

Electro-Optical Characterization of Stannous Oxide Based Conductive Glass Fabricated Locally with Stannous Chloride Dihydrate Precursor

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Abstract

Most commercially available conductive oxides such as indium doped tin oxide (ITO) and fluorine doped tin oxide (FTO) are expensive. This has made local production of alternative oxides necessary. This work demonstrates local production of transparent conducting stannous oxide (SnO) film via thermal decomposition of stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$). The films were then characterized optically and electrically using UV/VIS spectrophotometer and four point probe, respectively. The thickness of the film increased linearly with precursor mass. While the sheet resistance and optical transmittance decreased, the optical absorbance increased with increased thickness. Average optical transmittance ranged between 85% and 94% and the sheet resistance lies between $62.89 \Omega/\text{sq}$ and $84.57 \Omega/\text{sq}$. With these characteristics, the deposited film will be useful for optoelectronic applications.

1. Introduction

Semiconducting oxide thin films are materials with numerous applications in electronic and optoelectronic devices such as protective coatings and catalysis [1], thin film solar cells [2], dielectric layers in low emissivity coatings for windows [3], gas sensors applications [4], liquid crystal displays [5], development of new-fashioned thin film solar cells [6,7] and in tandem structures developed on flexible substrates [8]. Tin (iv) Oxide (SnO_2) is one of the most investigated thin films due to its mechanical, chemical and electrochemical stability [9] and wide band-gap of 3.6 - 3.8 eV [10]. In addition, it has low electrical resistivity because of its high carrier concentration due to oxygen vacancies and the substitutional fluorine dopant [11]. Un-doped tin oxide (SnO_2), has optical transparency of 85% and surface conduction due to oxygen vacancies [12]. SnO_2 nanostructures have been synthesized by methods such as hydrothermal methods, thermal evaporation of oxide powders, sol-gel method [13], chemical vapor deposition [14], pulsed laser deposition [15] and spray pyrolysis [16]. In addition, DC reactive magnetron sputtering using a metallic tin target and various plasma atmospheres such as $\text{Ar}/\text{O}_2/\text{CF}_4$, $\text{Ar}/\text{O}_2/\text{Freon}$ [17, 18] had been reported as methods of deposition. Studies on the effect of post annealing treatments [19], substrate temperature [20], texture [2], microstructure [21], and doping [22] have been published. The commercially available conductive glasses are Indium doped Tin Oxide (ITO) and Fluorine doped Tin Oxide (FTO) with sheet resistance less $10 \Omega/\text{m}^2$ and 75–85% visible light transmittance. They constitute a major component of optoelectronic [1] but their relatively high cost has initiated search for less expensive and equally effective alternatives.

The choice of precursor has great influence on the performance of fabricated conductive glass. $\text{SnO}_2:\text{F}$ thin films with a resistivity in the order of $2 \times 10^{-4} \Omega\text{cm}$, starting from stannous chloride (SnCl_2) and ammonium fluoride

(NH₄F) was reported [23]. For this study, local fabrication of SnO film coated conductive glass using Stannous Chloride Dihydrate (SnCl₂ · 2H₂O) precursor was investigated.

2. Experimental Procedure

The methods and procedures of deposition and characterization are discussed in this section.

2.1 Deposition of Stannous Oxide Film

Five (5) glass pieces (7 cm × 7 cm × 2 mm) and spacers (1cm × 1cm) were cut from transparent glass. The pieces were properly cleaned in alkali free detergent for two minutes and then rinsed in de-ionized (DI) water. Thereafter, they were rinsed in 0.1M HCl, acetone, isopropanol for 2 minutes consecutively. The samples were finally boiled in isopropanol for five minutes and air dried until the surfaces were completely dried. By thermal decomposition of SnCl₂ · 2H₂O, SnO thin film was deposited on the prepared transparent glass substrate (Eq. 2.1)



To estimate the mass of the deposit, each of the glass was weighed before and after deposition. About 0.1 g of the precursor was used to form a narrow pile very close to the edge of the square glass, and carefully lifted with the aid of two pairs of pickers onto a clean hot plate. Two spacers, one on top of the other, were placed at each corner of the square glass and covered with another glass. The side of the square glass where the pile of precursor was mounted was first covered with a piece of glass to avoid the molten precursor from dripping onto the hot plate during deposition. The hot plate was powered and the temperature adjusted to 450 °C with the aid of a thermocouple. The pile was viewed periodically from the top until the powder melted completely and began to fume. The side glass cover was then removed with the fume spreading uniformly towards the remaining three windows forming a thin layer of SnO on the glass until the fume stopped.

