorine doped tin oxide, opto-electronic properties

INTRODUCTION

Transparent and Conducting Oxide (TCO) films are a class materials of importance because of their applications in optoelectronics and solar cells (Smith *et al*., 1995). TCOs have high transmission in visible wavelength range (Arca *et al*., 2012) and high electrical conductivity close to that of metals (Arca *et al*., 2012; De la Garza-Guadarrama *et al*., 2001). Most commonly used TCOs are tin oxide (TO), indium oxide (IO), indium tin oxide (ITO), fluorine doped tin oxide (FTO), undoped zinc oxide (ZO), aluminium doped zinc oxide (AZO) and cadmium oxide (CdO) (Noh *et al*., 2012). Among these most commonly used transparent conducting oxides, FTO thin films plays in its origin because of its high optical transmittance and electrical conductivity. They are used in broad range of applications like electrode for thin film solar cells (Noh *et al*., 2012; Tatar and Duzgun, 2012), sensing material for gas sensor devices (Shamala *et al*., 2004; Korotcenkov *et al*., 2002), infrared reflective glass and transparent electrode for other optoelectronic devices (Aukkaravittayapun *et al*., 2006; Ravichandran and Philominathan, 2011).

The fluorine doped tin oxide can be prepared by both physical and chemical deposition methods including e^--beam evaporation (Elangovan and Ramamurthi, 2003; Chung *et al*., 1994), reactive sputtering (Chung *et al*., 1994; Thangaraju, 2002; Brown *et al*., 2000; Nelli *et al*., 2000; Stambolova *et al*., 2000; Ruske *et al*., 1999; Zhao *et al*., 2011), chemical vapour deposition (Elangovan and Ramamurthi, 2003; Belanger *et al*., 1985; Arias *et al*., 2000; Shewale *et al*., 2010), dip coating technique, sol-gel (Elangovan and Ramamurthi, 2003; Zhao *et al*., 2011; Varghese and Malhotra, 2000) and spray pyrolysis technique (Elangovan and Ramamurthi, 2003;

Thangaraju, 2002; Frank *et al*., 1983). Amongst, spray pyrolysis technique is the least expensive and it can produce films with large area, reproducibility, high film quality, high film growth rate, mass production capability and comparatively low-cost than other methods (Elangovan and Ramamurthi, 2003; Thangaraju, 2002; Nelli *et al*., 2000; Zhao *et al*., 2011; Lee *et al*., 2007).

The work in this study deals the deposition and characterization of fluorine doped tin oxide thin films prepared using nebulizer spray pyrolysis technique by varying the fluorine doping concentration and by keeping all other spray parameters as constant. The effect of varying doping concentration on the crystallinity, surface morphology, transparency, resistivity and mobility of the film has been studied by carrying out the respective characterizations. Based on the results obtained, optimized doping concentration was predicted those required for optoelectronic applications.

MATERIALS AND METHODS

Materials used: Stannous chloride ($SnCl_2.2H_2O$, 98%, Sigma-Aldrich), ammonium fluoride (NH_4F, 99%, Sigma-Aldrich), hydrochloric acid (HCl) and de-ionized water were used to prepare the precursor solution, as received without further purification.

Preparation of spray precursor: The 0.1 M of $SnCl_2.2H_2O$ was dissolved in 20 mL of de-ionized water and concentrated hydrochloric acid (HCl) was added and stirred to make the pH of the solution to ~2. The fluorine doping was done by varying the molarity of the NH_4F in the 20 mL of tin precursor solution.

Spray parameters:

- Precursor volume: 20 mL
- Substrate temperature: 350°C
- Substrate to nozzle distance: 50 mm
- Carrier gas pressure: 1.6 kg cm^{-2}

Spray process: The pre-cleaned glass slides of 20×10×1.5 mm were used as the substrates for the FTO films. Glass substrates were pre-heated to the optimized temperature. Substrate temperature was optimized and it was fixed at 350°C for all the films. After the spray deposition, the films were taken out of the furnace after the furnace temperature reached the room temperature.

