



Fabrication and Characterization of Spray-Deposited Fluorine-Doped Tin Oxide Thin Film

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Abstract: This paper reports the synthesis of fluorine-doped tin oxide (FTO) thin film on glass at 450°C via continuous spray pyrolysis in ambient atmosphere. The source to substrate distance was kept fixed, with a moderate flow rate at low pressure. Conventionally, scanning electron microscopy, X-ray diffraction, Spectrophotometer, Four point probe and Hall Effect measurement were used to investigate the structural, electrical and optical properties of the thin film. Structural analysis confirmed that the thin film was polycrystalline with preferred orientations at (110), (101), (200) and (211) planes. Thickness of the thin film was 285nm with a low resistivity of $3.3 \times 10^{-1} \Omega \cdot \text{cm}$.

Keyword: Transparent conducting oxide; doping; spray pyrolysis; thin film.

I. Introduction

In recent years there has been a growing interest in the use of transparent conducting oxide thin films as conducting solar window materials in thin film solar cells, heat reflectors for advanced glazing in solar applications, and as various gas sensors, flat panel displays, substrate material in electrolysis, passive counter electrode for electrochromic devices, frost preventing surfaces.

Tin oxide (SnO_2) is n-type wide bandgap semiconductor with high transparency in the visible region. Tin oxide also highly conducting and oxygen vacancies are responsible for the electron-carrier generation in SnO_2 . Hence, conductivity of tin oxide thin film can be controlled by controlling oxygen deficiency. Also, variety of dopants are introduced to induce conductivity in SnO_2 . Usually, donor doping is done by substitution of Sb^{5+} on the Sn^{4+} site and F^{1-} on the O^{2-} site [1,2]. Crystal lattice is always affected by donor doping. As oxygen ionic radii are similar to fluorine's, lattice distortion is minimized.

SnO_2 either doped or undoped can be synthesised by numerous techniques such as thermal evaporation [3], sputtering [4], chemical vapour deposition [5], metallo-organic chemical vapour deposition (MOCVD) [6], sol-gel dip coating [7], painting [8], spray pyrolysis [9-14], hydrothermal method and pyrosol deposition [15,16]. Among the various deposition techniques, the spray pyrolysis is commonly used low cost large-area deposition technique. Typically the spray solution contains SnCl_2 or SnCl_4 in solvent and the carrier gas mixture is the source of oxygen. In this method, films are deposited on hot substrates. Usually, substrate temperature varies at range 350°-550°C [17]. At elevated temperature substitution reaction of Cl by oxygen takes place.

The prime aim of this work is to fabricate fluorine doped tin oxide thin film using a low cost manually controlled home-made spray pyrolysis system and investigate its structural, optical and electrical properties. Different parameters like spray angle, source to substrate distance, spray nozzle position, spray rate, carrier gas pressure, hot plate temperature were manually controlled to fabricate a FTO thin film on glass substrate.

II. Experimental

The whole system is enclosed in an air-tight chamber provided with an exhaust to remove the gases and vapors produced during the spray pyrolysis process. An internal mix two fluid type spray nozzle was used in the system. The spray nozzle arrangement was made using simple glassware. Compressed air was used to atomize the liquid spray solution and source of oxygen. A PID temperature controller was used to control substrate temperature. A hot coil was introduced around the substrate to make a temperature gradient along the path from source to substrate.

The thin films of $\text{SnO}_2\text{:F}$ (FTO) were deposited on microscopic glass substrates ($76.2 \times 25.4 \times 1 \text{ mm}^3$). Stannic chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) was used as precursor for SnO_2 thin films and Ammonium fluoride (NH_4F)

was used as doping material. The first solution is made from 0.199 M of tin chloride pentahydrate in 150ml and the solution was stirred for at least 5h to obtain a clear solution. The second solution is made from 17.365 M ammonium fluoride in 4.00 ml DI water. The two solutions are admixed in a water bath at 60°C. The combined solution is allowed to stir overnight to ensure complete mixing, and the resulting solution was clear and stable. Fluorine doping is 28 wt% in this starting solution. This solution was used for deposition of FTO thin film on glass substrate.

