Fabrication and Characterization of Fluorine-Doped Tin Oxide Transparent Conductive Nano-Films

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ARTICLE INFO	ABSTRACT
	Fluorine-doped Tin Oxide (FTO) thin films supported on glass substrates have been fabricated by employing Ultrasonic Spray Pyrolysis (USP) technique. Precursor solution for the spraying was prepared by placing NH_4F and $SnCl_2.2H_2O$ at a weight ratio of 1 to 9 in a solution of acetic acid ? and distilled water. Three films of different thicknesses were prepared corresponding to spray times of 10, 20, and 30 minutes, resulting in 13, 22, and 45 nm thick films. The optical, structural, morphological, and electrical properties of the fabricated films have been investigated. X-ray diffraction studies revealed a polycrystalline fluorine-tin oxide phase with monoclinic crystalline structure, predominantly with (201), (130), (222), and (510) oriented films. The measured sheet resistances of the films were 38 Ω/cm, 150 Ω/cm, and 300 Ω/cm and the highest measured optical transmittance in the visible range were 87.4%, 70% , and 36% respectively.

Introduction

Tin-oxide (SnO_2) is one of the semiconducting oxides that has unique optical, electrical, transparent, and conductive properties and hence widely used as transparent conducting materials for variety of applications such as solar cells electrodes. Several researchers have carried out investigations on the physical and optical properties of doped SnO_2 thin films in order to achieve best transparency and conductivity. The best conductive and transparent FTO thin films were obtained to the precursor colloidal solution by using propane-2-ol as solvent comparative to methanol, ethanol, or double-distilled water [1]. E. Elangovan, K. Ramamurthi found that the sheet resistance decreased to a minimum of 1.75 Ω/□ with doping concentration 15 % wt of NH_4F, but increased thereafter [2]. The minimum sheet resistance observed is the lowest among the reported values for SnO_2:F films prepared from $SnCl_2$ precursor. The transmittance was found to increase with the increase in fluorine concentration. The highest optical transmittance obtained is 85 % at the wavelength of 800 nm for (NH_4F:$SnCl_2.2H_2O$) thin film with ratio 15% . The maximum reflectance in the infrared region approached to 50 % (for 15,30 wt% NH_4F) [2]. In the present work, highly transparent and conductive thin films were prepared from tin chloride hydrate doped with ammonium fluoride precursor and their electrical and optical properties were investigated. A good criterion to define the quality of the window material for thin film solar cells is the figure of merit, which is a function of sheet resistance and visible transmittance.

Experimental:

Nano thin films of fluorine doped tin oxide were fabricated applying aerosol assisted chemical vapor deposition (AACVD) technique by using ultrasonic frequency to spray pyrolysis of the precursor solution on heated glass substrates. 4.5g tin chloride ($SnCl_2.2H_2O$,purity-99.99%, Aldrich) and ammonium fluoride (NH_4F,purity- 99.99%,Aldrich) were dissolved in to 15 ml Acetic Acid (AcAc, Samchun chemical, 32%) and (30 ml) distilled water .The resulting mixture was stirred at 40°C for 30 min using an ultrasonic agitator in order to obtain a clear solution which was used for synthesizing then FTO films on microscopic glass slides . The latter slides (2.5cm x 7.5cm) were ultrasonically cleaned in acetone, ethanol and de-ionized water , and dried at 60°C . A glass slide was sprayed manually with the FTO synthesis solution at 400°C over a time period of 10 min utilizing the ultrasonic spray pyrolysis device .The FTO coated slide was then annealed at 450°C for 30 min. The preceding procedure was repeated with other glass slides over spray time periods of 20 and 30 min to obtain thin films of different thicknesses .The temperature of the FTO coated glass slides was monitored by an infrared temperature indicator through the experimental runs.

