# Spin Coated Tin Oxide Thin Film For Optical And Optoelectronic Material Applications

Sunday S. Oluyamo

Condensed Matter and Statistical Physics Research Unit, Department of Physics, Federal University of Technology, Akure, Nigeria

#### David B. Agunbiade

Ladoke Akintola University of Technology, Ogbomoso

Abstract: This work consists of the preparation of thin film of tin oxide using automated spin coating technique. Investigations of the surface morphology and optical characteristics of the deposited films were examined. Thin film of tin oxide  $(SnO_2)$  is a special class of transparent metal oxides that combine high optical conductivity with high transparency. Such Transparent Conducting Oxide (TCO) provides an important component for optoelectronic applications. The transmittance and reflectance spectra were obtained with a UV- Vis spectrophotometer while the microphotograph was obtained using a scanning electron microscope. The thin film produced has high transparency, wide band gap and low dielectric constant. Optical characterization was done over a range of wavelength of 250 nm to 1000 nm which corresponds to photon energy between 1.2 eV to 5.0 eV. The average transmittance is 85 %, average optical conductivity is  $0.032 \times 10^{16} \text{ S}^{-1}$ , average extinction coefficient is 1.25, average real dielectric constant is -7.5 and the band gap energy is estimated to be 3.78 eV. The SEM micrograph of the SnO<sub>2</sub> film shows the existence of some agglomerates of small rounded particles. Tin oxide thin films have a number of applications such as in optical coatings, high temperature superconductivity and communication, solar cell fabrication especially as an absorption layer and a transparent contact.

Keywords: Optical conductivity, transparency, optoelectronics, spin coating and superconductivity.

#### I. INTRODUCTION

Thin film technology for device applications are based on material structures created by thin-film deposition and characterization [1]. In recent time, there are growing demands for more efficient solar cell technology and also electronic devices that could operate at high power levels. Suitable thin films for these applications require wide band gap, high optical conductivity, high transparency and stability at higher temperature [2]. The numerous varieties of electronic, optical and solid state properties of metal oxides make them suitable materials for basic research that results in invention of novel systems and improvement on the exiting. Oxides have a wide range of properties from wide band-gap insulators, metallic to superconducting. Tin oxide belongs to a class of materials called Transparent Conducting Oxides (TCO), constituting an important component for optoelectronic applications [3].

Tin oxide thin films have some useful applications in visible light and infrared light. It has low electrical sheet resistance, rendering it suitable for a wide variety of applications as gas sensors, electrodes in solar cells, infrared reflectors for glass windows, transparent electrodes in electroluminescent lamps and displays [4, 5]. Other useful properties are high mechanical hardness and good environmental stability. Tin Oxide  $(SnO_2)$  is a n-type semiconductor with wide energy band gap (3.7 eV) [6]

The methodology employed for thin-film deposition ranges from very simple and cheap to complex and very expensive depending on the substrate type, material to be deposited and the required performance of the films [7]. In this work, the spin coating deposition which is a simple, quick and relatively cost effective technique was adopted. UV- Vis spectrophotometer and scanning electron microscopy are used to characterize the spin coated SnO<sub>2</sub> film grown on glass substrates at room temperature.

#### II. EXPERIMENTAL DETAILS

#### A. SUBSTRATE CLEANING

In order to obtain good adherence and uniformity of the films, it is important to prepare clean substrate before deposition. The microscopic glass slide (24.5mm x 25.0 mm) were washed thoroughly using alkali free detergent and a piece of gauze and rinsed several times in distilled water The glass slides were ultrasonically bathed with ethanol for 15 minutes and dried in a micro analysis oven at a temperature of **200**<sup>U</sup> C for 10 minutes

## B. THE DEPOSITION OF THE SNO<sub>2</sub> THIN FILMS

 $SnO_2$  thin films were deposited on the glass substrate using the spin coating technique. All the chemicals used were of analytical grade reagents Anhydrous Tin (II) chloride (SnCl<sub>2</sub>) was dissolved in the mixture of methanol (CH<sub>3</sub>OH) and acetic acid (CH<sub>3</sub>COOH) at room temperature in a conical flask. An accurately measured quantity (1g) of Tin chloride was dispersed in calculated volume (25.5 ml) of methanol and acetic acid. The solution was thoroughly mixed until a homogenous clear solution was obtained. The molar concentration of the SnO<sub>2</sub> solution formed was 0.2 M.

