Optical Characterization of Fluorine doped Tin Oxide (FTO) thin films deposited by spray pyrolysis technique and annealed under Nitrogen atmosphere

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ABSTRACT: Spray pyrolysis technique has been used to deposit Fluorine doped Tin Oxide (FTO) thin films. Optical constants such as refractive index (n), extinction coefficient (K) and the absorption coefficient (α) of the FTO thin films were determined using spectrophotometric measurement of transmittance, absorbance and reflectance in the spectral range from 172 to 1100nm. The maximum value of transmittance was in the range of 77% to 86%. Furthermore, the effect of annealing temperature and the annealing condition on optical band gap (E_g) was studied. The optical band gap was found to be within the range of 3.50 to 4.0 eV.

KEYWORDS: Fluorine doped Tin oxide (FTO), Optical properties, Extinction coefficient, refractive index.

1 INTRODUCTION

Transparent conducting oxides (TCOs) are electrical conductive materials with a comparably low absorption of light. They are usually prepared with thin film technologies. Glass fibers are nearly lossless conductors of light, but electrical insulators such as silicon and compound semiconductors are wavelength dependent optical resistors (generating mobile electrons), as well as dopant dependent electrical conductors. Transparent conducting oxides are highly flexible intermediate states with both of these characteristics. Their conductivity can be tuned from insulating via semiconducting to conducting as well as their transparency adjusted. As they can be produced as n-type and p-type conductivities, they open a wide range of power saving opto-electrical circuitries and technological applications [1].

Transparent conductive oxides (TCO) have become increasingly important in a large variety of applications due to demands for optically-transparent, conductive materials. Applications of these devices include thin-film solar cells, display devices, optoelectronic devices, polymer-inorganic composite solar cells, gas sensors, and frost-resistant surfaces. [1, 2]. A common TCO used in research and industry is tin-doped indium oxide (ITO). ITO is an n-type semiconductor where indium oxide (In_2O_3) has been doped with tin oxide in order to improve many of the material's properties, including its electrical conductivity. However, ITO experiences a reduction of electrical conductivity when exposed to oxygen at elevated temperatures (> 300[0]C) [3].

Fluorine doped Tin dioxide Thin Films belong to a special class of metal oxide thin films i.e. Transparent Conducing Oxide thin films which are a special part of nanostructured thin film solar cells. It offers the possibility of fabrication of low cost solar cells. As it permits the transmission of solar radiation directly to the active region with little or no attenuation, these solar cells have improved sensitivity in the high-photon-energy portion of the solar spectrum and make thin film solar cells

suitable for large scale application with high performance efficiency [4]. At higher temperatures, oxygen in the atmosphere combines with oxygen vacancies. When the number of oxygen vacancies decreases and the number of charge carriers reduces accordingly, the electrical conductivity decreases. Since many of the above-mentioned devices undergo thermal treatments, this reduction of conductivity becomes problematic. Therefore, FTO, which is much more thermally stable, is often used as an alternative to ITO. FTO is an ideal candidate for applications requiring TCO due to its ability to adhere strongly to glass, resistance to physical abrasion, chemical stability, high optical visible transparency, and electrical conductivity. In the case of FTO, fluorine (F) is doped into tin oxide where fluorine substitutes for O^{-2} and acts as an electron donor, resulting in an n-type degenerate semiconductor [3]. Many techniques have been employed to deposit FTO such as sputtering [5, 6], Inkjet printing technique [7], Aerosol assisted chemical vapor deposition (AACVD) [8], Sol gel [9], Atmospheric-pressure plasma deposition system [10], Spray pyrolysis [3, 11]. Spray pyrolysis has been chosen in this research because it is considered as a modification of vapour deposition using a fine spray of precursor solution (generated by a spray nozzle using compressed gas) that delivers the precursor metal organic molecules to the substrate surface for thermal reaction and film formation.

2 EXPIREMENTAL DETAILS

2.1 CLEANING OF THE MATERIALS

The soda lime glass, the beakers, and measuring cylinder were washed first with detergent and rinsed with distilled water, then washed with acetic acid and finally rinsed with ethanol.

