ISSN : 0974 - 7486 Volume 11 Issue 5

Materials Science

An Indian Journal

Full Paper

MSAIJ, 11(5), 2014 [189-194]

Analysis of dispersive optical constant of as deposited and annealed SnO_2 thin films

Sami Salmann Chiad[1], Hanan R.A.Ali[2]*, Ali Saddam Lafta[1]

[1]Al_Mustansiriyah University, College of Education, Physics Department/ Baghdad, (IRAQ)

[2]University of Tikrit, College of Education, Physics Department/ Tikrit, (IRAQ)

E-mail: ifaris38@yahoo.com

ABSTRACT

Films of SnO_2 were prepared by the spray pyrolysis technique onto glass substrate heated up to 500°C. Optical absorption measurements in the wavelength range 300-900 nm were studied and confirmed that annealing films at 550ºC for different annealing time has a significant effect on the optical properties of the films. The optical constants confirm that SnO_2 films have an indirect band gap that decreased from 3.3 to 3.1eV as the annealing time increases to 3hrs. The dispersion of the refractive index was analyzed using the concept of a single oscillator. The values of the single oscillator energy E_o were 6.6, 6.57, 6.48 and 6.18eV, while the dispersion energy E_d values were 94, 82, 77, and 70 for the as deposited and the annealed films for 1, 2, and 3hrs respectively. The increase in the density of localized states E_u from 595 to 667meV causes an expanding in the Urbach tail and consequently decreases the energy gap.

KEYWORDS

Tin oxide SnO_2;
Optical dispersion parameters;
Optical energy gap;
Spray pyrolysis.

INTRODUCTION

Transparent conducting oxide (TCO) thin films such as zinc oxide, indium oxide, tin oxide, and cadmium oxide have attracted considerable attention because of their low resistivity and high optical transmittance[1,2]. Due to their unique optical and electrical properties, their films are used for photovoltaic devices, phototransistors, liquid crystal displays, optical heaters, gas sensors, solar cells, transparent electrodes and other optoelectronic devices[3-8].

Among these TCOs, SnO_2 films are inexpensive, chemically stable in acidic and basic solutions, thermally stable in oxidizing environments at high temperatures and also mechanically strong, which are important attributes for the fabrication and operation of solar cells[9,10]. SnO_2 has a tetragonal structure, their property is resulted from its n-type semiconductor behavior, similar to the rutile structure with the wide band gap of E_g =3.6–4.0eV[11,12].

Thin films of SnO_2 can be produced by various techniques, such as chemical vapor deposition[13,14], canonray evaporation[15], sol–gel coating[16], pulsed laser deposition[17], magnetron sputtering[18,19], electron beam evaporation[20] and spray pyrolysis[21–22]. Among these techniques that used to form SnO_2 films spray pyrolysis technique is the best, it is simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings[23].

Full Paper

In reviewing of literatures, it can be seen that the effect of annealing time on the optical properties of SnO_2 films should be studied more sufficiently. In this paper, we report and discuss the characterization of the SnO_2 films prepared by spray pyrolysis technique and annealed to 550ºC for 1, 2, and 3 hrs.

EXPERIMENTAL DETAILS

Tin oxide SnO_2 thin films were deposited by the spray pyrolysis technique, using 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 clearly 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 nozzle and the substrate was about 29cm, solution flow rate 5 ml/min.

The samples were weighed before and after spraying to determine the mass of the films[24]. Knowing the dimensions of the substrates used, the thicknesses can be determined using the following equation[25]:

$$d = \frac{\Delta m}{\rho_m \, lL} \qquad (1)$$

Where Δm is the difference between the mass after and before spraying, ρ_m is the density, l the width and L the length. Optical transmittance and absorbance were recorded in the wavelength range (300-900 nm) using UV-VIS spectrophotometer (Shimadzu Company Japan). The effect of annealing time on the optical properties was investigated.

RESULTS AND DISCUSSION

The study of the optical absorption of the investigated SnO_2 films, particularly the absorption edge has proved to be very useful for elucidation of the electronic structure of these materials. The optical absorption spectra of the tested films as a function of annealing time are shown in Figure 1. The absorption at higher wavelengths in the visible region is low and at wavelength 350–380 nm, an intense absorption can be seen. These results were in a good agreement with that obtained by Patil et al.[26]. Moreover, it can be noticed that the absorbance tends to increase as the annealing time rises from 1 to 3 hrs.