# C. THIN FILM FORMATION

The glass substrate was positioned in the spin coater for film deposition. Table 1 shows the deposition control and

parameter	for each cycle.		
Step	Description	Speed (rpm)	Duration (s)
1	Spin Up	200	10
2	Spin Off	1000	20
3	Evaporation	2000	30
		. 1/	

*Table 1: Deposition control/parameter* 

#### D. CHARACTERIZATION OF THE SNO<sub>2</sub> THIN FILM

The deposited  $\text{SnO}_2$  film thickness was determined by the gravimetric method using analytical balance Adventurer (AR 3130) with 0.0001g readability. The thickness of films is given as:

$$t = \frac{(M_A - M_B)}{A\rho}$$

where A is the area of the film surface,  $M_A$  is mass of slide after deposition,  $M_B$  is the mass of slide before deposition,  $\rho$  is the density of bulk material [1]. The thickness of the SnO<sub>2</sub> thin film was found to be 420 nm.

The optical transmission of the film was obtained in the UV- Vis region up to 1000 nm using (AvaSpec- 204B) UV spectrophotometer at room temperature; blank measurements were performed on glass substrates as baseline spectra. The

microstructure of the sample was characterized using scanning electron microscope (SEM ASPEX 3020).

### III. RESULTS



Figure 1: Absorbance, Transmittance and Reflectance as a function of Wavelength for SnO<sub>2</sub> thin film

# B. ABSORPTION COEFFICIENT



Figure 2: Absorption Coefficient as a function of Photon Energy for  $SnO_2$  thin film

# C. EXTINCTION COEFFICIENT



Figure 3: Extinction coefficient as a function of Photon energy for  $SnO_2$  thin film

### D. REFRACTIVE INDEX



Figure 4: Refractive index as a function of Photon energy for SnO<sub>2</sub> thin film

# E. OPTICAL CONDUCTIVITY



for  $SnO_2$  thin film

# F. DIRECT BAND GAP ENERGY



Figure 6: Absorption Coefficient  $^2$  as a function of Photon energy for SnO<sub>2</sub> thin film

G. DIELECTRIC CONSTANT (REAL AND IMAGINARY PARTS)



Figure 7: Dielectric Constant (Real and Imaginary Parts) as a function of Photon energy for SnO<sub>2</sub> thin film

# H. PHOTOMICROGRAPH TIN OXIDE THIN FILM



Figure 8: SEM image for  $SnO_2$  thin film

### **IV. DISCUSSION**

Figure 1 shows the Absorbance, Transmittance and Reflectance of the  $SnO_2$  thin films The Absorbance (A) of  $SnO_2$  film was calculated from the reflectance and transmittance spectrum using the relation;

R+T+A = 1

where R is the reflectance, T the transmittance and A the absorbance. [8]. Absorbance is high (about 90%) at short wavelengths (below 300 nm), absorbance decreases sharply between 300 nm and 400 nm reaching 0 % at 460 nm. The increase of the absorption occurs when the photon energy became equal to the value of the energy [9] and consequently electronic transfers between the valance band and the

conduction band will begin. High absorbance in the UV region coupled with low absorbance in the Vis region could be used for prevention of house warming in buildings by screening off UV radiation and allowing visible radiation. [10]. the thin film exhibits a relatively high transmittance in the visible region, up to 92 %. The high transmittance of film throughout the UV-Vis regions makes it a suitable material for optoelectronic devices and especially as window layers in PC cells. [2]. The reflectance spectrum has very little decrease from initial value of 10.8 % at wavelength of 250 nm to 10.6 % at 280 nm. A steady increase in reflectance occurred from 1% at 250 nm to 13.4 % at wavelength of 350 nm. The reflectance of the thin film is moderately high in the NIR region, thereabout 15 %. This property makes the thin film useful as heat mirrors to reduce temperature in buildings [11].

The absorption coefficient ( $\alpha$ ) of the SnO<sub>2</sub> thin films is shown in Figure 2. The absorption coefficient of SnO<sub>2</sub> film was determined from the absorbance measurements, ( $\alpha$ ) calculated using the following equation:

$$\alpha = \frac{2.303 A}{t}$$

where A is the absorbance and t is the thickness of the film. [12]. The absorption coefficient of  $\text{SnO}_2$  film was calculated to be  $2.5 \times 10^7$  m<sup>-1</sup> at 3.78 eV photon energy. The films have good absorption at short wavelength region where absorption decreases with increase in wavelength. Increase in absorption occurred when the photon energy becomes equal to the value of the energy gap. At this point electronic transfer between the valance and the conduction band begins [13]. The high absorption coefficient of the thin film implies that the thin film have high ability to absorb light within the visible region.

The extinction coefficient (k) of the SnO<sub>2</sub> thin film is shown in Figure 3. The extinction coefficient k was determined from the following relation

$$k = \frac{\alpha \lambda}{4\pi}$$

where  $\alpha$  is the absorption coefficient and  $\lambda$  is the wavelength. [14]. Extinction coefficient is lowest in the low photon energy region. It increased steadily with photon energy in the Vis region and in the UV region extinction coefficient was found to be constant. The low extinction coefficient in the UV region is a result of high absorbance of the thin films in the region [17]. The extinction coefficient increases with photon energy up to a value of 4.2 eV and decreased afterwards.

