ISSN : 0974 - 7486 Volume 10 Issue 9

Materials Science

An Indian Journal

Full Paper

MSAIJ, 10(9), 2014 [397-401]

Physical characterization of sprayed SnO_2 thin films

Saad Farhan Oboudi[1], Nadir Fadhil Habubi[2]*, Sami Salmann Chiad[2]
[1]Baghdad University, College of Science, Physics Department, Baghdad, (IRAQ)
[2]Al_Mustansiriyah University, College of Education, Physics Department, Baghdad, (IRAQ)
E-mail : nadirfadhil@yahoo.com

ABSTRACT

SnO_2 films with different thicknesses (250, 300, 330 and 350 nm) were synthesized by spray pyrolysis technique. The substrates were heated to 500°C. Characteristics and optical constant of the films have been studied. Optical absorption studies in the wavelength range 300–900 nm in order to calculate the optical constants such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant. Results illustrate that both refractive index and extinction coefficient of the films are increasing with increasing film thickness, on the other hand, the values of real and imaginary parts of the dielectric are found to be decreased with increasing film thickness. The skin depth is found to be decreases as the film thickness increased to 350nm, so the skin depth is a transmittance related.

INTRODUCTION

Transparent conductive oxides (TCOs) films are used in a variety of applications because of their special optical and electrical properties such as wide band gaps, typically larger than 3 eV, and consequently high optical transparency in the visible spectral region. Also these films have low resistivity ($\rho < 10^{-4}\ \Omega$cm)[1-4]. Among them, tin dioxide SnO_2 seems to be the most appropriate material for different applications due to its optical and electrical properties. SnO_2 is chemically inert, mechanically hard and heat-resistant. In addition, they exhibit low electrical resistivity and high optical transmittance. Furthermore, tin dioxide films are more stable than other TCOs films such as zinc oxide (ZnO)[5–7]. Moreover, they have a lower material cost.

Different techniques are used to prepare tin dioxide films such as chemical vapor deposition[8,9], canonray evaporation[10], sol–gel coating[11], laser pulse evaporation[12,13], magnetron sputtering[14,15], electron beam evaporation[16,17] and spray pyrolysis[18,19]. Among these methods, the spraying technique is a simple, economic and commonly used method and it is well suited for the preparation of tin dioxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings[20,21]. In addition, the tin oxide prepared by the spraying technique is also physically and chemically resistant against environmental effects and adheres strongly to different substrates.

The growth of SnO_2 thin films on semiconductor substrate has attracted so much attention because of the interest in both fundamental physical properties and potential applications in promising devices[22-25], as a good example Alfonso et al.[26] has grown SnO_2 thin films on Si substrates. In this study, the optical characteristics of SnO_2 films deposited by spray pyrolysis technique on glass substrates are reported. It is intended the determination of optimum conditions that leads to the manufacturing of well crystallize, conductive and transparent tin oxide thin films. The optical constants of the films were examined in association with the increase in film thickness.

EXPERIMENTAL PROCEDURE

Thin films of tin oxide have been prepared by chemical pyrolysis technique. The starting solution was achieved by an aqueous solution of 0.1M $SnCl_4.5H_2O$ from Merck Chemicals, this material was dissolved in de-ionized water and ethanol, a few drops of HCl were added to make the solution clear, formed the final spray solution and a total volume of 50 ml was used in each deposition. The spraying process was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 500°C, with the optimized conditions that concern the following parameters, spray time was 7 Sec and the spray interval 3 min was kept constant to avoid excessive cooling, the carrier gas (filtered compressed air) was maintained at a pressure of $10^5 Nm^{-2}$, distance between the nozzle and substrate was about 29cm, solution flow rate 5 ml/min. Optical transmittance and absorbance were recorded in the wavelength range (300-900 nm) using UV-VIS spectrophotometer (Shimadzu Company Japan). In order to explore the influence of film thickness on the parameters under investigation, the films prepared with different thickness in the range of 250, 300, 330 and 350 nm.

