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Structural, Morphological, Optical and Electrical Properties of S_nO_2: F Thin Films via Nebulizer Spray and Electro-Spinning Techniques

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ABSTRACT

Fluorine highly doped tin oxide (FTO) thin films as a special kind of transparent conductive oxide material were prepared by Nebulizer spray and electro-spinning techniques. These transparent conductive films were prepared at a substrate temperature 500 0C. A solution of stannous chloride (SnCl2.2H2O) in methanol and glacial acetic acid was used as a precursor. Hydrofluoric acid (HF) was added to the precursor solution as a dopant. The crystal structure and surface morphologies of the prepared thin films were characterized by X-ray diffraction and scan electron microscope. The XRD patterns show polycrystalline structure in nature with tetragonal phase. The scanning electron microscope images showing the smoothality and the homogeneity of the prepared thin films. The optical and electrical properties of the films were investigated by using UV-vis spectroscopy in the visible range and four point probe technique. The characterization of the prepared films showing that the spray technique enhancing the electrical and optical properties rather than the electro-spinning technique. The results showed that the prepared FTO films can be used in solar energy applications especially as a heat mirror for solar collector.

Keywords:
Nebulizer spray, electro-spinning , polycrystalline structure, optical and electrical properties

1. Introduction

The transparent conducting oxide thin films, owing to its high optical transmittance and electrical conductivity, have wide applications [1, 2]. They are widely used in the photovoltaic and the opto-electronic applications which required high transmission, low electrical sheet resistance, high uniformity and larger substrate area [3, 4]. Among the different transparent conductive oxide materials, tin oxide (SnO2) which is chemically stable, mechanically hard, and can resist high temperature [5]. Doping SnO2 with foreign impurities such as fluorine (F) or antimony (Sb)

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enhances the electrical conductivity. SnO2 can be synthesized by numerous deposition techniques such as chemical vapor deposition CVD [6], spray pyrolysis [7], atomic layer deposition (ALD) [8], pulsed laser deposition (PLD) [9], RF sputtering [10], sol–gel technique [5], and electro-spinning technique [11]. Among the various deposition techniques, the spray pyrolysis is convenient for the preparation of doped tin oxide thin films because of its simple, inexpensive, reproducibility, high growth rate, suitable for mass production and ease of adding various for uniform large area coatings which are desirable for industrial solar cell application [5].

Indium tin oxide (ITO) and fluorine tin oxide (FTO) are the most commonly used TCOs in several researches and industry. ITO has advantages over the other TCOs in terms of electrical conductivity and optical transparency. However, a reduction in the electrical conductivity tack place as the temperature increases ($T \geq 300$ °C) [12]. For FTO thin films, Fluorine acts as the source of free electron (Donor atom) by substituting the oxygen sites, resulting in an n-type degenerate semiconductor. This phenomenon leads to high carrier concentration, and therefore to a decrease in the electrical resistivity. In this work, sets of high quality FTO coatings were prepared by Nebulizer spray and Electro-spinning techniques. From the structure, electrical, and optical properties of the prepared films, we choose the optimum preparation technique (Nebulizer spray or Electro-spinning) to be used in the optoelectronic applications.

2. Experimental Work

Fluorine doped SnO_2 thin films were deposited on glass substrate using Nebulizer spray and Electro-spinning techniques. The grains of stannous chloride ($SnCl_2$:$2H_2O$) was used as a precursor and Hydrofluoric acid (HF) was used as the source for the fluorine doping. 2g of stannous chloride dissolved in 45 ml of methanol and 5 ml of glacial acetic acid to form the precursor solution. 0.05M of HF was added to the precursor solution as dopant. The weight percentage of [F] / [Sn] ratio was kept 2.5 wt. %. The mixture was magnetically stirred at 70°C for 1 hour in a closed container until all the grains were dissolved. The glass substrates were cleaned by deionized water and methanol with the help of ultra-sonication for 30 min. The substrates were gradually heated to the required temperature 500°C and after the deposition process were allowed to naturally cool down to the room temperature on the hot plate. The prepared samples were grown at different deposition time ranging from 10 to 25 min. at the same substrate temperature 500°C.