The refractive index (n) of the  $SnO_2$  thin film is shown in Figure 4. The Refractive index (n) was determined from the reflectance spectrum using the following equation

$$n = \frac{(1+\sqrt{R})}{(1-\sqrt{R})}$$

where R is the reflectance of the thin film. Refractive index decreased in the visible range. The sharp decrease of refractive index between 3.3 eV and 3.5 eV shows the presence of characteristic absorption at the photon energy range. This is as a result of high density of tin within the lattice [15]. The refractive index achieved could be utilized as anti reflective coatings in solar cells to counter surface reflections [16].

The optical conductivity  $(\sigma_0)$  of the SnO<sub>2</sub> thin film is shown in Figure 5. The optical conductivity  $(\sigma_0)$  was determined using the following equation

$$\sigma_0 = \frac{dnc}{4\pi}$$

where  $\alpha$  is the absorption coefficient, c is the velocity of light,  $\sigma_0$  is the conductivity and n is the refractive index [17]. Optical conductivity is lowest in the low energy region and increased steadily with photon energy in the Vis region. The maximum optical conductivity was obtained at photon energy 4.5 eV for the thin films which is an indication that the minimum disorders within the crystal structure of the films are reached at this photon energy. SnO<sub>2</sub> thin films are suitable for use as transparent contacts in PV cells.

The Absorption Coefficient of the thin films varies with photon energy as shown in Figure 6. The direct optical band gap energy of the film was extrapolated from the plot of  $ahv^2$  against photon energy (eV). A linear fit was performed for the curve and the value was estimated from the intercept with the energy axis. Direct band gap energy of SnO<sub>2</sub> thin film was estimated to be 3.78 eV, the value of the optical energy gap for direct allowed transition of SnO<sub>2</sub> thin films prepared at precursor concentration of 0.2 M is in good agreement with previously reported value [8, 17]. The wide direct band gap makes SnO<sub>2</sub> thin films good material for potential applications in optoelectronic devices and in high power electronics [18].

Figure 7 shows the dielectric constant (Real and Imaginary Parts) of the SnO<sub>2</sub> thin film as a function of Photon Energy. Dielectric constant (Real Part)  $(\varepsilon_r)$  was determined using the following equation

$$\varepsilon_r = n^2 \cdot k^2$$

where n is the refractive index and k is extinction coefficient [19].

While the Dielectric constant (Imaginary Part) ( $\varepsilon_i$ ) was determined using the following equation

$$\varepsilon_i = 2lnk$$

where n is the refractive index and k is extinction coefficient [12].

The real part dielectric constant of the thin film is very low at higher photon energy. Materials with negative dielectric constant provide attraction between similar charges and unusual scattering to electromagnetic waves with possible profound implications for high temperature superconductivity and communications [20]. For the thin film dielectric constant (imaginary part) is lowest in the low photon energy region and increased steadily with photon energy in the Vis region. The low value of imaginary dielectric constant obtained makes the distance inside the SnO<sub>2</sub> crystal lattice shorter so that light can travel in high speed [21]. This material allows for high speed signal transmission to take place making it suitable for high speed transmission device application.

Figure 8 shows the micrographs of the film prepared at concentration of 0.2 M. The surface is apparently compact with evidence of crystal undergrowth. The undergrowth could be associated with the super-saturation of the tin oxide in the methanol solution. Undergrowths and outgrowths are evenly distributed across the surface of the thin films. There is evidence of granularity which is a feature seen in crystalline films [17]. The micrographs obtained are similar to previous results obtained by [11]. [13], [15] and [19]

# V. CONCLUSION

The deposition of  $\text{SnO}_2$  thin film was successfully done on a commercial glass substrate at room temperature using spin coating deposition technique. The film was characterized for optical and micro structural characteristics. Optical application of the tin film includes, anti reflective coatings and transparent contacts in PV cells. The thin film have wide band gap which is in agreement with reported values in literature and also have negative dielectric constant which indicates very low real part dielectric constant. Materials with negative dielectric constant provide attraction between similar charges and unusual scattering to electromagnetic waves with possible profound implications for high temperature superconductivity and communications.