RESULTS AND DISCUSSIONS

The optical properties of SnO_2 films by means of optical absorption in the UV-Vis region of (300–900) nm have been investigated. Figure 1 shows the optical absorbance spectra for all SnO_2 films. The position of the absorbance spectra is observed to shift towards the higher wavelength side with the increase of films thickness. This indicates that the band gap of ZnO material decreases with increasing the thickness. In our earlier study we showed that the value of the band gap (E_g) is enhanced from 3.7 to 3.5 eV by increasing the film thickness from 250 to 350 nm. Similar results of enhancement of the SnO_2 band gap were also pointed

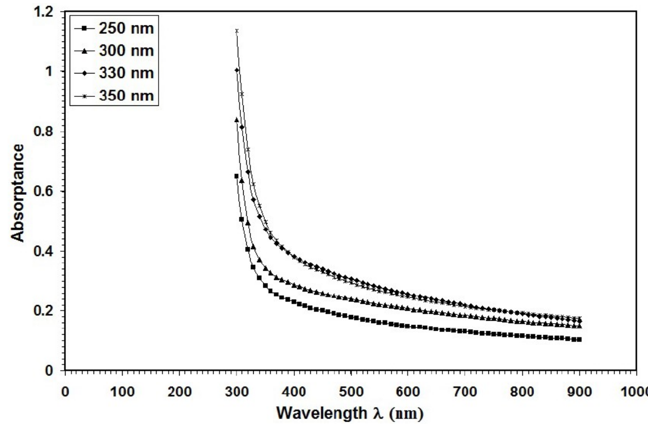

Figure 1 : Absorptance of different thicknesses of SnO_2 thin films versus wavelength.

out by other researchers[27,28].

Refractive index of the film is an important parameter for optoelectronic devices design such as optical filters, solar cells, high stability resistors, displays devices. In order to calculate the optical constant refractive index (n) and the extinction coefficient (k) of the films at different wavelengths, we can use the following relations[29,30]:

$$n = [1 + R/1 - R] + [\,4R / (1-R)^2 - k^2\,]^{1/2} \quad (1)$$

$$k = \alpha\lambda/4\pi \quad (2)$$

Where (α) is the absorption coefficient and λ is the wavelength. The refractive index of the films was calculated by using Eq. (1) and the variation of refractive index with wavelength for the films is shown in Figure 2. All films showed similar behavior in refractive index spectra. There is a little decrease in refractive index values for the films with increasing thickness. Refractive index values of the samples vary between (2.1–2.4) at long wavelengths. The lowering of refractive index can be attributed to the density and the surface roughness[31]. It can be noticed that all films have a similar k variation belonging to wavelength of polarized light, and a similar tendency was observed according to the curves of refractive index. The extinction coefficient of a material is directly related to its absorption characteristic. As shown in Figure 3, the k values are very small at long wavelengths where all films are nearly transparent. Both refractive index and extinction coefficient of the films are decreasing with increasing film thicknesses. The average refractive index and extinction coefficient values of the films at 500 nm are given in TABLE 1.

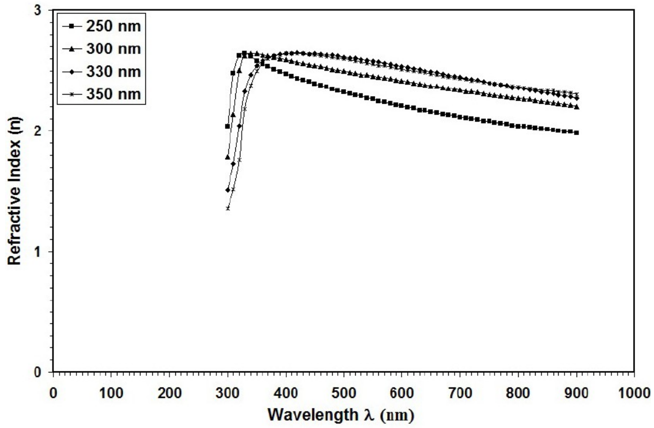

Figure 2 : Refractive index versus wavelength for SnO_2 thin films.

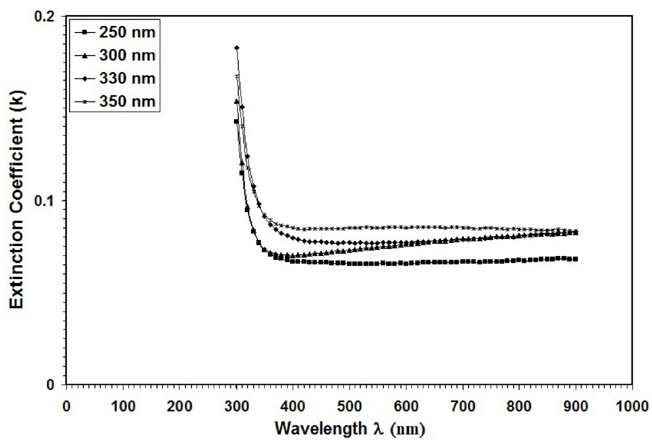

Figure 3 : Extension coefficient versus wavelength for SnO_2 thin films.