The glass substrates were ultrasonically cleaned in methanol, acetone and DI water for 45 minutes. After that the cleaned glass substrates were dried on hotplate. The spray rate was in the range of 0.1-0.5 ml/min. Compressed air was used as carrier gas and the optimum gas pressure was maintained at 0.5 bar. The source to substrate distance was fixed at 37 cm for each deposition. The substrate temperature was fixed at 450°C.

An etching solution was made by adding 1 ml nitric acid HNO₃ into 100 ml distilled water. Etching slightly improve the electrical properties of the films by removing the surface layer [18]. The SnO₂:F thin films were rinsed in this solution for 15s. Finally the films were rinsed in distilled water and then annealed in nitrogen atmosphere at 540°C for 30 min.

III. Characterization of films

The thickness of the thin films was determined using a stylus profilometer (Dektak150). The step height was measured at four different points and a thickness variation of ±5% was observed. The structural properties were determined using X-ray diffraction (BRUKER D8 XRD), using Cu Kα1 radiation according to the Bragg-Brentano configuration. The θ-2θ mode XRD measurements were collected between 10° and 70°. The thin film compositions and morphology were determined using FESEM with energy-dispersive X-ray spectroscopy (JEOL JSM-7600F). Sheet resistance of the SnO₂:F thin film was measured using four point probe method [19]. The four point probe set up consists of four equally spaced SS metal tips with finite radius. The probe spacing was 2mm. DAZHENG (RY1-3020D) DC power supply was used as constant current source for a current through the outer probe and the induced voltage across the inner probes was measured using KEITHLEY-197A auto ranging microvolt digital multimeter. The electrical property including mobility, resistivity and carrier concentration (N_a) of the films were measured using a Hall Effect measurement system (Ecopia HMS-3000). The optical properties were determined using a spectrophotometer (Shimadzu UV-1601) with a wavelength range of 190–1100 nm. An uncoated glass slide was used as a reference for transmittance measurements. The transmittance data was used to calculate the absorption coefficient (α); a plot of the variation of the absorption coefficient against the photon energy (hν) was used to determine the optical band-gap from extrapolation of the linear portion of the curve to zero absorption.

IV. Results and discussion

A. Structural properties:

The XRD pattern of the FTO film fabricated at substrate temperature 450°C, by the spray pyrolysis method is shown in Figure 1. The film is polycrystalline and the XRD studies shows that the preferred orientations were (110), (101), (200) and (211) at 2θ=26.6, 33.74, 38.04 and 51.68 respectively, can be indexed to SnO₂ phase (JCPDS 00-041-1445). No appreciable peak shift can be observed, which is reasonable considering the doping level is relatively small in the starting solution. The sizes of the crystallites FTO thin film were estimated from the XRD results using Scherrer's formula in the equation (1) and inserted in Table 1.

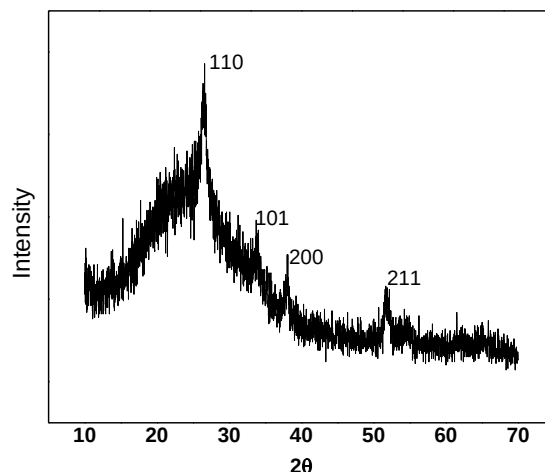
$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the grain size of the crystallite, λ (1.54059 Å) is the wavelength of the X-rays used, β is the broadening of diffraction line measured at the half of its maximum intensity in radians and θ is the angle of diffraction.

Table 1 Calculated values of the crystallites size at different plane orientation.

