Transactions of the Nigerian Association of Mathematical Physics
***Volume 18, (January – December, 2022 Issue*), pp1 – 6**
© Trans. of NAMP

PROPERTIES OF FLUORINE DOPED SnO_2 TRANSPARENT CONDUCTOR DEPOSITED BY ELECTROSTATIC ASSISTED CHEMICAL VAPOUR DEPOSITION (EACVD) METHOD

[1]Eyitayo E.T. and [2] Ekpekpo A.

[1,2]Department of Physics, Delta State University Abraka, Nigeria

Abstract

The experimental work deals with the properties of Fluorine doped Tin Oxide (SnO_2) thin film. It is aimed at ascertaining the optimized conductivity of the electrical and optical properties of the films as the temperature increase at constant volume. Five(5) samples of Tin oxide were grown at various temperatures at constant volume of 2.5 ml to ascertain the effect of temperature on the conductivity of the doped thin film. The Electrostatic spray-assisted chemical vapour deposition (EACVD) method was adopted for the Flourine doped thin oxide (FTO) preparation. The results show that the values of the band gap ranges from 2.23 eV to 2.42 eV. The profilometer readings shows that the thickness of the film changes as the temperature increases from 0.008µm, 0.012 µm, 0.006 µm, 0.5 µm, 0.001 µm for 0.4m, at 330ºC, 450ºC, 470ºC 490ºC and 510ºC respectively. The highest percentage of absorbance values across the different samples lies in between 300nm – 400nm at temperature 330ºC and the lowest absorbance was 954nm at 510ºC. This study therefore concludes that the exposure to high temperatures during annealing process improves on their electrical properties and optical properties of the films, by reduction of the sheet resistance from 1477.5 Ω cm to 4.62 Ω cm, 9.87 Ω cm, 22.711 Ω cm and 3.25 Ω cm as the temperature increases. This makes doped SnO_2 thin films stable and a good choice for making a transparent thin film efficient of different application.

1.0 INTRODUCTION

Transparent conducting films as the name implies are essentially made from optically transparent and electrically conductive materials called Transparent Conductive Oxide (TCO). These films are class of materials of importance because of their applications in optoelectronics and solar cells [1]. Research in tin oxide (SnO) is gaining remarkable interest among the wide-band gap semiconductor community because of its unique photoelectric and outstanding electrical conduction properties. Furthermore, doping of SnO_2 with metal and nonmetal ions has been used to tailor the properties of the base material, which in turn has resulted in an enhancement of the device performance. This makes SnO_2 thin films excellent candidates for large-scale applications in gas sensors [2], solar cells [3], lithium-ion batteries [4] low emission window [1], and UV photodetectors.

Tin oxide thin films that are both undoped and differentially doped can normally be deposited using a wide range of growth techniques. In general, a wide range of growth techniques, such as molecular beam epitaxy, pulsed-laser deposition (PLD), aerosol assisted chemical vapor deposition (AACVD) [5], atomic layer deposition (ALD), or spray pyrolysis, can be used to deposit both undoped and variously doped tin oxide thin films [6]. Among all this technique, Electrostatic assisted chemical vapor deposition (EACVD) is the least expensive and can produce film with large range with high film quality and has the advantages of being cost efficient [7].

In the fast growing electronics market, transparent conducting oxides (TCOs) have become essential components in a large number of modern devices including touch screens, portable electronics, flexible electronics, optics, biochemical/ environmental sensors, transparent heaters, multifunctional windows and solar cells [8]. This demand for

Correspondence Author: Eyitayo E.T., Email: editheyitayo@gmail.com, Tel: +2347034602460

flexible and improved technologies that will fit into the cashless society and globalized world. This is why this experimental work becomes essential to cover up these fast growing trends. The research believes that due to the abilities of semiconductor to be dope, it will enable this improvement come to pass by consciously and contentiously improve the properties of SnO_2 by doping and increasing the temperature and also using methods that are experimental friendly and those not attract high cost, which the electrostatic assisted chemical vapour deposition method fits in [9].