Characterization of film:

The electrical conductivity of the film was measured by a Multi high probe sheet resistance (Jandel RM3 Resistivity Meter). The thickness of film was measured by a thickness measurement (EPP-2000, Stellar Net Inc.) and Atomic Force Microscopy (AFM) (AA 3000 Scanning probe microscope, Angstron Advanced Inc.). The transmittance of FTO film coated was measured in the wavelength range of (190 - 1200) nm using a (SPECTRO UV/VIS Double Beam (UVD-3500) Labomed, Inc.). A blank sample of substrate was used as a reference in the measurement of optical transmittance and thickness. Composition and crystal structure studied by X- ray diffraction (XRD-Shimadzu 6000, Cu-Kα) for SPU coating. AFM investigation of the surface morphology of sample was studied .

Basic theory:

The optical properties of FTO thin films were studied. The Absorption coefficient (α), Extinction Coefficient (k_o) and Refractive Index (N_o) were measured as function of energy of photon incident. Equation (1) is based on the Beer-Lambert law for optical absorption, where I is the intensity of transmitted light of the film with thickness (t), Absorbance (A), and the Absorption coefficient (α) which shown in the following equation[3]:

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$$\alpha = \frac{1}{t} * ln\left(\frac{I_0}{I}\right) = 2.303 * \frac{A}{t} \quad ....(1)$$

We calculated the optical band gap of the thin film FTO from the equation (2) [3]:

$$hv * \alpha = B * \left[hv - E_g\right]^{1/2} \quad ...(2)$$

Where ,h is the Planck constant , v is the light frequency , E_g is the optical energy gap and B is empirical constant . The relation between the Absorption coefficient and the Extinction Coefficient (k_o) was shown in the following equation [3]:

$$K_0 = \alpha * \lambda / 4\pi \quad ....(3)$$

Where λ is the wave length of the incident light . The relation between the Extinction Coefficient and the Refractive Index (N_o) was shown in the following equation[3] :

$$N_0 = \left[\frac{4R}{(R-1)^2} - K_0^2\right]^{1/2} + \frac{(R+1)}{(R-1)} \quad ....(4)$$

Where the R is the reflection coefficient of the FTO film .The grain size of the crystallite thin film from the XRD data was calculated using the Debye–Scherrer formula [1]:

$$D = \frac{0.9 * \lambda}{\beta * \cos(\theta)} \quad ...(5)$$

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 .

Results and discussion
Structural studies

The XRD pattern of the FTO film fabricated by the ultrasonic spray technique is shown in Fig(1-a). The figure depict that the orientations were (110),(101),(200) and (211) in (2Θ=27.6,34,38.1 and 51.8), respectively, for thin film with sprayed time (30 min) . Some researchers [4] reported that XRD diffractogram of FTO films for different deposition temperature showed a preferential growth along the (110),(101),(200) and (211) directions as shown in fig (1-b). The sizes of the crystallites FTO thin film were estimated from the XRD results using Scherrer's formula in the equation (5) and inserted in table(1) .

Table 1. Explains the size of crystals and the plane orientation of crystals

The plane orientation of crystals	(110)	(101)	(200)	(211)
The sizes of the crystals (nm)	3.079	3.534	15.28	3.098

The grain size values obtained from the XRD studies were confirmed by the AFM image of the thin film with thickness (45.64 nm). The images of the samples manufactured with sprayed times (10,20,30 min) explained in fig (2) had thicknesses (13.55,22.62,45.64 nm) , respectively, measured by AFM probe microscope (Cont Al-G Scanning probes microscope, Budget sensors Inc) with silicon probes materials, Resonant frequency 13KHz, force constant 0.2N/m and Aluminum reflex coating . The thickness of the film closed to (45 nm) , as shown in Fig. 2(C), this value was agreement with the thickness of film determined by a thickness measurement (EPP-2000, Stellar Net Inc.). The sheet resistances of the films were measured by a Multi high probe sheet resistance (Jandel RM3 Resistivity Meter) with current range (10 nA-99.999 mA),needle radius (100μm) and needle material (metal Tungsten Carped) .and the Sheet resistances closed to (38.02 Ω/□, 150.02 Ω/□ , 300.02 Ω/□) of the films with sprayed time (30 min, 20 min, 10 min) , respectively . The surface morphology of sample