2.1 The Deposition Techniques

The first deposition technique is Electro-spinning that used to prepare a nanofiber layers or spun layers by using the main solution. The main solution of FTO is forced through a capillary which is subjected to an electrical field and the Coulombic interactions of charges are applied on the liquid. The applied field will cause the emission of charged droplets from the capillary in different spray modes owing to the applied electric field strength. The size of the droplets is proportional to the flow rate. The large droplets might not decompose into vapor and react when they reached at the heated substrate. For more details see Choy et al [13]. The distance between the nozzle and the substrate was in range of 2-10 cm. The liquid flow was controlled at flow rate 10-50 ml/h. The electrical potential of 15-20 kV was used in charging the liquid for droplet formation. More than one sample was prepared with different deposition time. The second deposition technique is the Nebulizer spray that turns the precursor solution in to a mist rather than the old spray techniques that produced a huge amount of small drops for this feature the electrical and optical properties were enhanced. The distance between the spray nozzle and was kept in the range 5cm. The structural properties of the films were studied by X-ray diffraction (XRD) system (Philips) using Cu-Ka radiation (λ = 1.540 A°). Scan electron microscope (SEM, JEOL JSM-6360 LA) was used to observe the surface morphology of the thin film. The electrical resistivity of all as-deposited samples was measured by the four point probe technique. UV vis. Spectroscopy was used to measure the optical transmittance over the wavelength ranging from 300 to 900 nm.

3. Results and Discussion

3.1 Structural Properties

The crystal structure of FTO thin films were analysed using X-ray diffraction over the angle (2θ) range 20° to 70°. Figure 1 showing the XRD pattern of the Nebulizer spray and Electro-spinning techniques at different annealing durations. The XRD pattern reveals that films tend to grow in specific crystallographic direction and no appreciable peak shift can be observed, which possibly implies that fluorine doping did not introduce any significant stress in the films indicating the (O) atoms were replaced by (F) atoms in the FTO thin films [14]. The diffraction peaks clearly reveal the polycrystalline nature of the deposited films.

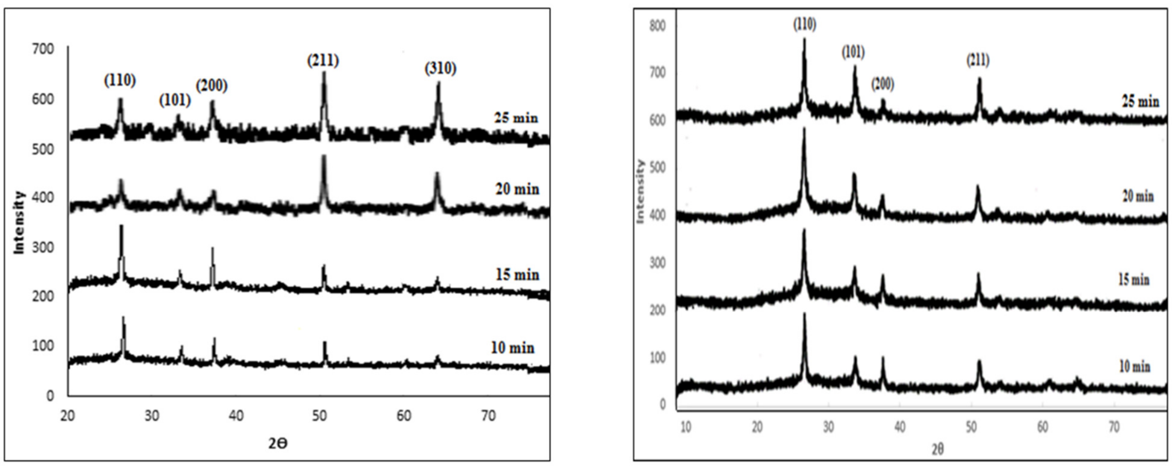

Fig. 1. XRD pattern of FTO thin films, Nebulizer spray (left), Electro-spinning techniques (right)

The grain sizes of the crystallites were calculated using the Scherrer equation $D = 0.9\lambda/\beta cos\theta$,where D is the grain size, λ is the wavelength of the X-ray source used, β is the full width half maximum (FWHM) of the specific peak, θ is the Bragg angle of that peak.