Characterization techniques used: Structural properties of the deposited FTO films were studied by using X-Ray Diffraction (XRD) analysis. The surface morphologies of films were observed by Scanning Electron Microscope (SEM). Hall Effect was used for the measurement of electrical properties such as resistivity, carrier concentration and mobility at the room temperature. Optical properties were studied by UV-Vis-NIR absorption spectra.

RESULTS AND DISCUSSION

Structural properties: All the deposited FTO thin films were transparent, have good adhesion to substrate, better uniformity, free from pinhole and stable for long period when kept in atmosphere. The X-ray diffractograms were recorded for FTO thin films deposited by the nebulized spray pyrolysis technique by varying the doping concentrations and are as shown in Fig. 1.

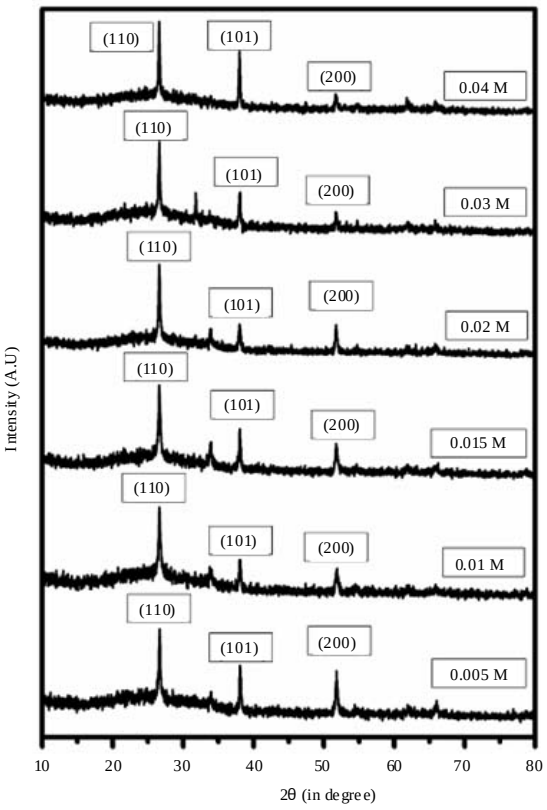

Fig. 1: XRD patterns of the FTO films deposited on glass substrates at different doping concentrations

The XRD analysis was carried out to determine the phase, micro-structure, crystallite size and lattice strain of the films deposited by varying the doping concentration. The XRD patterns of the films, prepared by different doping concentration, at the substrate temperature of 350°C revealed that the deposited films are polycrystalline in nature having the characteristic peaks of tetragonal structure of SnO_2.

The peaks observed are (110), (101), (200), (211) and among all the peaks the orientation of (110) peak is the high intensity peak observed in the patterns of all the films with different doping concentration. Gordillo *et al*. (1994) reported the results of XRD analysis for the doped and undoped SnO_2 films prepared by spray pyrolysis from $SnCl_2.2H_2O$ precursor, which also revealed the preferential growth along the (110) direction. In the present studies, (101) texturing is increasing with increasing doping concentration. But the films deposited with the doping concentration of 0.015 M shows the minimum texturing along (101) direction. The crystallite sizes of the deposited SnO_2: F films were determined from Scherrer's equation (Noh *et al*., 2012; Yadav *et al*., 2009; Memarian *et al*., 2010; Shen *et al*., 2005):

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{1}$$

where, D is the crystallite size in nanometers, β is the full width at half maximum of the diffraction line measured in radians and λ is the wavelength of X-ray used (λ = 1.5418 Å). The lattice strains of the films were also calculated using the relation (Wilson, 1949):

$$\varepsilon = \frac{\beta \cos\theta}{4\sin\theta} \tag{2}$$

Figure 2 shows the change in crystallite size and lattice strain with respect to different doping concentration. Figure shows that the crystallite size changes non-monotonically for the films deposited with the doping concentration of 0.005-0.015 M, then increasing monotonically from 0.015 upto 0.04 M. This evident that the crystallite size of the FTO thin films depends on the doping concentrations. The films deposited with the doping concentration of 0.015 M shows the minimum lattice strain which may be attributed to the substitutive doping of fluorine to the tin site and the films are having minimum interstitial defects. The calculated lattice constants a and c for the tetragonal phase was determined by the relation (Tatar and Duzgun, 2012):