The top cover and spacers were removed and the hot substrate was carefully lifted onto a pile of cotton wool to cool slowly at a uniform rate because subjecting it to stress or sudden change in temperature might cause it to break violently. The glass was left on the cotton wool to completely cool. The surface was tested for electrical conductivity with a multimeter set to continuity mode. This procedure was carried out with varying precursor mass for samples A (0.10 g), B (0.15 g), C (0.20 g), D (0.25 g) and E (0.3 g).

2.2 Estimation of film thickness

For uniform deposition, the thickness, *t*, of Tin (II) oxide film was determined from the mass of the substrate before deposition *M*₁ and mass after deposition *M*₂ (Eq. 2.2):

$$t = \frac{M_2 - M_1}{AD} \quad 2.2$$

Where *A* = area covered by the film, *D* = density of the SnO thin film (6.446g/cm³)

2.3 Optical and Electrical Characterization

The samples were characterized for optical absorbance and transmittance, and resistivity using Jenway 6405 UV/VIS spectrophotometer and Keithley 2400 series four point probe, respectively. For film of thickness *t*, the absorption coefficient *α* and the corresponding photon energy *E* (eV) were calculated using Eq. (2.3) and Eq. (2.4), respectively. The optical band gap for each film was determined by finding the x-intercept of tangent drawn along Tauc curve towards the photon energy axis.

$$\alpha = 2.303 \frac{A}{t} \quad 2.3$$

$$E = \frac{hc}{\lambda} \quad 2.4$$

where *A*, *h*, *c* and *λ* are the absorbance, Planck's constant, speed of light and wavelength, respectively.

3. Results and Discussion

The influence of film thickness on the optical and electrical properties are discussed in this section.

3.1 Thickness of Tin (II) oxide films

The masses of the substrate before deposition (M_1) and after deposition (M_2) for each sample of SnO film are presented in Table 3.1. The mass of the deposited film and the equivalent film thickness are also indicated. In agreement with the law of definite proportion, the SnO film thickness increases linearly with precursor mass (Figure 1).

Table 3.1: Masses and thicknesses of film samples

Sample	M_1	M_2	Mass of Film (g)	Thickness (nm)
A	31.01	31.0130	0.0030	94.98
B	32.23	32.2367	0.0067	212.12
C	31.98	31.9900	0.0100	316.60
D	31.74	31.7530	0.0130	411.58
E	30.11	30.1239	0.0139	440.08

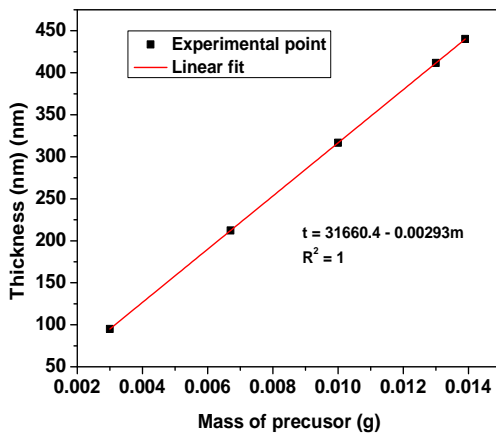


Figure 1: Variation of film thickness with precursor mass. In the fitting equation, t and m are thickness of the film and mass of precursor, respectively. The coefficient of regression is 1.

3.2 Optical and Electrical Properties of Tin (II) Oxide Film Samples

The absorbance and transmittance values of the samples are indicated in Figure 2(a) and 2(b), respectively. The optical transmittance of the SnO films is high (85 - 94 %) while the optical absorbance is low (0.02929 - 0.05672 %) in the visible and near infrared regions of the spectrum. This indicates that the average optical transmittance is good for optoelectronic applications when compared to 90% for industrial TCO glasses.