with sprayed time (30 min) was investigated by contact mode Photo Scan microscopy (PSM-500) as shown as in the Fig. (3), this image clear the homogeneous particle size in the film , no defects or cracks , and less flaws.
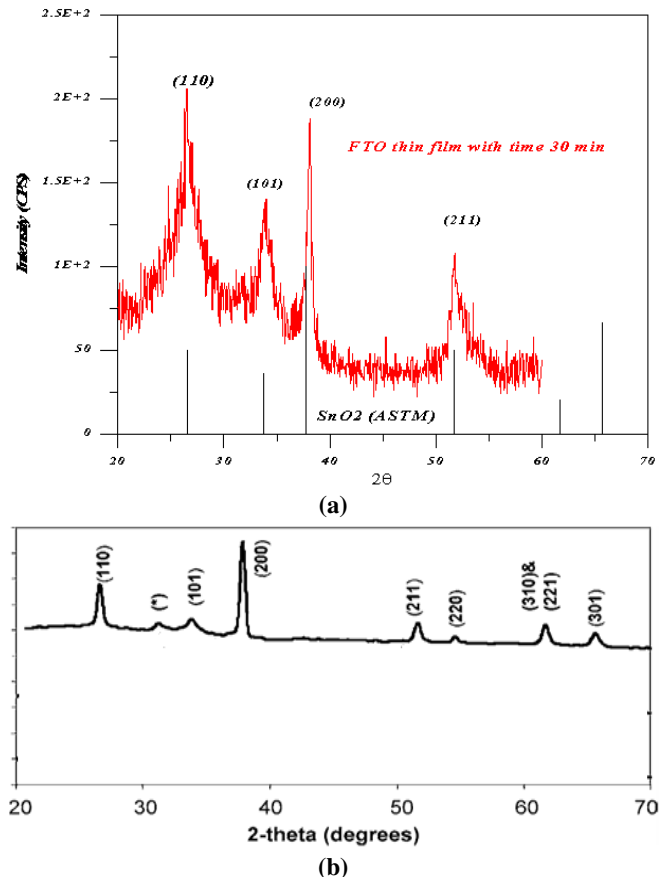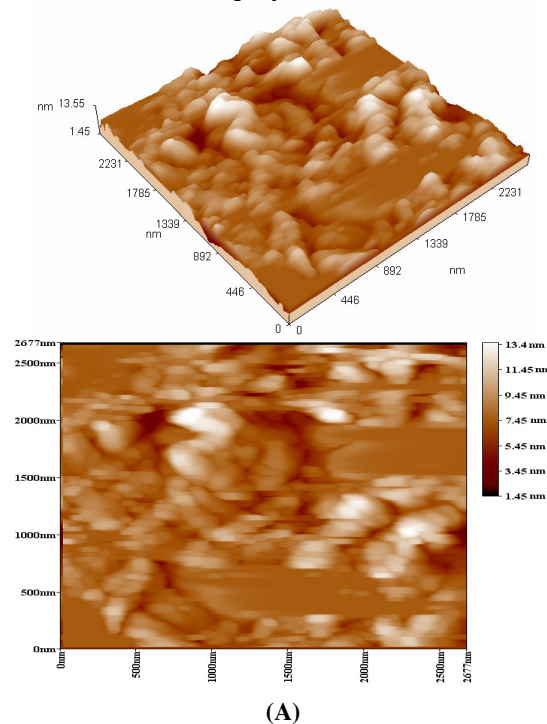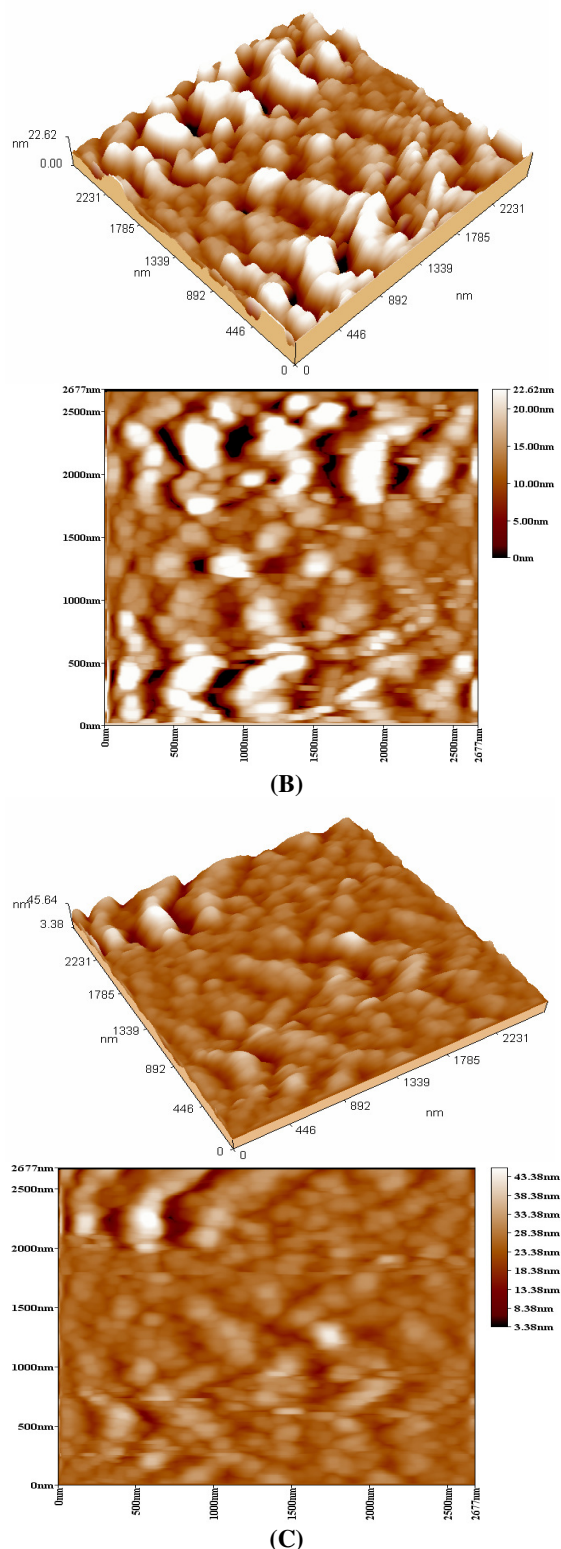