2.2 PREPARATION OF FLUORINE DOPED TIN OXIDE (FTO)

10.0g of tin tetrachloride pentahydrate ($SnCl_2.5H_2O$) was measured using the digital weighing machine (balance) and dissolved in 100ml of ethanol in a closed container. The solution was stirred continuously until all the tin chloride pentahydrate was completely dissolved in the ethanol. The solution was labeled A

2.0g of ammonium chloride was measured and dissolved in 4.0ml of ethanol in another container; the solution was stirred continuously until all the salt dissolved. And then the solution labeled B.

After both solutions have been allowed to fully stir, the tin chloride penthydrate solution is placed in a water bath and heated to 60℃. Next, the ammonium fluoride solution is then admixed. The combined solution is allowed to stir overnight to ensure complete mixing, and the resulting solution is clear and stable.

The Tin tetrachloride pent hydrate ($SnCl_2.5H_2O$, Ammonium fluoride (NH_4F), Ethanol (C_2H_5OH) and Acetic acid were of analytical grade of 4N purity and obtained from Sonopharm chemical reagent company limited.

2.3 SYNTHESIS OF FLUORINE DOPED TIN OXIDE (FTO) THIN FILMS

The spray pyrolysis technique was employed to deposit the fluorine doped tin oxide thin films. Soda lime glass was used as substrate. The precursor solution was the mixture tin chloride pentahydrate solution and ammonium fluoride solution. The solution was sprayed on the heated glass substrate using KM – 150 spray pyrolysis deposition machine (SPD). The deposition temperature and solution flow rate were maintained at 723K and 1.5ml/min respectively. Other parameters were kept constant. Film thickness of 100nm was deposited on the glass substrate at a nozzle – substrate distance of 11.0cm. The growth rate was approximately 25nm/min. The film thickness was measured using a taly step profilometer (roughness detector with a stylus Taylor Hobson model).

Four samples were prepared and labeled as FTO 273: as deposited sample, FTO 423: sample annealed under nitrogen atmosphere at 423K, FTO 573: sample annealed under nitrogen atmosphere at 573K, and FTO 723: sample annealed under nitrogen atmosphere at 723K. Deposition rate is defined as the thickness divided by deposition time, and it is important in film thickness control, especially for precise multi-layer coating [6].

2.4 ANNEALING OF THE SAMPLES

Three samples designated as FTO 423, FTO 573, and FTO 723 were taken to an oven one after the other and heated at temperatures $423K$, 573K and723K respectively under nitrogen atmosphere for one hour. The Nitrogen gas flow rate is 1 standard cubic centimeter per minute (sccm). The sample marked FTO 273 was unannealed to serve as reference sample.

2.5   CHARACTERIZATION

The transmittance spectra of the films were measured in the range of 172 to 1000nm using Avantes Avaspec 2048 UV–VIS-NIR spectrophotometer at room temperature.

3   METHOD OF CALCULATION

The study of the fundamental absorption edge provides useful complementary information concerning energy band structure and the type of transition of the charge carriers. The absorption coefficient α of the films was determined using the formula [12, 13].

$$\alpha = \frac{1}{d}Ln[\frac{1}{T}] \qquad (1)$$

Where T and d are the transmittance and thickness of the films respectively.

The optical energy band gap E_g was estimated from the optical measurements using the following expression [4, 14].

$$(\alpha h y)^2 = A(h y - E_g) \qquad (2)$$

Where A is a constant, $h\upsilon$ is the photon energy, E_g is the energy band gap and α is the absorptivity. E_g values were obtained by extrapolating the linear portion of the plots of $(\alpha h\upsilon)^2$ versus $h y$ to $\alpha = 0.0$.

The refractive index n was calculated from the following equation [12].

$$n = \frac{1+R^{\wedge}0.5}{1-R^{\wedge}0.5} \qquad (3)$$

Where R is the reflectance.

The coefficient of absorption k was calculated from the following equation [15].

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

Where α is the absorption, γ is the incident wavelength.