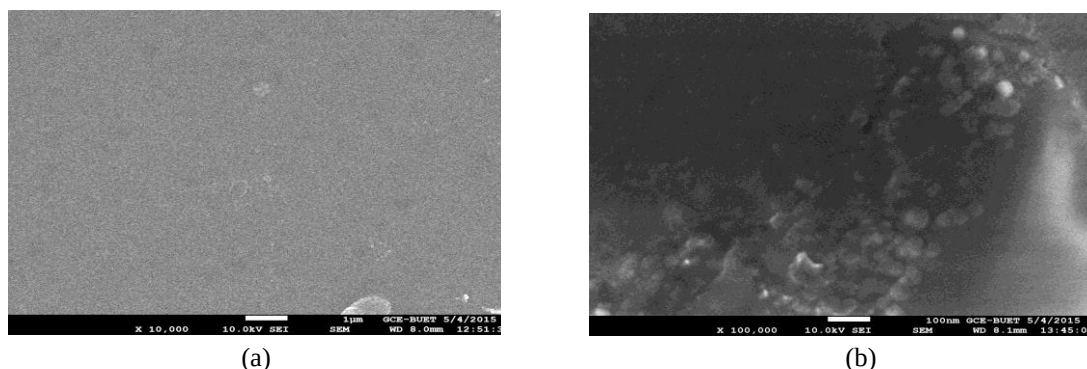
The plane orientation of crystals	(110)	(101)	(200)	(211)
The sizes of the crystals(nm)	4.04	10.12	7.39	10.15

Figure 1 XRD pattern for the FTO thin film in the present work



To observe the morphology of the thin film scanning electron micrograph images were taken at 10K and 100K magnification. Figure 2(a) shows uniform and dense microstructure apparently devoid of any cracks and voids. Whereas, the presence of grains can be observed from Figure 2(b).

Figure 2 Shows scanning electron micrograph image of the sample at (a) 10K magnification and (b) 100K magnification.



B. Electrical and optical properties:

To characterize the electrical properties of the thin films, Four Point probe and Hall Effect probe measurements at room temperature were employed. Sheet resistances of the FTO thin film with substrate temperature 450 °C was 11.77 K Ω /□, which is reasonable for small grain sizes (Table 1). The thickness of the thin film was 285nm, giving a low resistivity of 3.3x10⁻¹Ω.cm. This value similar to those obtained by S. A. YOUSAF AND S. ALI [20] and lower than A.N. BANERJEE et al [21] (~1Ω.cm). The Hall measurements showed that the conductivity of the films is of n-type. The fluorine doped tin oxide thin film has a mobility of 7.89 cm²/Vs and a corresponding carrier concentration (N_d) of 1.45×10¹⁷ cm⁻³, for 27 wt% fluorine doping in the starting solution. These values are similar to those reported elsewhere [22].

Transmittance of the FTO film was measured in the wavelength range 190-1100 nm using UV/VIS spectrometer, is shown in Figure 3(a). In between 400 nm and 1100 nm, transmittance varies from 68-78%, with a maximum transmittance of 78.34% at 1100nm. Hence, the FTO thin film is transparent in the visible region. As can be seen, the absorption coefficient of FTO thin film material was increased in the high photon energy

Figure 3 Shows the (a) transmittance (b) absorption coefficient of the sample.