(a)

(b)

Fig. (1-a) shows XRD of FTO film with spray time 30 minutes in the present work Fig. (1-b) XRD pattern for the FTO film sprayed at 440 ◦C [4]
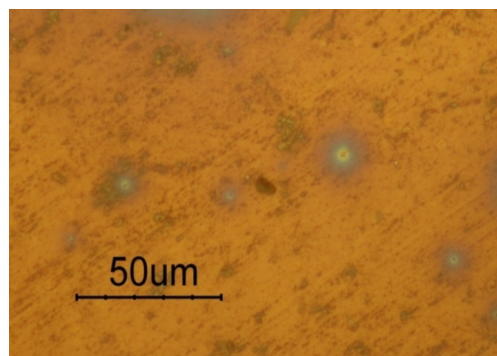

(A)

(B)

Fig. (3) Shows Photo Scan microscopy image of sample with sprayed time (30 min) and (PSM-500)

Optical studies:

The obtained transmittance of FTO films was measured in the wavelength range (190-1200) nm using a (SPECTRO UV/VIS Double Beam (UVD-3500) Labomed, Inc.) as shown in Fig 4. The maximum values of transmittance thin films grown with thicknesses (13.55,22.62,45.64 nm) in the wave length visible range have been obtained (85%, 65%,37%),respectively . Fig (5) depicted the absorption coefficient of (SnO:F) material as function of photon energy. As can be seen , the absorption coefficient (α) of FTO thin films material which calculated from the eq (1) was increased in the high photon energy, as shown as in fig(5) . Inset illustrates plots of $(\alpha*h\upsilon)^2$ versus photon energy(hυ) for three samples of FTO films were shown in Fig .6. Direct optical band gap energy (Eg) for SnO:F thin film was determined by fitting the absorption data to the direct transition equation (2). The optical band gap value was obtained by extrapolating the linear part of the curve $(h\upsilon*\alpha)^2$ as a function of photon energy, hυ , to intercept the (hυ) axis at α = 0. The plots $(\alpha*h\upsilon)^2$ versus photon energy (hυ) were depicted as an inset in Fig. 6. The optical band gap energy for three films grown with time sprayed (10,20 and 30 minuet) were estimated with values 4.033, 3.93 and 3.874 eV, respectively, as shown as in fig (6) .As consequence , Eg, values of FTO films were increased when the thickness films were decreased [5-8].

The thickness was independent on Resistivity of three films (Sheet Resistance * Thickness) as shown as in table (2). As consequence, the thinner sample (grown time was10min) apparently has higher Resistivity than thicker sample. This behavior may be because the optical energy gap was found to be larger in the thinner sample as shown as in table (2). An addition , optical band gap was related with the electric conductivity (σ =1/Resistivity) which was decreased in the insulator materials which have larger energy gap than conductive materials which , barely, didn't have energy gap , Their for, the Energy gap and Resistivity of the films had same behavior . Figure 7 was shown the refractive index, N_0, of the FTO films with grown time (10,20,30 min) as a function of photon energy. As clearly from Fig (7), The refractive indexes N_0 were decreased in the high photon energy about 3.6 to 4.3 eV with all the samples manufactured with grown times (10,20,30 min) . Sample with (t=10 min) film, a peak of the refractive index in Fig. 7 (square symbol) appears at 3.85 eV, which likely corresponds to the direct-band-gap energy Eg transition, lower than the typical value (4.033 eV). The direct-band gaps of SnO_2:F is closely coincides with the SnO_2:Sb thin film prepared by spray technique using perfume atomizer [8].

(C)

Fig(2-a) shows the morphology surface of (FTO) film with sprayed time (10 min), Fig(b) explains the morphology surface of (FTO) film with sprayed time (20 min) ,Fig(c) explains the morphology surface of (FTO) film with sprayed time (30 min)
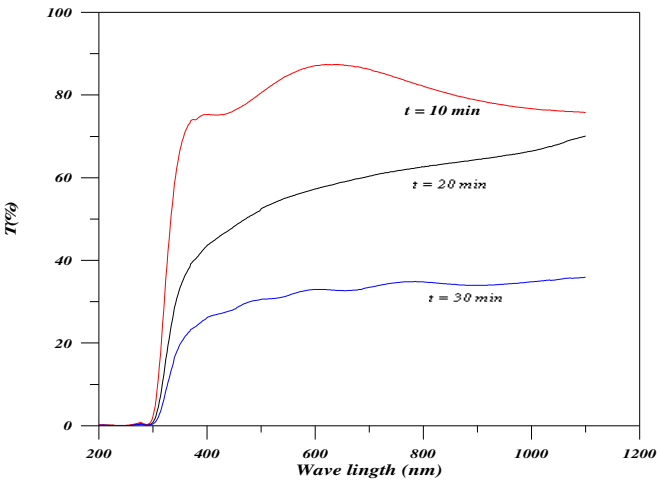
Fig 4. shows the Transmittance as function UV-vis wave length for three manufactured samples with variation sprayed times
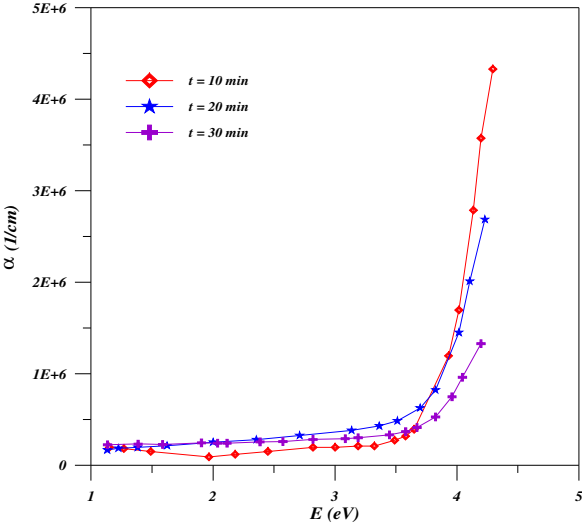