$$\left(\frac{1}{d^2}\right) = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{3}$$

where, d is the interplaner distance and (h, k and l) are Miller indices for the particular Bragg reflection. The calculated lattice constants a and c are found to vary from 4.7373(3)-4.7421(4) Å and 3.1864(8)-3.1901(1) Å, respectively. The changes in lattice constants for the FTO thin films over from the bulk material clearly indicate that the film grains are strained, which is attributed to the changes in the crystalline nature and doping concentration of fluorine to tin oxide (Shen *et al*., 2005).

Surface morphology: Surface morphology of FTO thin films deposited with different doping concentration was analyzed by JEOL JSM-6701F field-Emission Scanning Electron Microscope (FE-SEM).

Figure 3 shows SE micrographs of the FTO thin film samples with X5000 magnification. The results show that the surface of the films consist of uniform distribution of diamond shaped grains

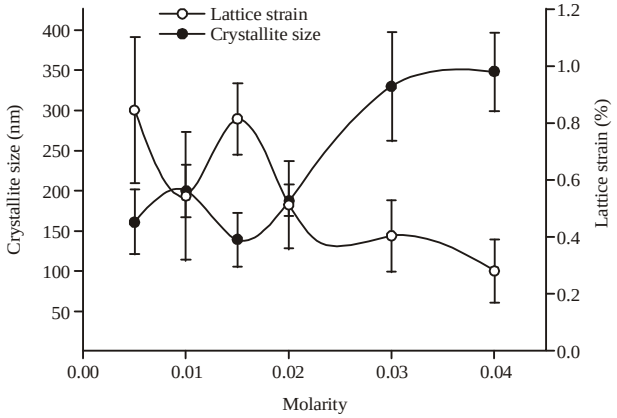

Fig. 2: Variation of crystallite size and lattice strain of the FTO films with doping concentrations

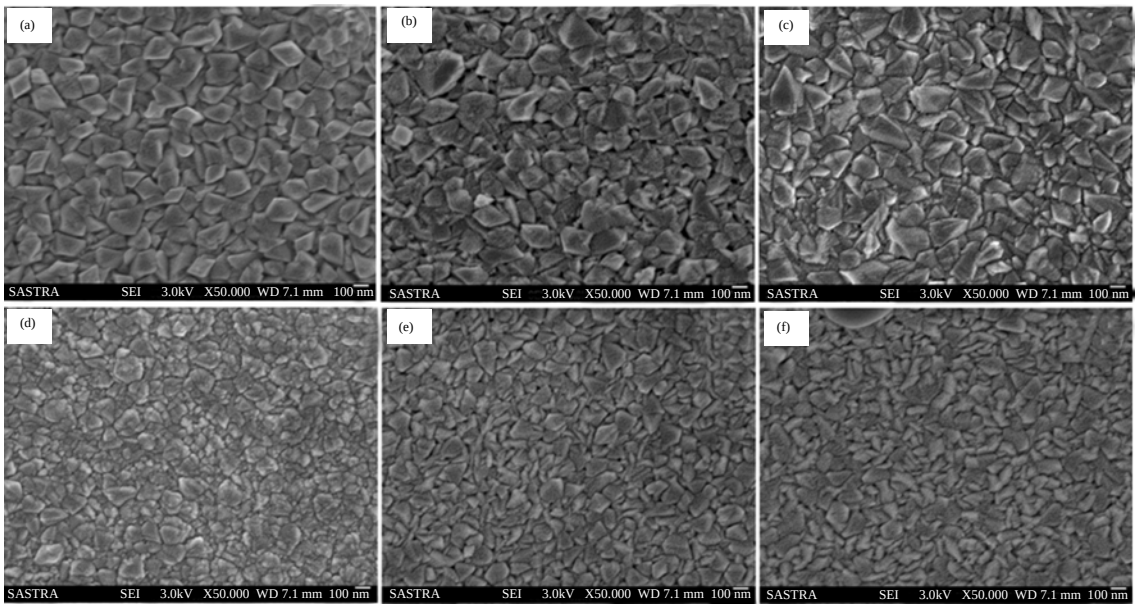

Fig. 3(a-f): Scanning electron micrographs of tin oxide thin films deposited at various doping concentration (a) 0.005 M, (b) 0.01 M, (c) 0.015 M, (d) 0.02 M, (e) 0.03 M and (f) 0.04 M