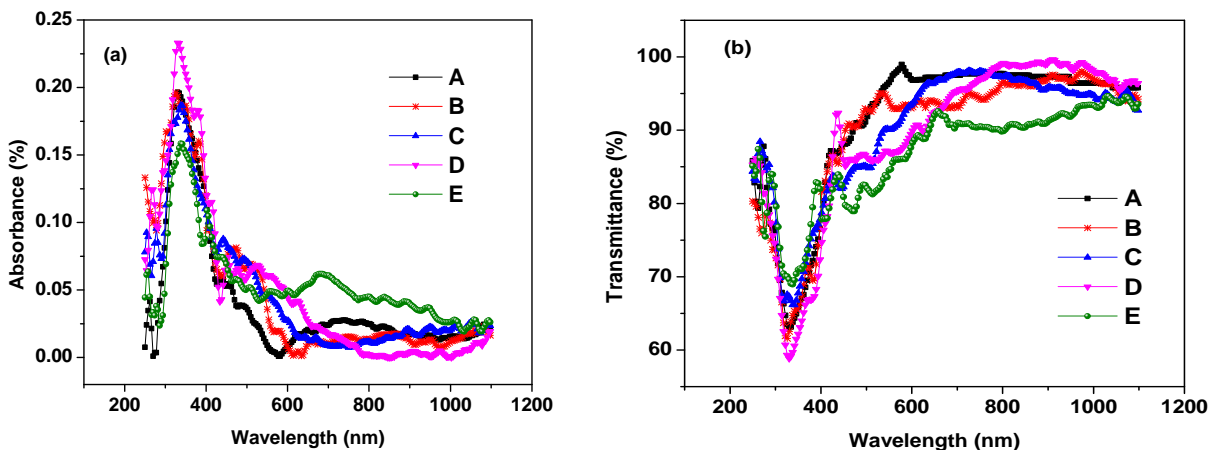


Figure 2: (a) Optical absorbance spectra and (b) transmittance spectra of SnO films

The average absorbance and transmittance within the visible region (400 nm - 700 nm) for the films were evaluated and plotted against thickness (Figure 3). The optical transmittance decreases with increasing film thickness while the optical absorbance increases. Higher absorbance is observed because more optical energy is absorbed, scattered and reflected by the individual atom as film grows thicker. Consequently, the increased absorbance together with increased optical scattering and reflection lower the optical transmittance of the film.

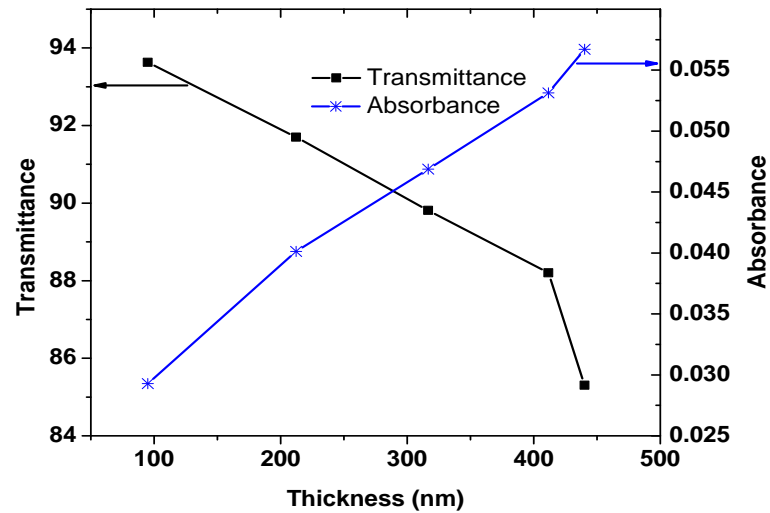


Figure 3: Optical transmittance and Absorbance against Thickness

The optical bandgap evaluated from the Tauc plots (2.4 – 2.55 eV) were in agreement with the theoretical value for Tin (iv) Oxide (Figure 4a). The variations of sheet resistance and optical band gap are shown in Figure 4(b). The sheet resistance decreased with increasing film thickness with average value of 70.39 Ohm/sq, 84.57 Ohm/sq maximum and 62.89 Ohm/sq minimum. The relatively high sheet resistance obtained might be attributed to non-uniform deposition occasioned by non-availability of standard CVD reactor. This can also be reduced by doping if appropriate tools are available. Also, the trends observed for optical and electrical properties are similar to those reported for SnO₂ thin films elsewhere.