The relation between the real dielectric constant ε and the wavelength, in the normal dispersion region is given by [12].

$$\varepsilon = n^2 - k^2 \qquad (5)$$

4   RESULTS AND DISCUSSION

4.1   OPTICAL CHARACTERIZATION

The optical properties of fluorine doped tin oxide thin films prepared and deposited by spray pyrolysis technique on a soda lime glass substrate (at a substrate temperature of 723K) and annealed at different temperatures (423K, 573K and 723K) have been studied. Transmission and absorption spectra were measured in the range from (380nm to 750nm)

4.2   TRANSMITTANCE

Fig. 1 shows optical transmittance spectrum of the FTO films. All the films show high optical transmittance in the visible region of the electromagnetic spectrum. The annealed samples have high transmittance more than the as deposited samples. The optical transmittance of the as-deposited, sample annealed at 423K, 573K, and 723K are 72.85%, 80.66%, 84.14% and 79.05% respectively.
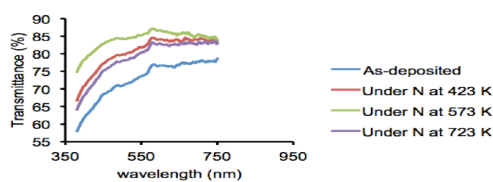
Fig. 1   A plot of optical transmittance versus wavelength for as-deposited and samples annealed under N$_2$ atmosphere.

Fig. 2 shows the plot of transmittance against temperature of the FTO films. It can be seen clearly that transmittance increases with an increase in annealing temperature. The transmittance keeps increasing when the films were heated from room temperature(273 K) to 723K, until it reaches a maximum value of 84.16% at 573K. Further increase in temperature leads to slight decrease in transmittance of about 5% at a temperature of 723K.

According to [12], the decrease of transmittance with increasing annealing temperature may be due to an improvement of the degree of crystallinity of the films and an increase of the grain size.
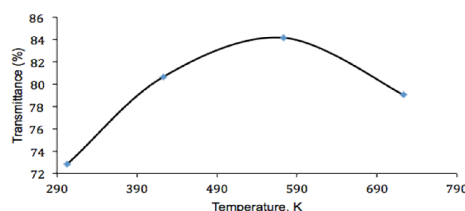

Fig. 2. Variation of transmittance with annealing temperature for as-deposited sample and samples annealed under N$_2$ atmosphere

Fig. 3 shows optical reflectance spectrum of the FTO films. All the films show low optical reflectance in the visible region of the electromagnetic spectrum. The annealed films have a low reflectance than the as-deposited sample. The optical reflectance of the films as-deposited sample and samples annealed at 423K, 573K, and 723K are 27.92%, 35.28%, 28.89% and 15.78% respectively.

The high transmittance and low reflectance properties of the films make them good materials for anti-reflection coatings and for solar thermal applications in flat plate collectors [13].
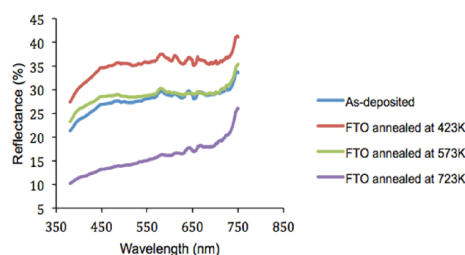

Fig. 3.   Plot of optical reflectance versus wavelength for as-deposited and samples annealed under N$_2$ atmosphere.

4.3   ABSORPTION COEFFICIENT (α)

The ability of a material to absorb light is measured by its absorption coefficient. Fig. 4 shows variation of absorption coefficient of FTO films with various wavelength regions annealed at different temperatures. It can be seen that the as-deposited films have higher absorption coefficient than the annealed samples. This implies that the as-deposited sample have high ability to absorb light within the visible region than the other samples annealed at different temperatures. The absorption coefficient of the FTO films is shown in table 1.

