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EFFECT OF FLUORINE DOPING ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF SPIN COATED TIN OXIDE THIN FILMS FOR SOLAR CELLS APPLICATION

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Abstract

Transparent conducting oxide (TCO) thin films are materials of significance for their applications in optoelectronics and sun powered cells. Fluorine-doped tin oxide (FTO) is an elective material in the advancement of TCO films. This paper reports the impact of fluorine doping on structural, optical and electrical properties of tin oxide thin films for solar cells application. The sol-gel was prepared from anhydrous stannous chloride, SnCl_2 as an originator, 2-methoxyethanol as a solvent, di-ethanolamine as a preservative and ammonium fluoride as the dopant source. FTO precursor solution was formulated to obtain 0, 5, 10, 15 and 20 % doping concentration and deposited on glass substrates by means of spin coater at the rate of 2000 rpm for 40 seconds. After pre-heated at 200 °C, the samples were annealed at 600 °C for 2 h. The structural, optical and electrical characteristics of prepared films were characterized using X-ray diffraction (XRD) analysis, UV-visible spectroscopy and electrical measurement. X-ray diffraction (XRD) investigation of the films demonstrated that the films were polycrystalline in nature with tetragonal-cassiterite structure with most extraordinary pinnacle having a grain size of 17.01 nm. Doping with fluorine decreases the crystallite size. There was increment in the absorbance of the film with increasing wavelength and the transmittance was basically reduced with increasing fluorine doping in the visible region. The energy band gaps were in the range of 4.106-4.121 eV. The sheet resistance were observed to decrease as the doping percentage of fluorine increased with exception at higher doping of 15 and 20 %. In view of these outcomes, FTO thin films prepared could have useful application in transparent conducting oxide electrode in solar cell.

Keywords: Fluorine-doped tin oxide, Doping, Sol-gel spin coating, Grain size, Energy band gap, Sheet resistance

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Introduction

Transparent conducting oxides (TCOs) are electrical conductive materials with comparably low absorption of light. The optical band gaps of TCOs are ≥ 3.1 eV with its properties based on the preparation and deposition methods (Yadav *et al.*,

2009). Examples of TCOs are indium tin oxide (ITO), cadmium oxide (CdO), tin oxide (TO), indium oxide (IO), aluminium doped zinc oxide (AZO), undoped zinc oxide (ZO) and fluorine doped tin oxide (FTO) (Noh *et al.*, 2012).

The most common TCO is ITO, but it has a lot of disadvantages such as expensive source, scarcity and highly toxic nature of indium itself. Several methods such as chemical vapour deposition (CVD) (Noh *et al.*, 2012), atmospheric photo CVD (Hassanien *et al.*, 2016), spray pyrolysis (Hassanien *et al.*, 2016), sol-gel dip coating (Kar and Kundoo, 2013) and sol gel spin coating (Kahatta *et al.*, 2016) have been successfully tried to produce devices of quality films. It was observed that the use of sol gel spin coating technique have been scarcely reported in the production of fluorine-doped tin oxide in the literature. Fluorine-doped tin oxide (FTO) is an alternative material in the development of TCO thin film due to the availability, non-toxicity and inexpensive source of fluorine. Sol gel spin coating techniques were used to produce undoped and doped tin oxide thin films. Structural characteristics were verified using X-ray diffractometer, optical and electrical properties were investigated by UV-vis spectroscopy and four point probes, respectively.

Materials and Methods

The glass substrates with dimension 25.4 mm x 76.2 mm were rinsed in de-ionized water. They were then cleaned in a breaker containing ethanol and the beaker was put on VWR ultrasonic cleaner at room temperature for 30 min. The cleaned glass slides were dried in a stream of nitrogen gas. All glass slides received the same cleaning process. Fluorine-doped tin oxide precursor solutions were prepared from stannous chloride as metal source, 2-methoxyethanol as a solvent, di-ethanolamine as a stabilizer and ammonium fluoride as a dopant. The starting materials, stannous chloride and 2-methoxyethanol were ensured to be free of impurities. Stannous chloride (0.2 M) was dissolved in 10 ml of 2-methoxyethanol and was mixed for 30 min at 60 °C until the mixture turned milky. Di-ethanolamine

of 10 ml was added little by little under steady mixing until milky solution was cleared. The resultant solution was stirred continuously for another 90 min until a colourless, homogeneous and transparent solution was obtained. Ammonium fluoride was added to the stannous chloride solution and stirred with magnetic stirrer for 3 h at 60 °C until it was totally dissolved (a transparent thick milky colour was obtained). The solution was kept in a closed container for 40 h at 27 °C for aging and also to obtain high thickness. The mixture prepared was deposited on a glass substrate using sol-gel spin coating method. Spin coating parameters were as follows: 2 ml of solution per deposition with a speed of 2000 rpm for 40 sec each by using LAURELL WS-400-6NPPSS spin coater. The films were pre-heated in ambient atmosphere at 200 °C for 10 min to evaporate the solvent. The FTO thin films were annealed at 600 °C for 2 h using a furnace.