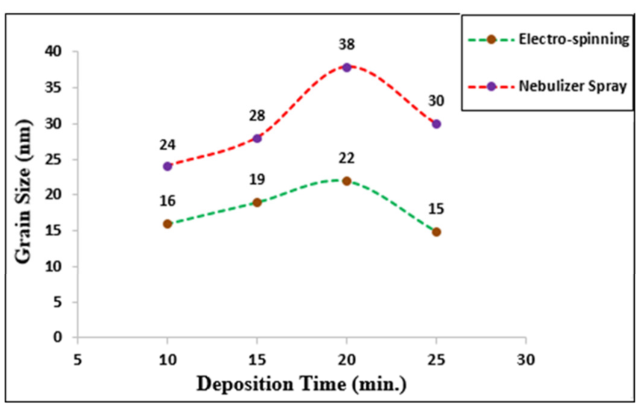

Fig. 2. The grain size of FTO at different deposition time

3.2 Morphological Properties

The surface morphologies of the FTO thin films investigated by using Scanning Electron Microscope. SEM images were given in Figure.3,4 Revealed that films are uniform and homogenous, these images strongly support the XRD data result.

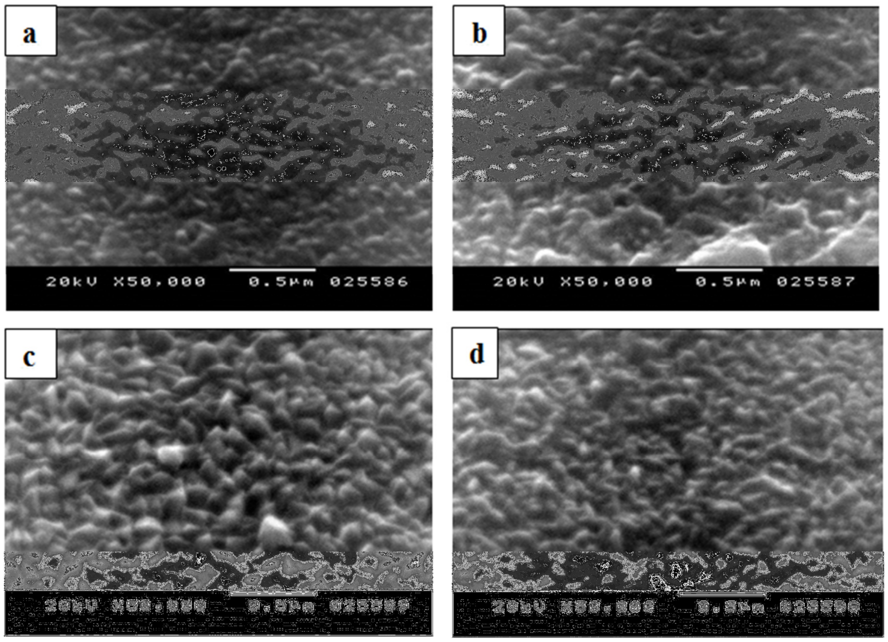

Fig. 3. SEM of FTO films prepared by Nebulizer spray technique a) 10 min., b) 15 min., c) 20 min., d) 25 min