Sanusi Abdullahi, A.U. Moreh, B. Hamza, U. Sadiya, Z. Abdullahi, M. A. Wara, H. Kamaluddeen, M. A. Kebbe, and U. F. Monsurat

According to [13], this higher value of absorption coefficient (α) for as- deposited FTO films with steeper optical absorption edge indicates better crystallinity of the films and lower defect density near the band edge.
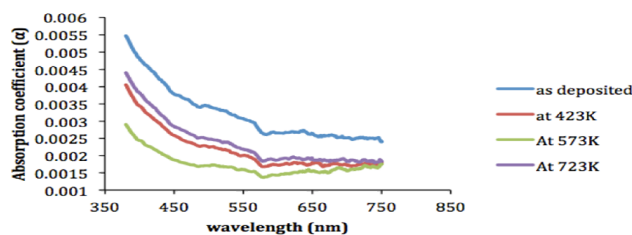

Fig.4. Plot of Absorption coefficient versus wavelength for as-sample and samples annealed under N_2 atmosphere

Table 1.   Absorption coefficient for as-sample and samples annealed under N_2 atmosphere.

SAMPLE	ABSORPTION COEFFICIENT, α (cm^{-1})
As-deposited FTO films	*0.0032*
FTO films annealed at 423K	*0.0022*
FTO films annealed at 573K	*0.0017*
FTO films annealed at 723K	*0.0024*

4.4   OPTICAL BAND GAP (EG)

The plot of $(\alpha h \gamma)^2$ versus $h\gamma$ is shown in Figures 5a, b, c and d. By extrapolating the linear portion of the graph to $h\gamma$ axis, band gap have been obtained at the intercept. The obtained values of E_g are listed on table 2, where E_g increases with increase in annealing temperature.

This increase in E_g is due to quantum size effect. And that during the annealing process the films will have time for some atomic rearrangement to take place. Therefore, some defects will be removed which will result in reducing the density of dangling bonds, redistributing atomic distances and bond angles and optical gap then increases. Physically, the band gap growth effect in FTO system may originate from the change in nature and strength of the interaction potentials between the donors and host crystals. It is generally believed that this increase in the band gap is due to Burstein-Moss shift that is due to increase in carrier concentration, the absorption edge shifts to higher energy level [4, 12]. This increase is also connected to a reduction in the resistances of the films, implying enhancement of the carrier concentration [5].
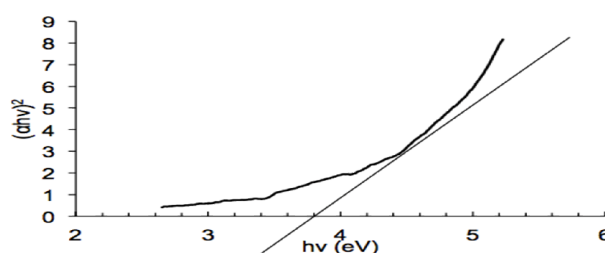

Fig. 5a.   A plot of $(\alpha h \upsilon)^2$ versus hv for as-deposited sample.
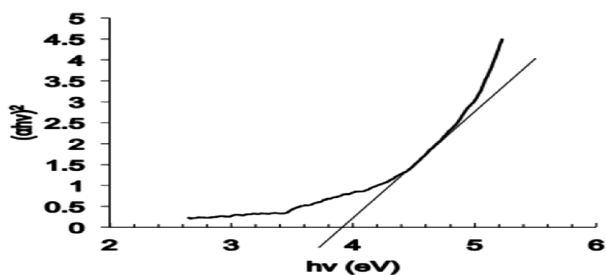
Fig. 5b.   A plot of $(\alpha h v)^2$ versus hv for FTO annealed under N_2 at 423K.
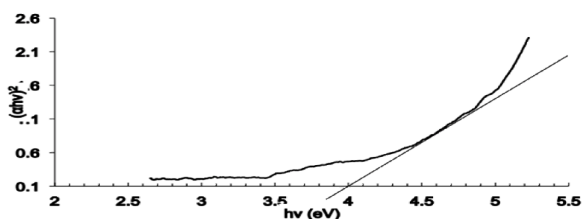

Fig. 5c.   A plot of $(\alpha h v)^2$ versus hv for FTO annealed under N_2 at 573K
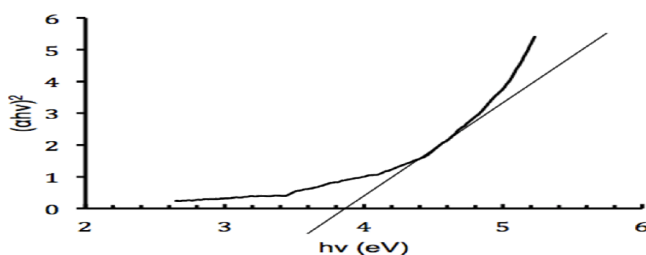

Fig. 5d.   A plot of $\alpha h v^2$ versus hv for FTO annealed under N_2 at 723K

Table 2.   Energy band gap for as-sample and samples annealed under N_2 atmosphere.