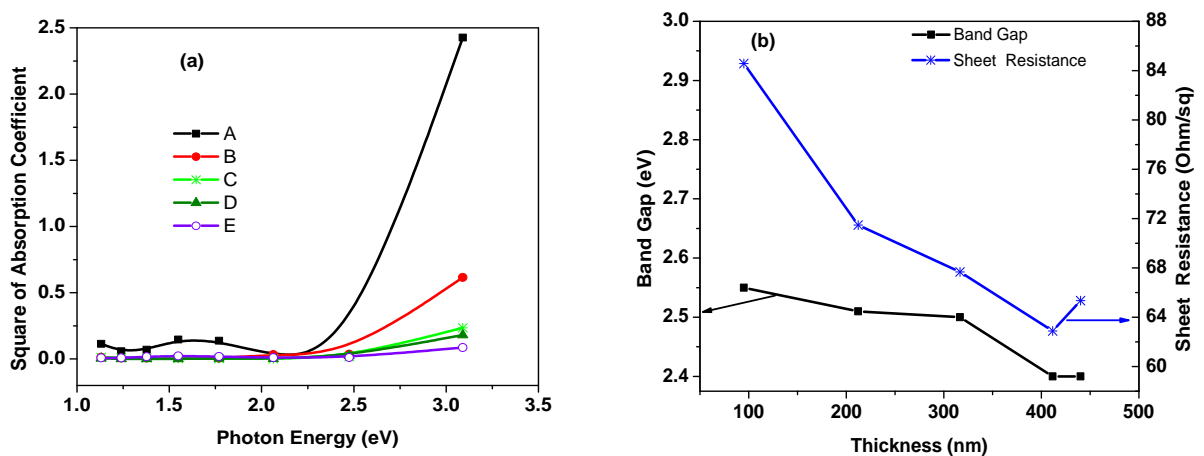


Figure 4: (a) Tauc Plots and (b) Influence of thickness on band gap and sheet resistance

For optoelectronic applications, it is desirable to have a film with low resistivity and high optical transmittance. In spite of the local technique adopted, the film is useful in this regard. For example, sample D was chosen for

solar cells electrodes because it has the lowest sheet resistance and relatively good average optical transmittance among other samples.

4.0 Conclusion

Stannous Oxide (SnO) film deposition on ordinary glass was achieved by thermal decomposition of Stannous Chloride Dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$). The films have average transmittance range between 85% to 94% and sheet resistance range between 62.89 Ω/sq and 84.57 Ω/sq . The result indicated that the average optical transmittance is good for optoelectronic applications when compared to 90% for industrial TCO glasses.