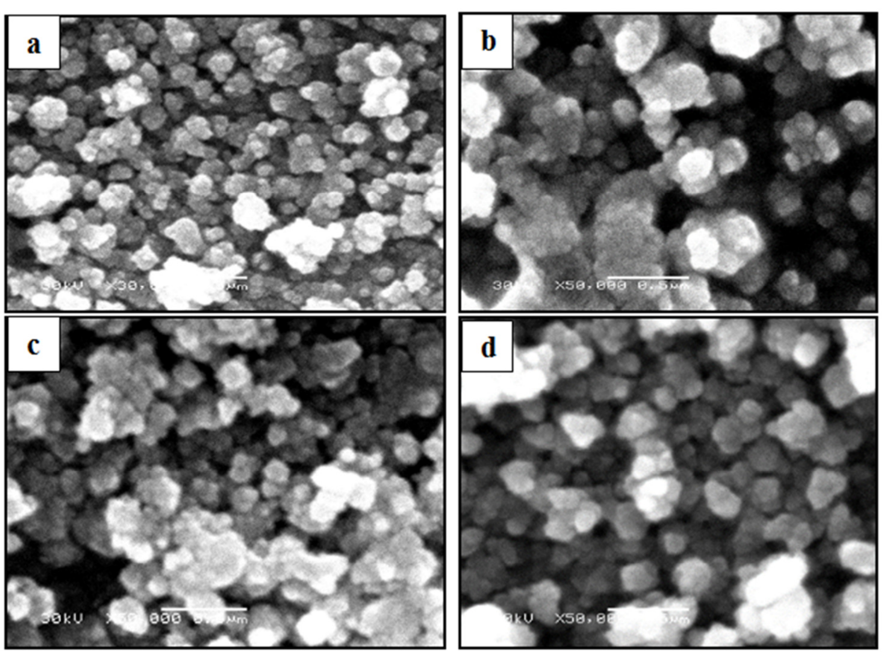

Fig. 4. SEM of FTO films prepared by Electro-spinning technique a) 10 min., b) 15 min., c) 20 min., d) 25 min

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The EDX spectra in figures 5 indicate well defined peaks corresponding to Sn, O and F which indicates that the final film stoichiometry is FTO thin films.

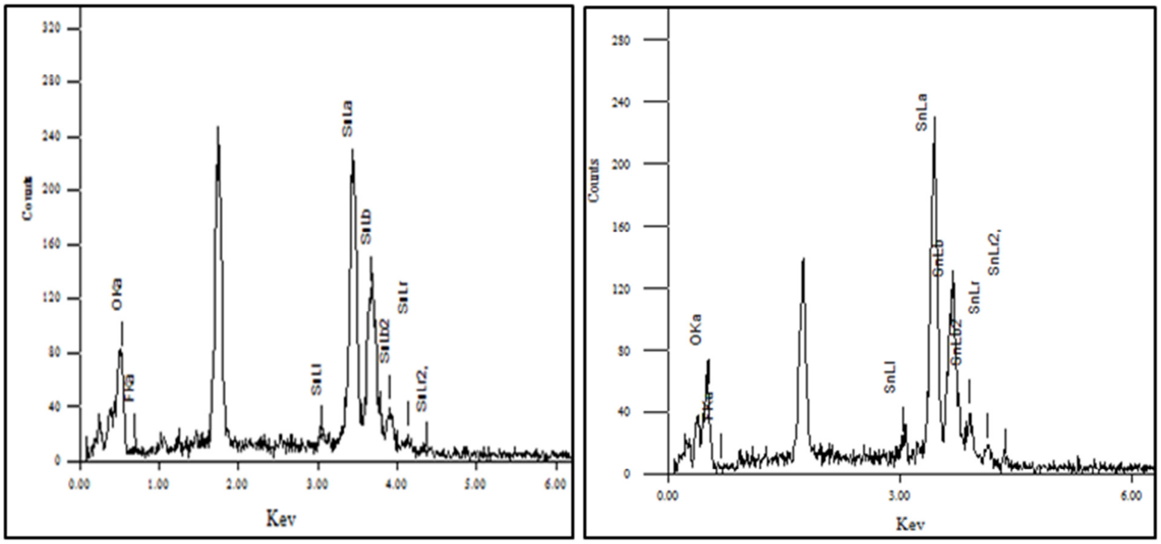

Fig. 6. EDX spectra of FTO, Nebulizer spray technique (left), Electro-spinning technique (right)

3.3 Optical Properties

The optical properties of FTO thin films were characterized by measuring the optical transmittance using UV vis. Spectroscopy. As the deposition time of the film increases, the optical transmittance will be decreases which indicated in the Figure 7.