2.0 MATERIALS AND METHODS

This is the description of the tools, materials and the method used for data collection of this experimental work that deals with the characterization and deposition of a thin film of fluorine-doped tin oxide ($F:SnO_2$). The objective of this research is to identify the characteristics of transparent conductive thin films and the impact of temperature on the conductivity of thin $F:SnO_2$ films. The electrostatic assisted chemical vapour deposition (EACVD) technique was adopted for the preparation of the film. Five (5) samples of thin films were grown at different temperature at constant volume [10]. The Electrostatic spray-assisted vapour deposition (ESAVD) method is to allows deposition of both thin and thick layers of a coating onto a variety of substrates, by put chemical precursors that is sprayed across an electrostatic field toward a heated substrate, where they undergo a controlled chemical reaction and deposit the necessary coating [11].
The level of the solution may affect how quickly material is deposited onto the glass substrate. The experiment started with production of the Tin. Flourine doped thin oxide (FTO) was prepared by using Tin tetrachloride $SnCl_4$ as the source of thin oxide, ammonium fluoride as the dopant (NH4F). 0.1m of ammonium fluoride and 0.4m tin tetrachloride was dissolved in 20m of methanol before spraying was performed with the machine. Doping was carried out for 330ºC, same procedure and precautions were taken as the experiment was carried out repeatedly for 450ºC, 470ºC, 490ºC and 510ºC respectively. After the electrostatic assisted chemical deposition method EACVD, the following optical characteristics were performed.

3.0 RESULTS AND DISCUSSION

Optical properties and characterization

The optical properties of the fluorine doped tin oxide (SnO_2) tin oxide thin films, prepared and deposited by Electrostatic Assisted Chemical Deposition EACVD method is as shown below. The absorbance spectra was measured in range of wavelength from 300nm – 1100nm for the 5 samples at temperature 330ºC, 400ºC, 450ºC 470ºC, 490ºC and 510ºC respectively for Fluorine dope tin, the graph below show the relationship between absorbance and wavelength.

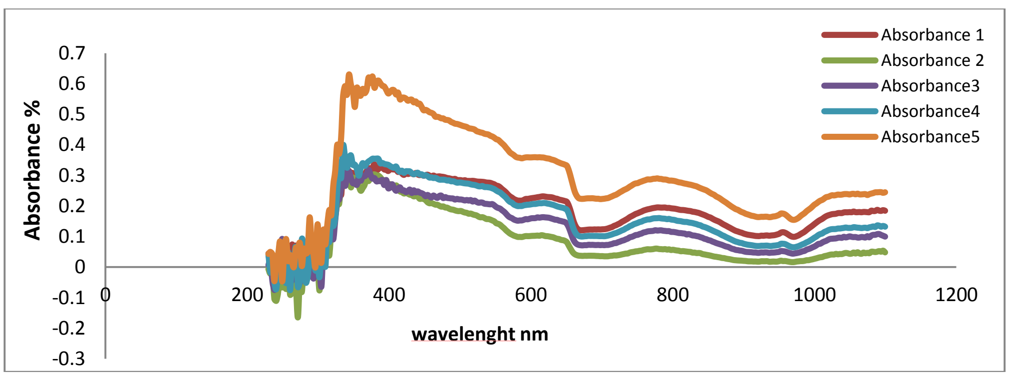

Figure 1: Absorbance graph of Fluorine Dope Tin Oxide at variance temperature

As seen from the figure above, all the samples absorbed light in the wavelength range of 300 nm to 1100 nm. Between 300 and 400 nm is where the maximum absorbance values are seen among the various samples. The absorbance of fluorine-doped materials was highest at 343.57 nm at 330 ºC, while the lowest absorbance was at 954 nm at 510 ºC. This shows that increasing the deposition temperature decreases the absorbance of fluorine-doped tin oxide material. Fluorine-doped tin oxide thin film has maximum absorbance in the ultra violet region of the electromagnetic spectrum. This shows that it can be used for window coating in the temperate part of the world.