Fig. 4: EDAX of 0.015M doping concentrations of FTO thin film

with good crystallinity, surface with relatively high density, high smooth and devoid of pin-holes. This might have decreased grain boundary scattering and resulted into lowering of electrical resistivity and it may lead to more conductivity (Patil *et al*., 2003). The EDAX analysis of fluorine doped tin oxide thin film with 0.015 M doping concentration revealed the presence of tin, oxygen, fluorine and silicon shown in Fig. 4.

Electrical properties: The Hall measurements were investigated using Van-der Pauw configuration at room temperature. The values of mobility (μ), carrier concentration (n) and resistivity (ρ) were determined from the Hall Effect measurements and plotted as a function of doping concentrations. Figure 5 shows the resistivity, mobility and carrier concentration of SnO_2:

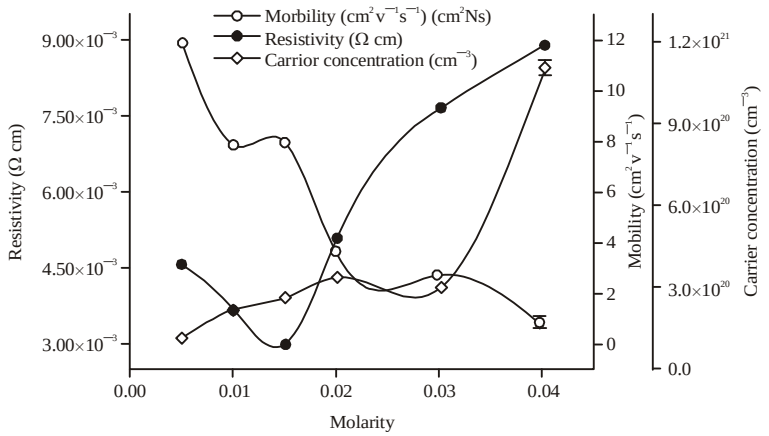

Fig. 5: Variation of resistivity, mobility and carrier concentration as a function of fluorine doping concentration

F films as a function of varying doping concentration. A decrease in the resistivity was observed with the increase of doping concentrations. As the fluorine doping is increasing from 0.005-0.015 M the resistivity (ρ) of the films are decreasing and then again increasing for molarities varying from 0.02-0.04 M. Carrier concentration (n) and Hall mobility (μ) are also varying with respect to the varying doping concentration.

Optical properties: The optical transmittance spectra of fluorine doped SnO_2 thin films were studied by TECHCOMP 2301 UV-vis-NIR spectrophotometer in the range of 300-1100 nm. The variation of optical transmittance (T) with respect to the wavelength for the SnO_2: F films with different doping concentration is as shown in Fig. 6. Figure 6 shows that the maximum transmittance is nearly 90%. The transmittance was maximum at lower wavelength range. The increase in transmittance in the wavelength range of 350-700 nm may due to the well-crystallization of the film (Moholkar *et al*., 2008), which supports the results of the XRD pattern and SEM.

Transmittance value is slowly decreasing in higher wavelength range by increasing the doping concentration, which may be attributed to the increasing free carrier absorption because of the surface oscillating electrons of the film. The observed oscillations of transmittance may be due to the better optical quality of the films (Batzill and Diebold, 2005).

Optical band gap: Since, SnO_2 is a degenerate semiconductor with direct band gap energy (E_g) (Czapla *et al*., 1989; Rakhshani *et al*., 1998). Figure 7 shows the plot of $(\alpha h\nu)^2$ to photon energy for SnO_2: F thin films with different doping concentration.