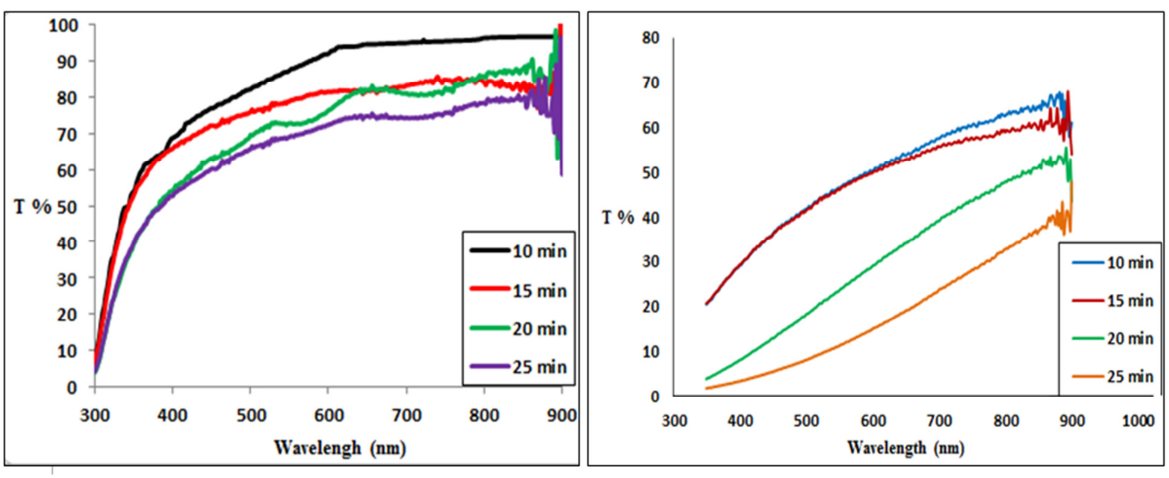

Fig. 7. Optical transmission of FTO, Nebulizer spray technique (left), Electro-spinning technique (right)

According the optical transmission curves of the FTO thin films prepared by Nebulizer spray and Electro-spinning technique the optimum conditions that give a TCOs material that have high optical transmittance and low electrical sheer resistance so that can be used in the optoelectronic applications.

3.4 Electrical Properties

As there are more than one sample were prepared with different deposition time, the optimum value can be calculated by using Figure of Merit (FOM) that is an important parameter for evaluating FTO thin films where it used in solar cell application [5].which calculated by the following relation

$$\emptyset_m = \frac{T^{10}}{R_{sh}} \tag{1}$$

The FOM maximizing the optical transmittance and minimizing the electrical sheet resistance so according to Table 1 the optimum condition in FTO thin films using Nebulizer spray (Deposition time 20 min, Sheet resistance 15 Ω/□, the optical transmittance 83.2 %) also the optimum condition for the Electro-spinning technique (Deposition time 10 min, Sheet resistance 262 Ω/□, the optical transmittance 58.2 %). For these conditions the Nebulizer spray technique is a convenient preparation method for the optoelectronic applications rather than the Electro-spinning technique.