TABLE 1 : Average refractive index and extinction coefficient values for all films at 500 nm.

Thickness nm	n at λ= 500 nm	k at λ= 500 nm
250	2.32	0.065
300	2.51	0.072
330	2.62	0.078
350	2.65	0.087

The real ε_1 and imaginary ε_2 parts of the dielectric constant were obtained using the formula as[32]:

$$\varepsilon_1 = n^2 - k^2 \quad (3)$$

$$\varepsilon_2 = 2nk \quad (4)$$

The variation in the real (ε_1) and imaginary (ε_2) parts of the dielectric constant for all SnO_2 films are shown in Figures (4) and (5). The values of the real part are higher than those of the imaginary part. The values of real and imaginary parts of the dielectric are found to be decreased with increasing film thickness.

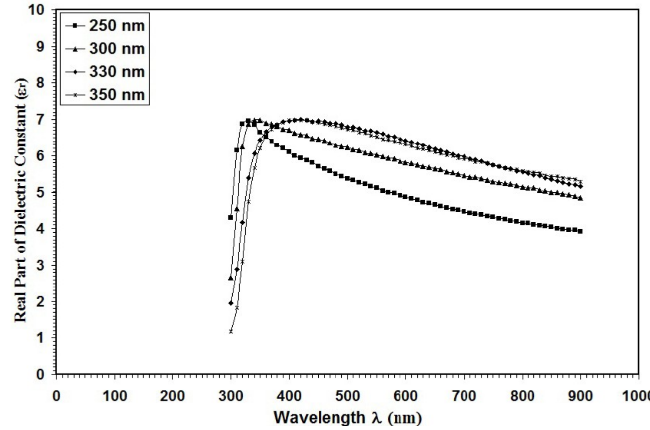

Figure 4 : Real part of the dielectric constant versus wavelength for SnO_2 films.

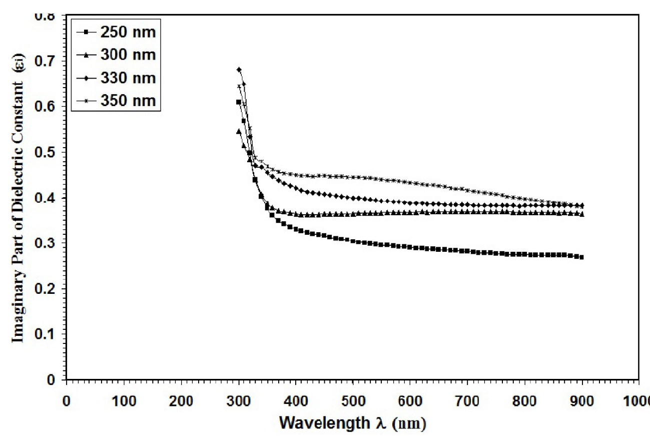

Figure 5 : Imaginary part of the dielectric constant versus wavelength for SnO_2 films.

The skin depth could be calculated using the following relation[33]:

$$\chi = \lambda / 2\pi k \quad (5)$$

Where λ is the wavelength of the incident photon, k is the extinction coefficient. Figure (6) Shows the variation of skin depth as a function of wavelength for all

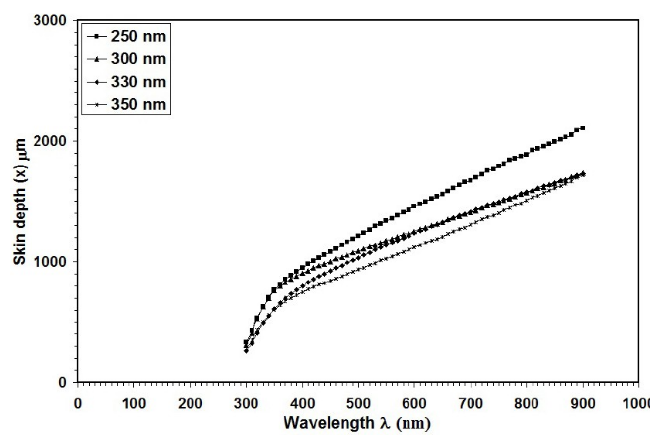

Figure 6 : Skin depth versus wavelength for SnO_2 films.

films. It is clear from the figure that the skin depth increase as the wavelength increase, this behavior could be seen in all samples, but the skin depth decreases as the film thickness increases to 350nm, which means that the skin depth is a transmittance related.