Results and Discussion

Structural analysis of FTO Thin Films

FTO thin films structure was investigated through X-ray diffraction (XRD) technique. From Figure 1, it was observed that with increasing fluorine doping percentage, the crystallinity of FTO thin film decreased. It was also observed from the spectra that no peaks were added to the spectra which indicated right replacement of doped atoms with host atoms.

The more prominent diffraction peaks were (110), (101), (211) and (301), which exhibited tetragonal-cassiterite structure reported for SnO₂ (JCDPS No. 21-1250) with a preferred orientation along (110). The grain size (D) of the films was obtained from the XRD spectrum using Deybe Scherrer's formula (Awodugba and Adedokun, 2011):

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where k is a constant to be taken 0.9, β is Full Half Maximum (FWHM) in radian, λ is the wavelength of X-ray used and θ is Bragg's angle. The grain size decreased with increasing fluorine doping percentage as shown in Table 1. This may be due to

different size radii which caused the strain field or stress that disturb grain growth process. This implies that the grain size depend on doping % concentration. This result is similar to reported work of Bakr *et al.* (2016).

Table 1: Variation of average grain size of FTO thin films with doping

Doped thin film (%)	Crystalline size (nm)
0	17.01
5	14.93
10	13.62
15	11.83
20	9.90

Optical Properties of FTO Thin Films

Figure 2 demonstrates the optical transmittance spectra of FTO thin films annealed at 600 °C for 2 h using UV-vis spectrophotometer from 250-800nm at

different doping percentage. The transmission values of the films were observed to be low in the infrared region and high at visible region. This means that the films behaved as a translucent material at longer wavelengths.

Figure 1: XRD pattern of un-doped and doped SnO₂ thin film

It was also evident from the graph that as doping concentration increased, the transmittance of doped tin oxide film decreased as shown in Figure 2, which is because of increment essential absorption as photon striking increases with increment in transporter concentration (Shanthi *et al.*, 1999)

Figure 3 shows the absorption spectra for the films at different doping percentage, the absorbance of the films increases with

increasing wavelength. Absorbance increased with increase in doping percentage because there is fusion of fluorine atoms in the structure of the thin films (Noh *et al.*, 2012). It was clear that absorbance reduced rapidly within short wavelengths (Nabeel *et al.*, 2016). The absorption of all the films was different from each other and absorbance increased with increase in thickness of the film because of scattering losses.

Figure 2: UV-vis transmittance spectra for un-doped and doped SnO₂ thin films

Figure 3: Absorption spectra for un-doped and doped SnO₂ thin films

The optical conductivity spectra of the thin films were presented in Figure 4. From the result, it was perceived that doping increased the optical conductivity of the SnO₂. FTO 15 % have the highest optical conductivity of $4.4 \times 10^{15} \text{ cm}^{-1}$ at 4.1eV, followed by FTO 20 % with the optical conductivity of $4.4 \times 10^{15} \text{ cm}^{-1}$ at 4.0eV. From the graph of $(\alpha h\nu)^2$ against photon energy, the energy band gap, E_g of the prepared FTO thin films can be determined. The optical band gap of FTO thin film was approximated from the calculation of the linear relationship between $(\alpha h\nu)^2$ and $h\nu$ according to the

equation 2 (Awodugba and Adedokun, 2011).

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (2)$$

Figure 5 showed the energy band gap for 0, 5, 10, 15, and 20 % of FTO which were obtained as 4.126, 4.049, 4.097, 4.018 and 4.044eV, respectively. Doping reduced the energy band gap of SnO₂. These applies to the development of grain measure and the expansion in imperfection states close to the optical bands which actually diminished the estimated value of the energy gap (Nasir *et al.*, 2013).

Figure 4: Optical conductivity spectra for un-doped and FTO doped SnO₂ thin films

Electrical Properties of FTO Thin Films

There are two determinants of sheet resistance namely; carrier concentration and mobility (Zheng *et al.*, 2017). The sheet resistance was found to be decreasing as the doping percentage of fluorine increased, which was in contrary with the result of Moholkar *et al.* (2008). Fluorine doping concentration reached a stage, where the sheet resistance rose

(FTO 20 %). This is due to the incomplete ionization of fluorine particles in semiconductor at high doping ratio and therefore decreased the mobility (Russo and Cao, 2008; Obaida *et al.*, 2015). The sheet resistance and the sample transmittance for prepared thin films are as shown in Table 2. The sheet resistance at FTO 10 % showed the minimum value of $1.778 \Omega \text{sq}^{-1}$ that satisfied 75 % of average transmittance which is in accordance with

the results of Benhaoua *et al.* (2014). FTO films produced more free electrons and

reduced the value of the sheet resistance.