Table 1
FOM of FTO thin films prepared by Nebulizer spray and Electro-spinning techniques

Deposition Technique	Deposition Time (Min.)	Sheet Resistance R_{sh}(Ω/□)	Optical Transmission (%)	FOM (Φ_M×10^{-6})
Nebulizer Spray	10	130	95.3	4700
	15	61	83.2	2600
	20	15	81.3	8100
	25	35	75	1600
Electro-spinning	10	262	58.2	17.9
	15	258	56.4	12.6
	20	511	40.3	0.221
	25	620	25.2	0.0016

The optical bandgap properties of the investigated thin films are shown in Figure 8. The optical transmittance (T) was recorded over the wavelength range of 300–900 nm, and the absorption coefficient (α) was determined by

$$T = e^{-\alpha t} \tag{2}$$

where, t is the thickness of the film. The absorption coefficient, α, was then used to estimate the direct optical energy bandgap, E, using the following equation

$$\alpha h\upsilon = k(h\upsilon - E_g)^{1/2} \tag{3}$$

where k is a constant for direct transition, h is Planck's constant, and υ is the frequency of the incident photon. The direct optical energy bandgap (E) was estimated by constructing the (αhυ)2 versus hυ plot and then extrapolating the straight line portion to the energy axis

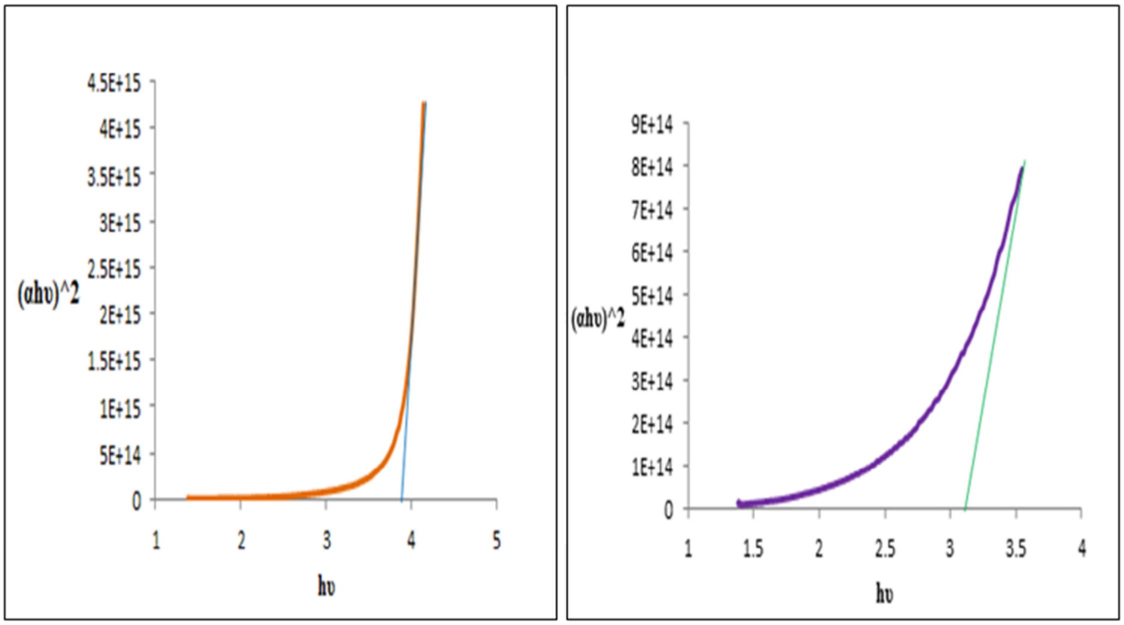

Fig. 8. Optical bandgap of FTO films, Nebulizer spray technique (left)), Electro-spinning technique (right)

4. Conclusion

Fluorine doped tin oxide thin films S_nO_2:F were prepared by Nebulizer spray and Electro-spinning techniques at a substrate temperature 500°C.X-ray diffraction pattern studies revealed that the materiel is a polycrystalline with tetragonal structure. More than one sample of FTO thin films were prepared with different deposition time .The optimum preparation conditions can be calculated by figure of merit. In this study the usage of a new spray technique (Nebulizer spray) that give a high optical transmittance (81.3%) and low electrical sheet resistance (15 Ω/□) can be used strongly in solar cell application.

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