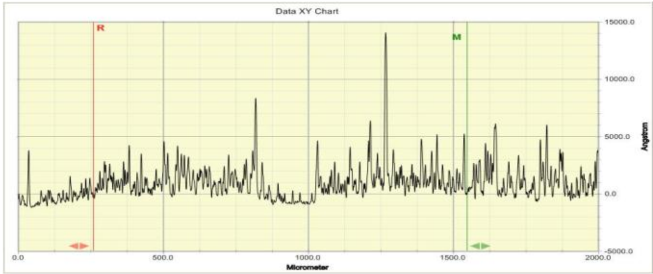

Figure 2: Profiler result showing film thickness 0.5 at temperature 330^{o}C

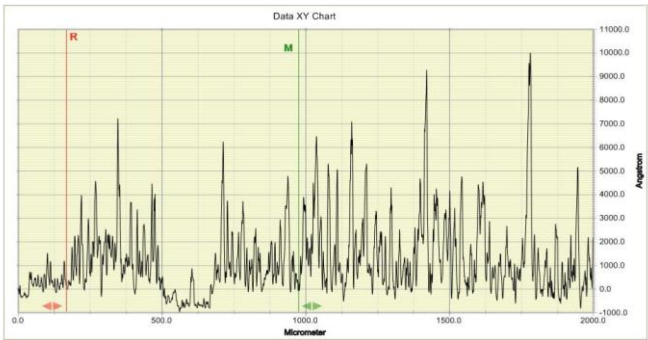

Figure 3: Profiler result showing film thickness 0.006 at temperature 450^{o}C

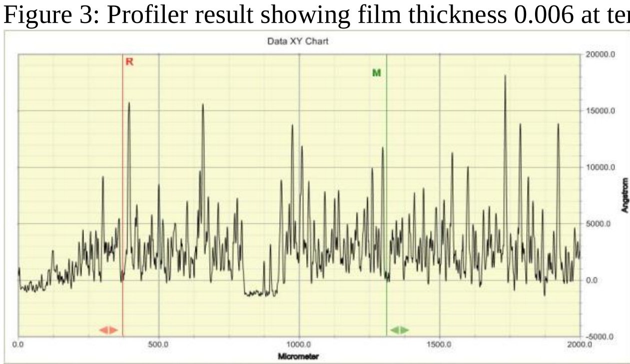

Figure 4: Profiler result showing film thickness 0.012 at temperature 470^{o}C

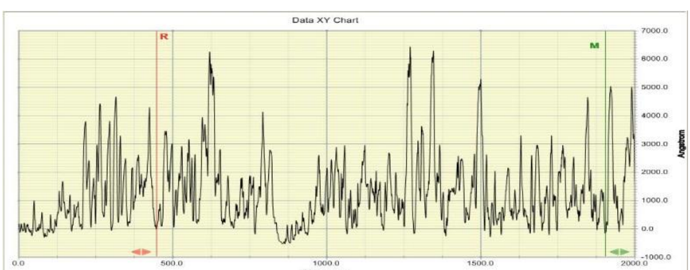

Figure 5: Profiler result showing film thickness 0.008 at temperature 490^{o}C

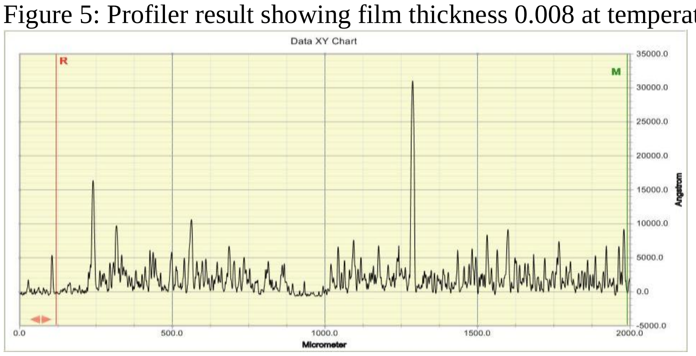

Figure 6: Profiler result showing film thickness 0.0001 at temperature 510^{o}C

Effect of Thickness on Conductivity

As illustrated in Figures 2 to 6, the results reveal that the thickness of five doped nanoparticles ranges from 0.008 µm, 0.012 µm, 0.006 µm, 0.5 µm and 0.001 µm, respectively, at 330 ºC, 400 ºC, 450 ºC, 470 ºC, and 510 ºC. These results show the variation of film thickness with deposition temperature for fluorine doped thin oxide films deposited at different temperature. The result reveals that increase in temperature reduce the thickness of the deposited fluorine doped thin oxide thin film. The thin film deposited at 330 ^{0}C has the highest thickness of 0.500µm while the film deposited at 510 ^{0}C has the least thickness of 0.001 µm.

Table 1: Film Thickness of increasing temperature of Fluorine dope thin film

Temperature ºC	Thickness µm
330	0.5
450	0.006
470	0.012
490	0.008
510	0.001

Analysis of the Absorption Coefficient (α)