The band gap (E_g) is determined by extrapolating the straight-line region of the $(\alpha h\nu)^2$ curve to the energy axis. The intercept of the extrapolation on energy axis at zero absorption indicates the value of band gap energy E_g and the values determined are in the range of 3.95-4 eV. The energy bandgap value is not monotonically increasing with doping concentration, which may be due to the changes in carrier concentration (Patil *et al*., 2003). The bandgap value is minimum for the films deposited with the doping concentration of 0.015 M. The absorption of the light by the free

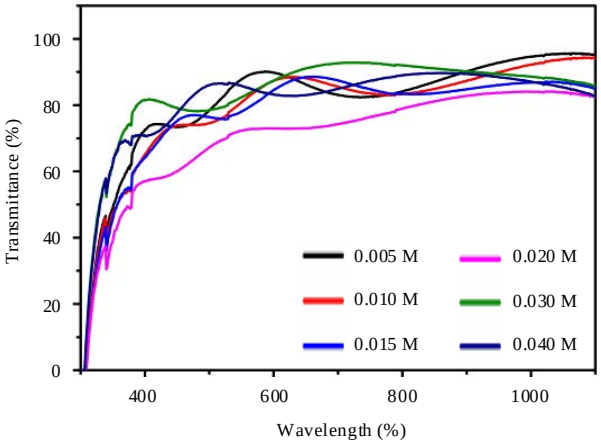

Fig. 6: Optical transmission spectra of SnO_2:F thin films

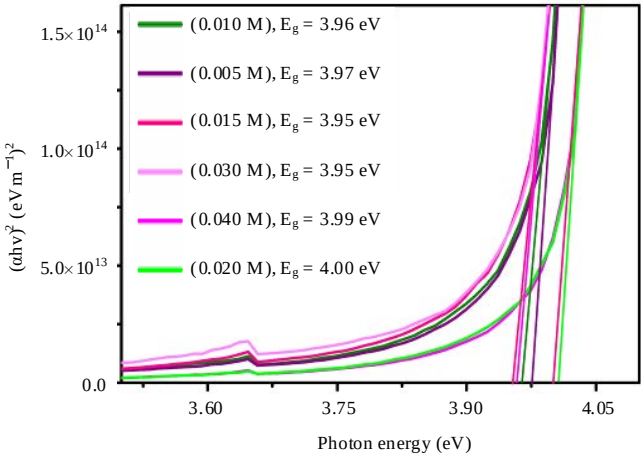

Fig. 7: Plot of $(\alpha h\nu)^2$ to photon energy for SnO_2: F thin films

carriers also increases with increase in carrier concentration and this leads to higher absorption coefficient (Patil *et al*., 2003). When the carrier concentration decreases, the light absorption by free carriers also decreases.

CONCLUSION

The SnO_2: F thin films were successfully deposited using different doping concentration of fluorine at the substrate temperature of 350°C from $SnCl_2.2H_2O$:NH_4F precursor using advanced and cost effective nebulized spray pyrolysis to study the opto-electronics properties of films. The XRD analysis revealed that the films were polycrystalline and the presence of tetragonal structure with (110), (101) and (200) orientations. The scanning electron micrograph showed the nano-structural growth, devoid smooth surface and good uniformity of the deposited FTO films. The obtained EDAX spectrum of the deposited films shows that the presence of tin, oxygen and fluorine elements. The detailed analyzes of electrical properties revealed that the resistivity was as low as 2.9×10^{-3} Ω cm. The maximum carrier concentration and the mobility were 11.05×10^{20} cm^{-3} and 11.88 $cm^2 Vs^{-1}$, respectively. Optical studies revealed the maximum transmittance of 90% and the

optical band gap due to its direct transitions was varying from 3.95 to 4 eV. The studies revealed that the nebulized spray deposited transparent conducting SnO_2: F films are useful for the application of low cost electrode for photovoltaic devices and crystalline hetero junction solar cells.

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