CONCLUSION

The optical properties of SnO_2 films grown on glass substrates have been investigated. Results indicate that the optical parameters are strongly dependent on the film thickness. As the SnO_2 film thickness increases, the energy gap of the SnO_2 film decreases, but both the refractive index and the extinction coefficient increases. The real and imaginary parts of dielectric constant were calculated and they are tending to increase with increasing film thickness, on the other hand the skin depth decreases as the film thickness increases. These present observations can help improve the understanding of the optical parameters of SnO_2 thin films.

REFERENCES

[1] A.Facchetti, T.J.Marks; Transparent electronics: from synthesis to applications, John Wiley and Sons,; **(2010)**.

[2] Mohsen Ghasemi Varnamkhasti, Hamid Reza Fallah a,b, Mehdi Zadsar; Effect of heat treatment on characteristics of nanocrystalline ZnO films by electron beam evaporation, Vacuum, **86**, 871-875 **(2012)**.

[3] S.S.Pan, C.Ye, X.M.Teng, L.Li, G.H.Li; Localized Exciton Luminescence in Nitrogen-incorporated SnO2 Thin Films, Appl.Phys.Lett., http://dx.doi.org/10.1063/1.2416070, **89**, 251911 **(2006)**.

[4] R.Dolbec, M.A.El Khakani, A.M.Serventi, R.G.Saint-Jacques; Influence of the nanostructural characteristics on the gas sensing properties of pulsed laser deposited tin oxide thin films, Sens.Actuators B, **93**, 566-571 **(2003)**.

[5] T.Minami, S.Tukata, H.Sato; Properties of transparent zinc-stannate conducting films prepared by radio frequency magnetron sputtering, J.Vac.Sci.Technol.A, http://dx.doi.org/10.1116/1.579592, **13(3)**, 1095-1099 **(1995)**.

[6] Xina Wang, Haojun Zhu, Yeming Xu, Hao Wang, Yin Tao, Suikong Hark, Xudong Xiao, Quan Li; Aligned ZnO/CdTe Core"Shell Nanocable Arrays on Indium Tin Oxide: Synthesis and Photoelectrochemical Properties, ACS Nano, **4(6)**, 3302–3308 **(2010)**.

[7] Brijesh Tripathi, Malkesh Patel, Abhijit Ray, Manoj Kumar; Influence of optical properties of ZnO thin-films deposited by spray pyrolysis and RF magnetron sputtering on the output performance of silicon solar cell, IOP Conference Series: Materials Science and Engineering, conference 1, doi:10.1088/1757-899X/43/1/012002, **43**, **(2013)**.

[8] J.R.Brown, P.W.Haycock, L.M.Smith, A.C.Jones, E.W.Williams; Response behavior of tin oxide thin film gas sensors grown by MOCVD, Sensors and Actuators, **B63**, 109-114 **(2000)**.

[9] K.H.Kim, J.S.Chun; X-ray studies of SnO_2 prepared by chemical vapour deposition, Thin Solid Films, **141**, 287–295 **(1986)**.

[10] C.A.Pan, T.P.Ma; High Quality Transparent Conductive Indium Oxide Films Prepared by Thermal Evaporation, Appl.Phys.Lett., **37**, 163 **(1980)**.

[11] S.C.Lee, J.H.Lee, T.S.Oh, Y.H.Kim; Fabrication of tin oxide film by sol–gel method for photovoltaic solar cell system, Sol.Energy Mater.Sol.Cells, **75**, 481-487 **(2003)**.

[12] C.K Kima, S.M Choia, I.H Noha, J.H Leea, C Hongb, H.B Chaeb, G.E Jangc, H.D Parkd; A study on thinfilm gas sensor based on SnO_2 prepared by pulsed laser deposition method", Sensors and Actuators B: Chemical, **77**, 463–467 **(2001)**.

[13] R.D.Vispute, V.P.Godbole, S.M.Chaudhari, S.M.Kanetkar, S.B.Ogale; Deposition of tin oxide films by pulsed laser evaporation, Journal of Materials Research, **3**, 1180-1186 **(1988)**.

[14] Tadatsugu Minami, Toshihiro Miyata, Takashi Yamamoto; Work function of transparent conducting multicomponent oxide thin films prepared by magnetron sputtering, Surface and Coatings Technology, **108,109**, 583–587 **(1998)**.

[15] S.I.Rembeza, T.V.Svistova, E.S.Rembeza, O.I.Borsyakova; The microstructure and physical properties of thin SnO_2 films, Semiconductors, **35**, 762-765 **(2001)**.