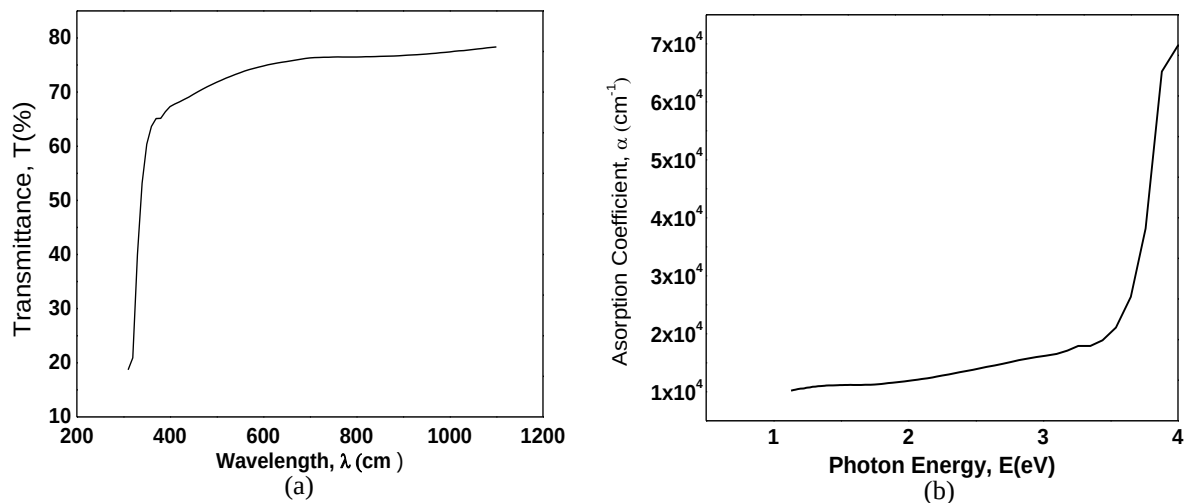
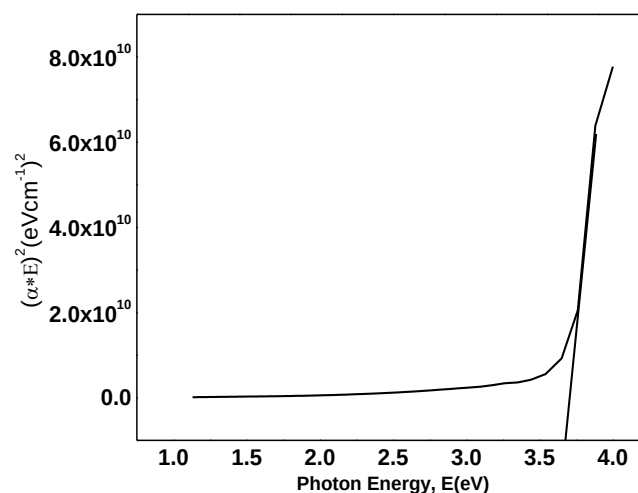


Figure 4 illustrates the plots of $(\alpha \cdot E)^2$ versus photon energy for the sample of FTO thin film. The optical band gap value was obtained by extrapolating the linear part of the curve $(\alpha \cdot E)^2$ as a function of photon energy ($h\nu$), to intercept the $(h\nu)$ axis at $\alpha=0$. The estimated band gap of the thin film material was 3.7 eV, which is comparable to literature value [1, 2].

Figure 4 Inset plot of $(\alpha h\nu)^2$ versus photon energy (E) to the FTO sample.



V. Conclusion

SnO₂:F thin film have successfully been fabricated by using manually controlled home-made spray pyrolysis system. Structural, electrical and optical properties were relevant to other literatures. The present work shows that FTO films with good crystal structure and low resistivity can be prepared by using relatively inexpensive raw material and simple manually controlled non vacuum system. Grain size was obtained from XRD pattern of the thin film. Small grain size introduces more grain boundaries, which in turn are responsible for increase in sheet resistance.

To improve sheet resistance doping concentration of the starting solution, thickness of the thin film [23], substrate temperature [24] may be optimized in future work. Also there are scopes to study on spray nozzle condition, carrier gas type etc.

Reference

- [1]. B. Stjerna, E. Olsson, and C. G. Granqvist, Optical and electrical properties of radio frequency sputtered tin oxide films doped with oxygen vacancies, F, Sb, or Mo, J. Appl. Phys. 76 (1994)3797.
- [2]. E. Shanti, V. Dutta, A. Banerjee, and K. L. Chopra, Electrical and optical properties of undoped and antimony-doped tin oxide films, J. Appl. Phys. 51 (1980) 6243.
- [3]. Properties of Amorphous SnO₂ Thin Films, Prepared by Thermal Evaporation; Shadia J. Ikhmayies; International Journal of Materials and Chemistry 2012, 2(4): 173-177