The absorption coefficient can be attained from the measured transmission T or from the absorbance spectra A gotten from the UV spec. applying the equation given below the absorbance coefficient can be deduces as shown below [12]:

$$\alpha = 2.303\frac{A}{d} \quad (1)$$

Where A is the absorption gotten from the UV spec and d is thickness of the film and 2.303 is constant of proportionality. Table 1 shows the absorbance coefficient at different thickness. The graph of the absorbance coefficient was plotted against the photon energy at the different thickness of samples doped with Ammonia fluorine as shown below.

Energy band gap

The absorbance spectra of the thin films with various dopant contents were recorded in order to learn more about the energy band gap of SnO_2 as well as the influence of the deposition circumstances. The Tauc equation was used to investigate the optical absorption edge [12].

$$\alpha h\nu = A(h\nu - E_g)^m \quad (2)$$

Where m is equal to 1/2 for direct transitions and 2 for indirect transitions, where A is the optical constant, the absorption coefficient, Eg the optical band gap, and the absorption coefficient [13].

Tauc equation can be used to determine the direct band gap energy Eg, which is 3.6 eV. From the points where the straight line and the energy axis connect for m=1/2. According to Figures 7 and 8 below, the band gap values vary from 2.23 eV to 2.6 eV

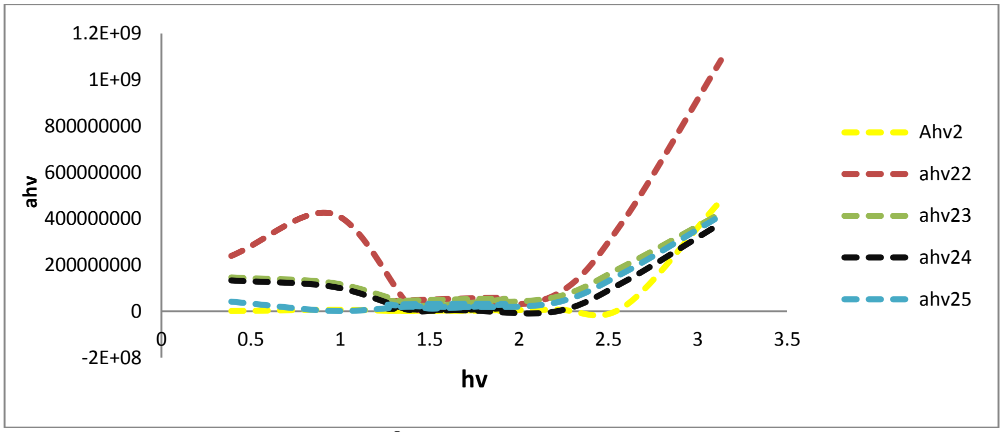

Figure 7: Typical variation of $(ah\nu)^2$ as a function of photon energy used for optical band gap determined as temperature increase from 330-510^{O}C.