Table 2: Sheet resistance (Rs) and transmittance of FTO thin films

Sample	Sheet resistance (Ωsq^{-1})	Transmittance (%)
SnO ₂	8.922	80
FTO 5 %	5.506	56
FTO 10 %	1.778	75
FTO 15 %	2.068	56
FTO 20 %	7.453	50

Conclusion

In this research, SnO₂ and FTO films were prepared by the easier method of sol-gel spin coating by using economical materials which included SnCl₂, NH₄F, di-ethanolamine and 2-methoxyethanol as the starting materials because of easier availability, low cost and for greater degree of incorporation of fluorine atoms in SnO₂. X-ray diffraction patterns confirmed the proper phase formation of FTO thin film. Optical transmittance spectra of the films showed considerable high transparency (75 %) in the visible region and the transparency decreased with the increase of fluorine doping. The optical studies revealed that increasing the doping concentration decreased the energy band gap from 4.039eV to 3.918eV. The FTO (10 at % F) film has lowest sheet resistance (1.778 Ωsq^{-1}) making it to be highly conductive. The thin films properties observed confirmed that they would be good materials for solar cell application.

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References

- Awodugba, A.O. and Adedokun, O. 2011. On the physical and optical characteristics of CdS thin films deposited by chemical bath deposition technique: *The Pacific Journal of Science and Technology* 12 (2): 336-341.
- Bakr, N.A., Salman S.A. and Ali, M.N. 2016. Effect of fluorine doping on structural and optical properties of SnO₂ thin films prepared by chemical spray pyrolysis method. *Advances in Materials* 5(4): 23-30.
- Benhaoua, A., Rahal, A., Benhaoua, B. and Jlassi O. 2014. Effect of fluorine doping on the structural, optical and electrical properties of SnO₂ thin films prepared by spray ultrasonic. *Superlattices and Microstructures* 749(70): 61-69.
- Hassanien, A.E., Hashem, H.M., Kamel, G., Soltan, S., Moustafa, A.M., Hamman, M. and Ramadan, A.A. 2016. Performance of conducting fluorine-doped tin oxide films for application in energy efficient devices. *International Journal of Thin Films Science and Technology* 5(1): 55-65.
- Kahatta, C., Noonuruk, R. and Pecharapa, W. 2016. Influence of annealing

temperature on optical properties of fluoride doped Tin oxide films grown by the sol-gel spin coating method. *Integrated Ferroelectrics* 175(1): 138-145.

Kar, S. and Kundoo, S. 2013. Synthesis and characterization of pure and fluorine doped Tin oxide nano-particles by sol-gel methods. *International Journal of Science and Research* 4(1): 530-533.

Moholkar, A.V., Pawar, S.M., Rajpure, K.V. and Bhosale, C.H. 2008. Effect of concentration of SnCl_4 on sprayed fluorine doped tin oxide thin films. *Journal of Alloys and Compound* 455(1-2): 440-446.

Nabeel, A.B., Sabah, A.S. and Mohammed, N.A. 2016. Effect of fluorine doping on structural and optical properties of SnO_2 thin films prepared by chemical spray pyrolysis method. *Advanced Materials* 5(4): 23-30.

Nasir, E.M., Iqbal, S.N. and Alias, M.F.A. 2013. Characterization of Cadmium Tin Oxide thin films as a window layer for solar cell. *International Journal of Application or Innovation in Engineering & Management (IJAEM)* 2(9): 189-194.

Noh, S.I., Ahn, H.J. and Riu, D.H. 2012. Photovoltaic property dependence of dye sensitized solar cells on sheet resistance of FTO substrate deposited via spray pyrolysis. *Ceramic International* 38(5): 3735-3739.

Obaida, M., Moussa, I. and Boshta, M. 2015. Low sheet resistance F-doped SnO_2 thin films deposited by novel spray pyrolysis technique. *International Journal of Chemical Technology Research* 8(12): 239-247.

Russo, B. and Cao, G.Z. 2008. Fabrication and characterization of fluorine-doped tin oxide films and nanorod arrays via spray pyrolysis. *Applied Physics A* 90(2): 311-315.

Shanthi, S., Subramanian, C. and Ramasamy, P. 1999. Investigations on the optical properties of undoped, fluorine doped and antimony doped tin oxide films. *Crystal Research Technology* 34(8): 1037-1046.

Yadav, A.A., Masumdar, E.U., Moholkar, A.V., Neumann-Spallart, M., Rajpure, K.Y. and Bhosale, C.H. 2009. Electrical, structural and optical properties of SnO_2 :F thin films: Effect of the substrate temperature. *Journal of Alloys and Compounds* 488(1):350-355.

Zheng, W., Zhang, Y.N. and Tian, J.Q. 2017. Effect of fluorine doping concentration on semiconductive property of tin dioxide. *Chalcogenide Letters* 14(7): 275-281.