S/NO.	SAMPLE	Energy Band Gap, E_g (Ev)
1	As deposited	3.80
2	Annealed at 423K	3.90
3	Annealed at 573K	4.00
4	Annealed at 723K	3.90

4.6   REFRACTIVE INDEX (N)

Fig. 6 shows variation of refractive index with wavelength of the FTO films. Refractive index decreases with increase in wavelength indicating that all the films exhibit anomalous dispersion. The refractive index of the FTO films for as-deposited, annealed at 423K, 573K, and 723K are 1.47, 1.41, 1.46, and 1.68 respectively. According to [12], the decrease in refractive index with increase in wavelength confirms the semi conductor behavior of the films.
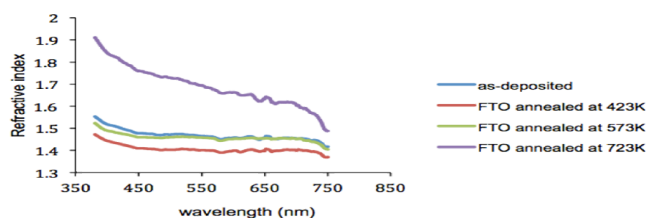
Sanusi Abdullahi, A.U. Moreh, B. Hamza, U. Sadiya, Z. Abdullahi, M. A. Wara, H. Kamaluddeen, M. A. Kebbe, and U. F. Monsurat

Fig. 6. A plot of optical reflective index versus wavelength for as-deposited and samples annealed under N_2 atmosphere.

Fig. 7 is a plot of refractive index versus annealing temperatures. The refractive index for FTO films annealed at 723K is higher than the rest of the films annealed at 423K, 573K, and as-deposited. According to [12], this could be due to increase in the packing density as the annealing temperature increases. Also according to [6], the increase in the refractive index could be due to the re-crystallization, oxidation, and diffusion of tin from the deposited films into glass matrix.
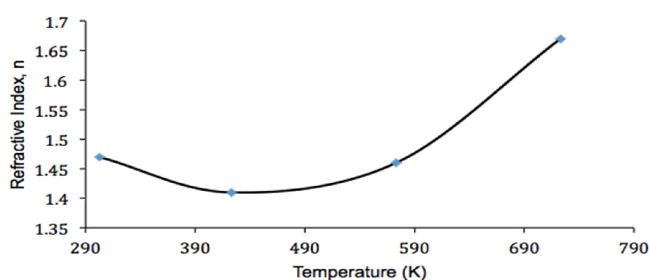

Fig. 7.   Variation of refractive index with annealing temperature for as-deposited sample and samples annealed under N_2 atmosphere.

4.7 EXTINCTION COEFFICIENT (K)

This is a measure of the rate of attenuation of transmitted light through scattering and absorption for a medium. Fig. 8 shows a plot of extinction coefficient against wavelength for FTO films. The value k decreases as the wavelength of the incident light increases to 550nm, and then starts to increase, as the incident wavelength increases. The average values of extinction coefficient (k) of the FTO films for as-deposited sample and samples annealed at 423K, 573K and 723K are 0.138, 0.093, 0.076, and 0.102 respectively. The variation in the value of k spectra was quite different between ultraviolet (UV) region (above 3.0 eV and the near infrared (NIR) region (below 1.75eV).
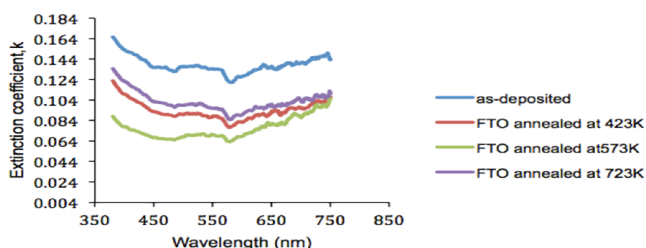

Fig. 8 A plot of extinction coefficient versus wavelength for as-deposited and samples annealed under N_2 atmosphere.