Electrical Properties

To determining the electrical resistivity and electrical conductivity of the $F:SnO_2$ thin films was carried out using a four-point probe machine [14]. The results gotten from the machine was given in Table 2 with the film thickness below

Table2: Values of sheet resistance and resistivity of F:SnO_2 films

Thickness nm	Sheet Resistance Ω/cm	Resistivity Ω
0.5	1477.5	738.766
0.006	4.6	0.027618
0.012	9.87	0.1184
0.008	22.711	18.1688
0.001	3.25	0.0032464

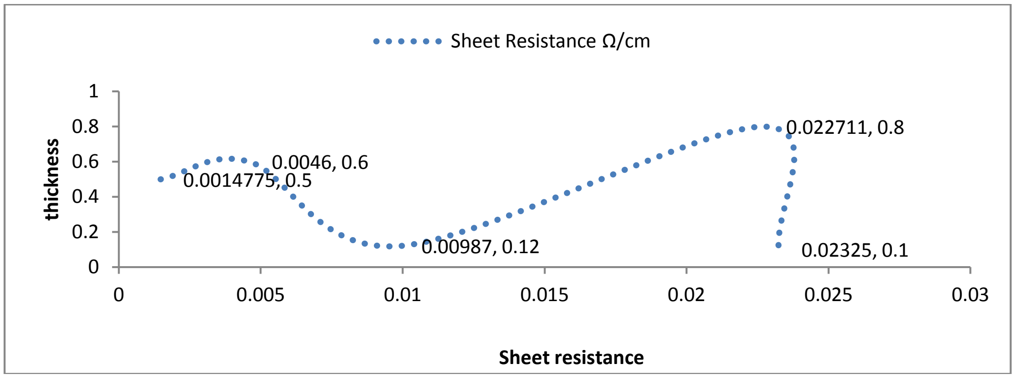

Figure 8: Graph showing the relationship between sheet resistance and thickness

The resistivity of the F:SnO_2 thin films was calculated before the sheet resistance. Equation (3) was used to determine the material's sheet resistance, which is illustrated below.

$$R_S = \frac{\rho}{t} \tag{3}$$

Where ρ is the resistivity of the film [Ω-cm], $R_s$is the sheet resistance of the film, and t is the thickness of the film [nm]. The electrical properties of the F: SnO_2 can be seen from the resistivity values and sheet resistance of the different samples at different thickness at constant volume 2.5 ml.

Where Rs is the film's sheet resistance, t is the film's thickness [nm], and ρ is the film's resistivity [-cm]. The resistivity values and sheet resistance of the various samples at various thicknesses at constant volume of2.5 ml allows one to observe the electrical properties of the F: SnO_2.

The thickness increases and decreases as the temperature changes, it decreases from 0.5µm to 0.001 µm resistivity and sheet resistance (R_s) of the films deposited on a glass substrate also show similar behavior as shown in the diagram above. This result was consistent with other measurements mentioned previously [15]. Especially, sheet resistance (R_s) is a useful parameter in comparing thin films, particularly, those of the same material deposited under similar conditions [16]. This also leads to a rise in carrier concentration as the thickness decreases.

4.0 CONCLUSION

It has been demonstrated that as the temperature rises, an increase in wavelength causes reduction in the absorbance spectrum across the various samples. The highest absorbance values across the different samples lies in between 300nm – 400nm. The highest absorbance for doped was at 343.57nm at temperature 330°C why the lowest absorbance was 954nm at 510^{0}C. However, this shows that it can be used window coating in the temperate part of the world. For electronic applications, SnO_2 based thin films produced by EACVD typically exhibit good optoelectronic characteristics. With negligible effects on absorbance and reflectance as well as a small influence on the computed band gap energy value for SnO_2, F:SnO2 thin films, their exposure to high temperatures during the annealing process increases their electrical conductivity. Doped SnO_2 thin films become stable as a result. Therefore, in its various applications, this is a viable option for producing a clear thin film.

REFERENCES

[1] Smith M Hampden, (1995) "*Aerosol processing of materials*". (New York: Wiley-Vch) 421.