[16] K.S.Shamala, L.C.S.Murthy, K.Narashima Rao; Studies on tin oxide films prepared by electron beam evaporation and spray pyrolysis methods, Bull.Mater.Sci., **27**, 295-301 **(2004)**.

[17] D.Debajyoti, R.Banerjee; Properties of electron-beam-evaporated tin oxide films, Thin Solid Films, **147**, 321-331 **(1987)**.

[18] T.Fukano, T.Motohiro; Low-temperature growth of highly crystallized transparent conductive fluorine-

doped tin oxide films by intermittent spray pyrolysis deposition, Sol.Energy Mater.Sol.Cells, **82**, 567-575 **(2004)**.

[19] E.Elangovan, K.Ramesh, K.Ramamurthi; Studies on the structural and electrical properties of spray deposited SnO_2:Sb thin films as a function of substrate temperature, Solid State Commun,**130**, 523-527 **(2004)**.

[20] Pramod S.Patil; Versatility of chemical spray pyrolysis technique, Materials Chemistry and Physics, **59**, 185–198 **(1999)**.

[21] A.V.Moholkar, S.M.Pawar, K.Y.Rajpure, C.H.Bhosale; Effect of concentration of $SnCl_4$ on sprayed fluorine doped tin oxide thin films, Journal of Alloys and Compounds, **455**, 440–446 **(2008)**.

[22] W.Dazhi, W.Shulin, C.Jun, Z.Suyuan, L.Fangqing; Microstructure of SnO_2, Phys.Rev.B, **49(20)**, 14282–14285, 282 **(1994)**.

[23] R.E.Cavicchi, J.S.Suehle, K.G.Kreider, B.L.Shomaker, J.A.Small, M.Gaitan, P.Chaparala; Growth of SnO_2 films on micromachined hotplates, Appl.Phys.Lett., http://dx.doi.org/10.1063/1.113429, **66**, 812-814 **(1995)**.

[24] D.Davazoglou; Determination of optical dispersion and film thickness of semiconducting disordered layers by transmission measurements: Application for chemically vapor deposited Si and SnO_2 film, Appl.Phys.Lett., http://dx.doi.org/10.1063/1.118379, **70**, 246 **(1997)**.

[25] M.W.J.Prins, K.O.Grosse-Holz, G.Müller, J.F.M.Cillessen, J.B.Giesbers, R.P.Weening, R.M.Wolf; A ferroelectric transparent thin-film transistor, Appl.Phys.Lett., http://dx.doi.org/10.1063/1.115759, **68**, 3650 **(1996)**.

[26] C.Alfonso, A.Charai, A.Armigliato, D.Narducci; Transmission electron microscopy investigation of tin sub-oxide nucleation upon SnO_2 deposition on silicon, Appl.Phys.Lett., http://dx.doi.org/10.1063/1.115970, **68**, 1207 **(1996)**.

[27] F.Atay, V.Bilgin, I.Akyuz, E.Ketenci, S.Kose; Optical characterization of SnO2:F films by spectroscopic ellipsometry, Journal of Non-Crystalline Solids, **356**, 2192–2197 **(2010)**.

[28] P.M.Gorley, V.V.Khomyak, S.V.Bilichuk, I.G.Orletsky, P.P.Horley, V.O.Grechko; SnO_2 films: formation, electrical and optical properties, Materials Science and Engineering B, **118**, 160–163 **(2005)**.

[29] M.R.Islam Podder; Optical properties of ZnO nano fiber thin films grown by spray pyrolysis of zinc acetate precursor, J.Cryst.Res.Technol., **44**, 286-292 **(2009)**.

[30] H.E.Atyia; Influence of deposition temperature on the structural and optical properties of InSbSe3 films, Optoelectron.Adv.M., **8**, 1359-1366 **(2006)**.

[31] F.Karipcin, E.Kabalcilar, S.Ilican, Y.Caglar, M.Caglar; Synthesized some 4-(2-thiazolylazo) resorcinol complexes: Characterization, thermal and optical properties, Spectrochim.Acta A, **73**, 174-180 **(2009)**.

[32] F.Buet, J.Olivier-Fourcade, Y.Bensimon, P.Belougne; Complex Impedance Study of Chalcogenide Glasses, Solid State Communications, **77(1)**, 29-32 **(1991)**.

[33] J.F.Eloy; Power Lasers, National School of Physics, Grenoble, France, John Wiley and Sons, **59**, **(1984)**.