## REFERENCES

- [1] Achour R, Said B, and Boubaker B. (2013). The effect of the film thickness and doping content of SnO<sub>2</sub> thin films prepared by the ultrasonic spray method. *Journal of Semiconductors* Vol. 34, No. 9, p 2-4
- [2] Adel H, Shymaa K, and Hussian M. (2013). Structural and Optical characterization of Nanocrystalline SnO<sub>2</sub> thin film prepared by spray pyrolysis technique. *Journal of Kufa – Physics* Vol.5 No.1 p 2-3, 5
- [3] Anthony O, (2012). Investigating the Optical Properties of Zinc Sulphide Thin Films Deposited from Chemical Acidic Baths, *Kwame Nkrumah University of Science and Technology*. M. Sc Thesis p 3, 35, 62
- [4] Assia S and Ratiba O (1999). Optical reflectance of pure and doped tin oxide: from thin films to poly-crystalline silicon/thin film device, International Journal of Chemical and Biological Engineering, vol 2(1), 48–51.
- [5] Awodugba A, Adepoju M and Familusi T. (2013) Preparation and Characterization of SnO<sub>2</sub> thin films deposited by Chemical Bath Deposition method. *http://meetings.aps.org/link/BAPS.2013.APR.S2.30.* p1 and 2
- [6] Baco S and Chik A (1999) Study on optical properties of tin oxide thin film at different annealing temperature, Journal of Science and Technology, vol 4, 61–72.
- [7] Batzill M, and Diebold U (2001). The surface and materials science of tin oxide, Progress in Surface Science, vol 79(2-4), 47–154
- [8] Bernardus M (2000). Chemical vapor deposition of tin oxide thin films, Ph.D Thesis, Technische Universiteit Eindhoven
- [9] Chopra, K.I. and Kaur. I. (1983). Thin Film Device Applications. *Plenum press, New York* Third edition p 3
- [10] Chu C. Chen F, Shulman J, Tsui, Y Xue, Wen W and Sheng P. (2013) A Negative Dielectric Constant in Nano-Particle Materials Under An Electric Field At Very Low Frequencies. *International Journal of Applied Sciences, Research and Innovation* Vol. 5, p 1-3

- [11] Fatema Chowdhury, Shamima Choudhury, Firoz Hasan, and Tahmina Begum, (2011) Study of Synthesis Variables in the Nanocrystal Growth Behavior of Tin Oxide Processed by Thermal Evaporation, *International Journal for Innovative Research in Advanced Engineering*, Vol. 17. p 4, 5 and 7
- [12] Fenz G Vard C and Neumann Spallart M (2013) Optical and electrical properties of tin oxide films prepared by Spray Pyrolysis technique. *Research and Reviews in Materials Science and Chemistry*. Vol. 4, Issue 1, Page 2
- [13] Mahrov J, Lindroos, S., Kannianen, T. (2004) Tin Oxide Thin Films. *Journal of Research in science*. Vol. 2. p 5
- [14] Majid H, Yasmeen D and Asmaa N. (2013). Investigation of tin concentration dependence of solution processed indium oxide thin film. *Advances in Physics Theories and Applications* Vol.24. p 4
- [15] Moreh Media El Mahdi, and Kadi Mohamed (2014) Optical Characterization of Fluorine doped Tin Oxide (FTO) thin films deposited by spray pyrolysis technique and annealed under Nitrogen atmosphere. *International Journal of Innovation and Applied Studies ISSN 2028-*9324 Vol. 9 No. 2. p. 2 and 4
- [16] Muranoi T, and Furukoshi M (2001). Properties of stannic oxide thin films produced from the  $SnC1_4$ -H<sub>2</sub>O and  $SnC1_4$ -H<sub>2</sub>O<sub>2</sub> reaction systems, Thin Solid Films, vol 48(3), 309–318
- [17] Nada M. Saeed (2013). Structural and Optical Properties of ZnS Thin Films Prepared by Spray Pyrolysis Technique. *Journal of College of Science, University of Baghdad, Baghdad-Iraq* Vol. 5. .p 2- 4
- [18] Quijada, M, Simpson H, Shreekala R. Ramesh M, Rajeswari K and Venkatesan T (1998), Optical Conductivity of Manganites Crossover From Jahn-Teller Small Polaron To The Ferromagnetic State, *Journal of Physical Review B* Vol. 58 p 99-102
- [19] Sanusi Abdullahi, Hamza, U. Sadiya, Z. Abdullahi, M. A. Wara, H. Kamaluddeen, M. A. Kebbe, and U. F. Monsurat (2014) Optical Characterization of Fluorine doped Tin Oxide (FTO) thin films deposited by spray pyrolysis technique and annealed under Nitrogen atmosphere, *International Journal of Innovation and Applied Studies ISSN 2028-9324* Vol. 9 No. 2 pp. 2 and 3
- [20] Smaali Assia, Outemzabet Ratiba, Media El Mahdi, and Kadi Mohamed (2008) Optical Reflectance of Pure and Doped Tin Oxide: From Thin Films to Poly-Crystalline Silicon/ Thin Film Device, World Academy of Science, Engineering and Technology Vol. 2 p 3
- [21] Uhuegbu Chidi Chukwuemeka (2007) Growth and Characterization Of Ternary Chalcogenide Thin Films For Efficient Solar Cells And Possible Industrial Applications. *Department of Physics, Covenant University, Nigeria* PhD thesis p 1, 4, 15, 17 and 57