[2] Cheng S.H., Ning Z.Y., Ge S.B, Chao Y., Gang Z.Q., Zhang Y.X., Liu Z.G. (2006), Preparation and characterization of ZnO:Al films by pulsed laser deposition. *Thin Solid Films.*

[3] Singh M., Mehta B.R. (2006), Effect of structural anisotropy on electronic conduction in delafossite tin doped copper indium oxide thin films. *Applied Physics Letters*; 9: 233-256

[4] Ali S., Tayebeh S., and Jaber F., (2011)."ITO-free organic solar cells using highly conductive phenol-treated PEDOT:PSS anodes". *Organic Electronics.* **24**: 188–194.

[5] Vallejos, S., Di Maggio, F., Shujah, T. & Blackman, C. (2017), Chemical vapour deposition of gas sensitive metal oxides. *Chemosensors* **4**, 4.

[6] Martijn F. J. Vos, Harm C. M. Knoops, Wilhelmus M. M. Kessels, Adriaan J. M. Mackus. (2021), Reaction Mechanisms during Atomic Layer Deposition of AlF3 Using Al(CH3)3 and SF6 Plasma. *The Journal of Physical Chemistry***,** *125* (7)

[7] Kim, K.S., Yoon, S.Y., Lee W.J and Kim, K.H. (2012) "Surface morphologies and electrical properties of antimony-doped tin oxide films deposited by plasma enhanced chemical vapor deposition". *Surface and Coatings technology.* 138 (2-3), 229-236.

[8] Lewis F., (2011) "Effect of $SnCL_4$ concentration on F: SnO_2, deposited by chemical spray pyrolysis". *In the proceedings of international Renewable Energy Congress,* Souse, Tunisia, 2, 276-279.

[9] Jain, V.K.; Kumar, P.; Vijay, Y.K. (2012) "Preparation of nanostructure ZnO-SnO_2 thin films for optoelectronic properties and post annealing influence". *World Acad. Sci. Eng. Technol.*, 72, 1575–1577.

[10] Ekpekpo A., Iyayi S.E., Aiyehuyin E.O (2010). Phase Transitions for Unconventional Superconductivity. *International Journal of Research and Reviews in Applied Sciences*, **5**(3), 305-309.

[11] Rupp, Joel; Guffy, Eri; Jacobsen, Gary. (2012) "Electrostatic spray processes". TW Ransburg Electrostatic Systems, in *Metal Finishing 2012 Organic Finishing Guidebook*.Elsevier.126-127.

[12] Mehta S.K., Kumar S., Chaudhary S., Bhasin K.K. (2009). Nucleation and growth of surfactant passivatedCdS and HgS NPs: Time dependent Absorption and Luminescence profiles. *The Royal Society of Chemistry.*

[13] Igwe H.U and Ugwu E.I. (2010) "Optical Characteristics of NanocrystalineThermal Annealed Tin Oxide (SnO_2) Thin Film samples Prepared by Chemical Bath Deposition Technique". *Journal of Advance in Applied Science Research*, 1(3), 240-246.

[14] Odari, B.M., Mageto, M.J., Musembi, R.J., Othieno, H., Gaitho, F., and Muramba, V. (2013) "Optical and Electrical Properties of Pd Doped SnO_2 Thin Films Deposited by Spray Pyrolysis". *Australian Journal of Basic and Applied Sciences*, 7 (2): 89-98.

[15] Menarian, F., Guillen – Gervauntes , A., Nieto-Zapeda, K.E., Quinones- Galvan, JG., Hernandez- Hernandez. A., Olvera, M.G and Melendez- Lira, M. (2010) "SnO_2 Thin Films Deposited by RF Magnetron Sputtering: Effect of the SnF_2 Amount in the Target on the Physical Properties". *Revista Mexicana de Fisica*, 59, 335-338.

[16] Ravichandran, E.A., Makdisi, Y and Ramazaniyan, A.H. (2009) "Electronic and optical properties of fluorine-doped tin oxide films". *Journal of Applied Physics*, 83, 1049-1057.