- [4]. Optical properties of non-stoichiometric tin oxide films obtained by reactive sputtering; A. Czapla, E. Kusior, M. Bucko, *Thin Solid*; Volume 182, Issues 1–2, 20 December 1989, Pages 15–22
- [5]. Thickness dependence of transport properties of doped polycrystalline tin oxide films; D. Belanger, J.P. Dodelet, B.A. Lombos, J.I. Dickson, *J. Electrochem. Soc.* 1985 132(6): 1398-1405
- [6]. The use of tin oxide thin films as a transparent electrode in PPV based light-emitting diodes; A.C. Arias, L.S. Roman, T. Kugler, R. Toniolo, M.S. Meruvia, I.A. Hummelgen, *Thin Solid Films* Volume 371, Issues 1–2, 1 August 2000, Pages 201–206
- [7]. Studies of ambient dependent electrical behavior of nanocrystalline SnO₂ thin films using impedance spectroscopy; O.K. Varghese, L.K. Malhotra, *J. Appl. Phys.* 87(2000)7457
- [8]. A simple and novel technique for the deposition of conducting tin dioxide films ;M.K. Karanjai, D.D. Gupta, *J. Phys. D: Appl. Phys.* 21(1988)356
- [9]. Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped SnO thin films from SnCl precursor; B. Thangaraju; *Thin Solid Films* 402(2002)71–78
- [10]. Fabrication and characterization of fluorine-doped thin oxide thin films and nanorod arrays via spray pyrolysis; B. Russo & G.Z. Cao; *Appl. Phys. A* 90, 311–315 (2008)
- [11]. Using HF rather than NH₄F as doping source for spray-deposited SnO₂:F thin films; S. J. Ikhmayies, R. N. Ahmad-Bitar; *J. Cent. South Univ.* (2012) 19: 791–796
- [12]. An alternative fluorine precursor for the synthesis of SnO₂:F by spray pyrolysis; E. Arca, K. Fleischer, I.V. Shvets; *Volume 520, Issue 6*, 1 January 2012, Pages 1856–1861.
- [13]. The relationship between the doping levels and some physical properties of SnO₂:F thin films spray-deposited on optical glass; DEMET TATAR and BAHATTIN DÜZGÜN; *Vol. 79, No. 1* July 2012 pp.137-150
- [14]. Microstructural investigation and SnO₂ nanodefects in spray-pyrolyzed SnO₂ thin films; ChanchanaThanachayanont, VisittapongYordsri, Chris Boothroyd; *Materials Letters* 65 (2011) 2610–2613.
- [15]. Relation between solution chemistry and morphology of SnO₂-based thin films deposited by a pyrosol process; A. Smith, J.M. Laurent, D.S. Smith, J.P. Bonnet, R.R. Clemente, *Thin solid films* 266(1995)20,
- [16]. A Pyrosol Technique to Deposit Highly Transparent, Low-Resistance SnO₂:F Thin Films from Dimethyltin Dichloride; K. Omura, P. Veluchamy, M. Murozono, *J. Electrochem. Soc.* 146(1999)2113
- [17]. *Handbook of transparent conductors*, David S. Ginley, Hideo Hosono and David C. Paine; Springer
- [18]. Effect of Processing on the Electrical Properties of Spray-Deposited SnO₂:F Thin Films; Shadia J. Ikhmayies and Riyadh N. Ahmad-Bitar; *American Journal of Applied Sciences* 5 (6): 672-677, 2008
- [19]. <http://www.pveducation.org/pvcdrom/characterisation/four-point-probe-resistivity-measurements>
- [20]. The effect of fluorine doping on optoelectronic properties of tin-dioxide (F:SnO₂) thin films; S. A. Yousaf and S. Ali; *CODEN JNSMAC Vol. 48, No.1 & 2* (April & October 2008) PP 43-50
- [21]. Synthesis and characterization of nano-crystalline fluorine-doped tin oxide thin films by sol-gel method; A.N. Banerjee, S. Kundoo, P. Saha and K.K. Chattopadhyay; *Journal of sol-gel science and technology* 28, 105–110, 2003
- [22]. Electrical and optical properties of fluorine doped tin oxide thin films prepared by magnetron sputtering, Ziad Y. Banyamin , Peter J. Kelly , Glen West and Jeffery Boardman; *Coatings*, 2014, 4, 732-746
- [23]. A study on low cost-high conducting fluorine and antimony-doped tin oxide thin films; E. Elangovan, K. Ramamurthi; *Applied surface science* 249(2005) 183-196
- [24]. Effect of substrate temperature on the crystal growth orientation of SnO₂:F thin films spray-dposited on glass substrates; Dengkui Miao, Qingnan Zhao, Shuo Wu, Zhendong Wang, Xingliang Zhang, Xiujian Zhao; *Journal of non-crystalline solids* 356(2010)2557-2561.

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