Fig 5. shows the Absorption Coefficients as function photon energy for three manufactured samples with variation sprayed times
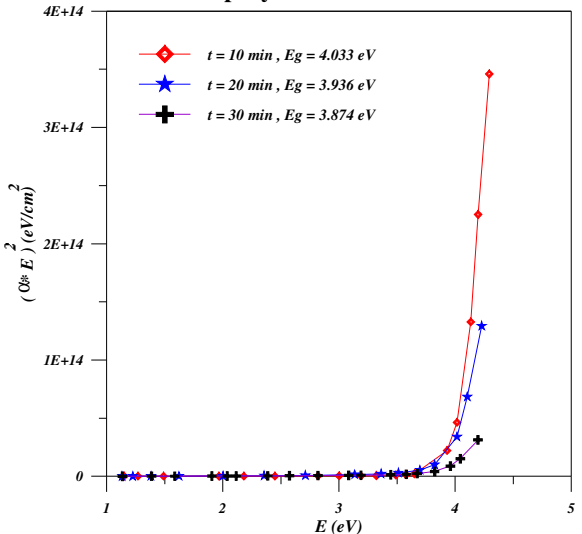

Fig 6. Inset illustrates plots of $(\alpha h\upsilon)^2$ versus photon energy (E) to the FTO samples.
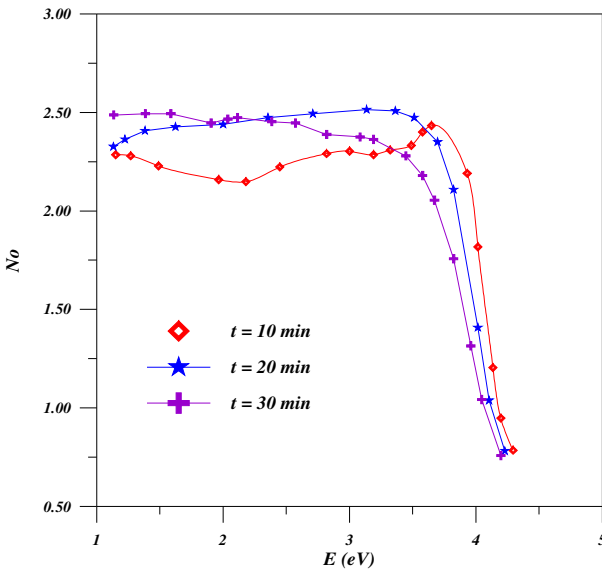

Fig 6. Inset illustrates plots of refractive index (N_0) versus photon energy (E) to the FTO samples

Table 2. Explains the optical and electrical properties of the manufactured thin films

Grown time (min)	Sheet Resistance ($\Omega/\square$)	Resistivity (Ωcm)	Max Transmittance in Vis light (%)	Thickness (nm)	Energy gap (eV)
10	300	$4.065*10^{-4}$	87.4	13.55	4.033
20	150		70	22.62	3.936
30	38	$3.393*10^{-4}$	36	45.64	3.874
		$1.735*10^{-4}$			

Conclusion

In an attempt to prepare low-cost transparent and conducting oxides, Aerosol assisted Chemical vapor deposition technique by using Ultrasonic frequency has been employed to prepare fluorine doped tin oxide thin films from $SnCl_2$:NH_4F precursor. Sheet Resistance, Optical energy gap, Resistivity and maximum value of transmittance in visible wave length for three samples have same behavior which is decreased when thickness film or grown time film is increased. The refractive index of FTO thin film was increased in visible light and decreased in UV range in the light spectrum. The high transmittance together with high conductivity makes these films suitable for window materials in thin film solar cells.

Acknowledgement

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