References

1. Malato S., Fernández-Ibáñez P., Maldonado M. I., Blanco J. and Gernjak W., (2009), "Decontamination and Disinfection of Water by Solar Photocatalysis: Recent Overview and Trends," *Catalysis Today*, 147(1)1-59.
2. Kim, C.Y., Riu D.H., (2011), Texture control of fluorine-doped tin oxide thin film. *Thin Solid Films*, 519, 3081–3085.
3. Gerhardinger, P.F., McCurdy R.J., (1996). Float line deposited transparent conductors—Implications for the PV industry. *MRS Proc.*, 426, 399–410.
4. Sankara, S., N., Santhi, B., Sundareswaran, S., Venkatakrishnan, K.S., (2006), Studies on Spray Deposited SnO_2 , Pd: SnO_2 And F: SnO_2 Thin Films for Gas Sensor Applications. *Synth. React. Inorg. Metal-Organic Nano-Metal Chem.* 36: 131–135.
5. 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)350-358
6. Li B., Wang L. D., Kang B. N., Wang P. and Qiu Y., (2006), "Review of Recent Progress in Solid-State Dye-Sensitized Solar Cells," *Solar Energy Materials & Solar Cells*, 90(5)549-573.
7. Chunjoong Kim, Mijung Noh, Myungsuk Choi, Jaephil Cho, and Byungwoo Park (2005), Critical Size of a Nano SnO_2 Electrode for Li-Secondary Battery, *Chem. Mater.* 17, 3297-3301.
8. Krebs F. C., (2009), "Fabrication and Processing of Polymer Solar Cells: A Review of Printing and Coating Techniques," *Solar Energy Materials & Solar Cells*, 93, 394-412.
9. Tesfamichael, T., Will, G., Colella, M., Bell J. (2003) Optical and electrical properties of nitrogen ion implanted fluorine doped tin oxide films. *Nucl. Instrum. Methods Phys. Res. B Beam Interact. Mater. Atoms* 201, 581–588.
10. Gnanam S. and Rajendran V. (2010) Luminescence Properties Of Eg-Assisted SnO_2 Nanoparticles By Sol-Gel Process Digest. *Journal of Nanomaterials and Biostructures*, 5(3)699-704
11. Subba Ramaiah, K and Sundara Raja, V. (2006), Structural and electrical properties of fluorine doped tin oxide films prepared by spray-pyrolysis technique. *Appl. Surf. Sci.* 253, 1451–1458.
12. Liu Y., Koep E., Liu M. (2005) A highly sensitive and fast-responding SnO_2 sensor fabricated by combustion chemical vapor deposition. *Chem Mater*, 17, 3997
13. Cachet, H. (2005), Films and powders of fluorine-doped tin dioxide. In Fluorinated Materials for Energy Conversion; Tsuyoshi, N., Henri, G., Eds.; Elsevier Science: Amsterdam, *The Netherlands*, 513–534.
14. Sheel D.W. and Gaskell J.M., (2011) Deposition of fluorine doped indium oxide by atmospheric pressure chemical vapour deposition. *Thin Solid Films*, 520, 1242–1245.
15. Kim, W.J., Koo, W.H., Jo, S.J., Kim, C.S., Baik, H.K., Lee, J., and Im, S. (2005), *Appl. Surf. Sci.* 252: 1332.
16. Elangovan E., Ramamurthi K., (2005) "Studies on Micro-Structural and Electrical Properties of Spray-Deposited Fluorine-Doped Tin Oxide Thin Films from Low-Cost Precursor," *Thin Solid Films*, 476(2) 231-236.
17. Martel A., Caballero-Briones F., Fandiño, J, Castro-Rodríguez R., Bartolo-Pérez P., Zapata-Navarro A., Zapata-Torre S.M., Peña, J.L., (1999), Discharge diagnosis and controlled deposition of SnO_x :F films by DC-reactive sputtering from a metallic tin target. *Surf. Coat. Technol.*, 122, 136–142.
18. Mientus, R. and Ellmer K., (1998) Structural, electrical and optical properties of SnO_2-x :F-layers deposited by DC-reactive magnetron-sputtering from a metallic target in $\text{Ar-O}_2/\text{CF}_4$ mixtures. *Surf. Coat. Technol.*, 98, 1267–1271.

19. Sundaram K.B. and Bhagavat G.K., (1983), "High-Temperature Annealing Effects on Tin Oxide Films," *Journal of Physics D: Applied Physics*, 16(1)69-76.
20. Lin C.C., Chiang M.C. and. Chen Y.W, (2009) "Temperature Dependence of Fluorine-Doped Tin Oxide Films Produced by Ultrasonic Spray Pyrolysis," *Thin Solid Films*, 518(4)1241-1244.
21. Jadsadapattarakul D., Euvananont C., Thanachayanont C., Nukeawa J. and Sooknoi T.,(2008). "Tin Oxide Thin Films De-positied by Ultrasonic Spray Pyrolysis," *Ceramics International*, 34(4)1051-1054.
22. Zhang B., Tian Y., Zhang J. X. and Cai W., (2011), "Structural, Optical, Electrical Properties and FTIR Studies of Fluorine Doped SnO₂ Films Deposited by Spray Pyrolysis," *Journal of Materials Science*, 46(6)1884-1889.
23. Luyo C., Fábregas I., Reyes L., Solís J. L, Rodríguez J., Estrada W. and Candal R. J, (2007), "SnO₂ Thin-Films Prepared by a Spray-Gel Pyrolysis: Influence of Sol Properties on Film Morphologies," *Thin Solid Films*, 516(1) 25-33.
24. M.K.M. Ali, K. Ibrahim, O. S. Hamad, M.H. Eisa, M.G. Faraj, F. Azhari (2011), Deposited Indium Tin Oxide (ITO) Thin Films By Dc- Magnetron Sputtering On Polyethylene Terephthalate Substrate (PET), *Rom. Journ. Phys.*, 56(5-6)730-741