Fig. 9 shows a plot of extinction coefficient versus temperature. It is clear that the value of k decreases with increase in annealing temperature until when temperature is 423K, and with further increase in temperature it also increases. This according to [16] is due to crystallization of film structure by increasing the grain size, and slightly, the absorption edge shift to smaller wavelength (higher photon energy) with increasing annealing temperature. The decrease of k with increasing annealing temperatures are due to the increasing value of energy gap.
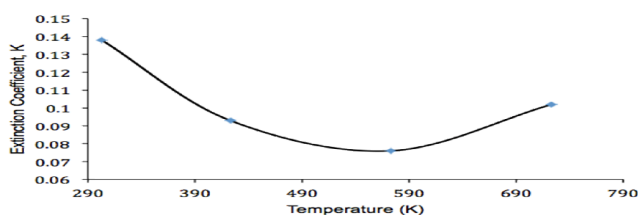
Fig. 9. Variation of extinction coefficient with temperature for as-deposited sample and samples annealed under N₂ atmosphere

4.8   DIELECTRIC CONSTANT (ε)

Fig. 10 is a plot of dielectric constant versus wavelength. The value of the dielectric constant decreases with increase in wavelength within the visible region of the spectrum. The dielectric constant of the FTO films for as –deposited sample and samples annealed at 423K, 573K, and 723K are 2.137, 1.967, 2.120, and 2.846 respectively.
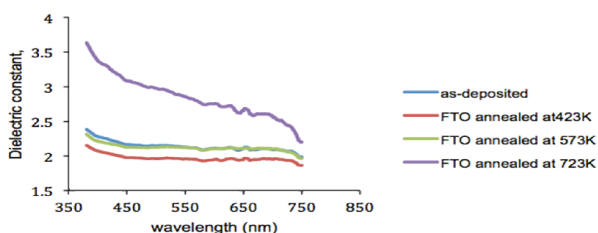

Fig. 10. A plot dielectric constant versus wavelength for as-deposited sample and samples annealed under N₂ atmosphere.

Fig. 11 shows the variation of dielectric constant of as-deposited FTO thin films and annealed at different annealing temperatures (423, 573,723K). It is interesting to see that dielectric constant increases with increasing annealing temperatures. This behavior according to [16] is due to increase in the reflection on which the refractive index depends on it.
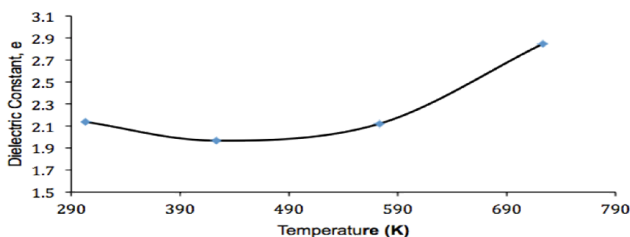

Fig. 11 Variation of dielectric constant with temperature for as-deposited sample and samples annealed under N₂ atmosphere.

Table 3. Values of transmittance,T, Reflectance,R, Absorption, A, absorption coefficient, extinction coefficient and Dielectric constant

S/No.	SAMPLE	T (%)	R (%)	A	α	K	ε
1.	As-deposited	72.85	27.92	0.138	0.003	0.138	2.137
2.	Annealed at 423K	80.66	35.28	0.093	0.002	0.093	1.967
3.	Annealed at 573K	84.16	23.89	0.075	0.001	0.076	2.12
4.	Annealed at 723K	79.05	15.78	0.102	0.002	0.102	2.846

5   CONCLUSION

This work reported the preparation growth and characterization of fluorine doped tin oxide thin films annealed under Nitrogen atmosphere at various temperatures. These films were deposited by spray pyrolysis technique. It is concluded that annealing under N₂ atmosphere influences some of the optical constants of the films.

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