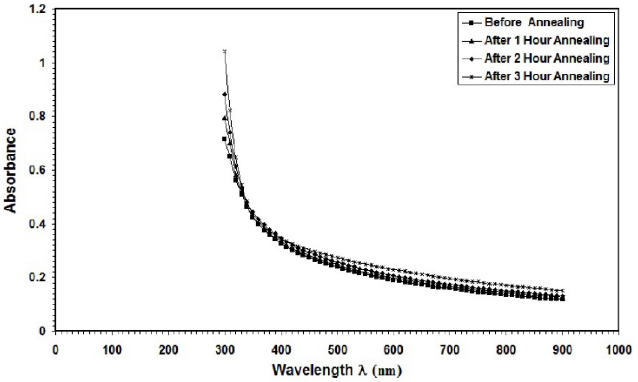

Figure 1 : Absorbance of as deposited and annealed SnO_2 films versus wavelength

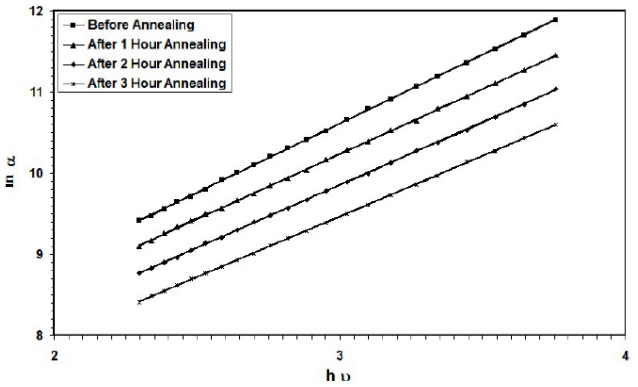

Figure 2 : lnα versus photon energy for as deposited and annealed SnO_2 films

The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach[27]. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as[28,29]:

$$\alpha = \alpha_o \exp(h\upsilon / E_U) \qquad (2)$$

Where α_o is a constant, E_U is the Urbach energy, which characterizes the slope of the exponential edge. Figure

TABLE 1 : The optical parameters

Sample	E_d (eV)	E_o (eV)	E_g (eV)	ε_∞	n(o)	M_{-1}	M_{-3} eV^{-2}	$S_o x10^{13}$ m^{-2}	λ_o nm	U_{tail} meV
Before annealing (as deposited)	94	6.60	3.30	15.20	3.90	15.20	0.326	2.20	612	595
Annealing for 1 hr	82	6.57	3.28	13.50	3.67	12.50	0.289	1.85	599	625
Annealing for 2 hrs	77	6.48	3.24	12.90	3.59	11.90	0.283	1.74	580	645
Annealing for 3 hrs	70	6.18	3.10	12.36	3.51	11.36	0.272	1.60	572	667

2 shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of lná vs. hõ and is given in TABLE 1. E_U values change inversely with the optical band gap. The Urbach energy values of the films increase with the increasing of annealing time. The increase of E_U suggests that the atomic structural disorder of SnO_2 films increases by increasing annealing time. This behavior can result from increasing the grain size. The size of the grains varies with annealing temperature and influences the values of the optical energy gap. It is well known that the size of crystallites is in direct relationship with the increase of the temperature and the annealing time, more the temperature is high more the size of the grains is important and more the annealing time is important more the grain is large. Such result was also confirmed by Hemissi *et al.*[30]. So, this increase leads to a redistribution of states from band to tail and may be attributed to the improvement of crystallinity. As a result, both a decrease in the optical gap and expanding of the Urbach tail have taken place.

According to inter-band absorption theory, the optical band of the SnO_2 films can be calculated using Tauc's relation[28]:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \quad (3)$$

where α is the absorption coefficient, A a constant, h is Planck's constant, υ the photon frequency, E_g the optical band gap and n is an index which could take different values according to the electronic transition. For allowed direct transitions the coefficient n is equal to 1/2 and for indirect allowed transitions n = 2. The curves $(\alpha h\upsilon)^{1/2}$ for the direct allowed transition does not present evidence linearity, this seems to suggest that SnO_2 has

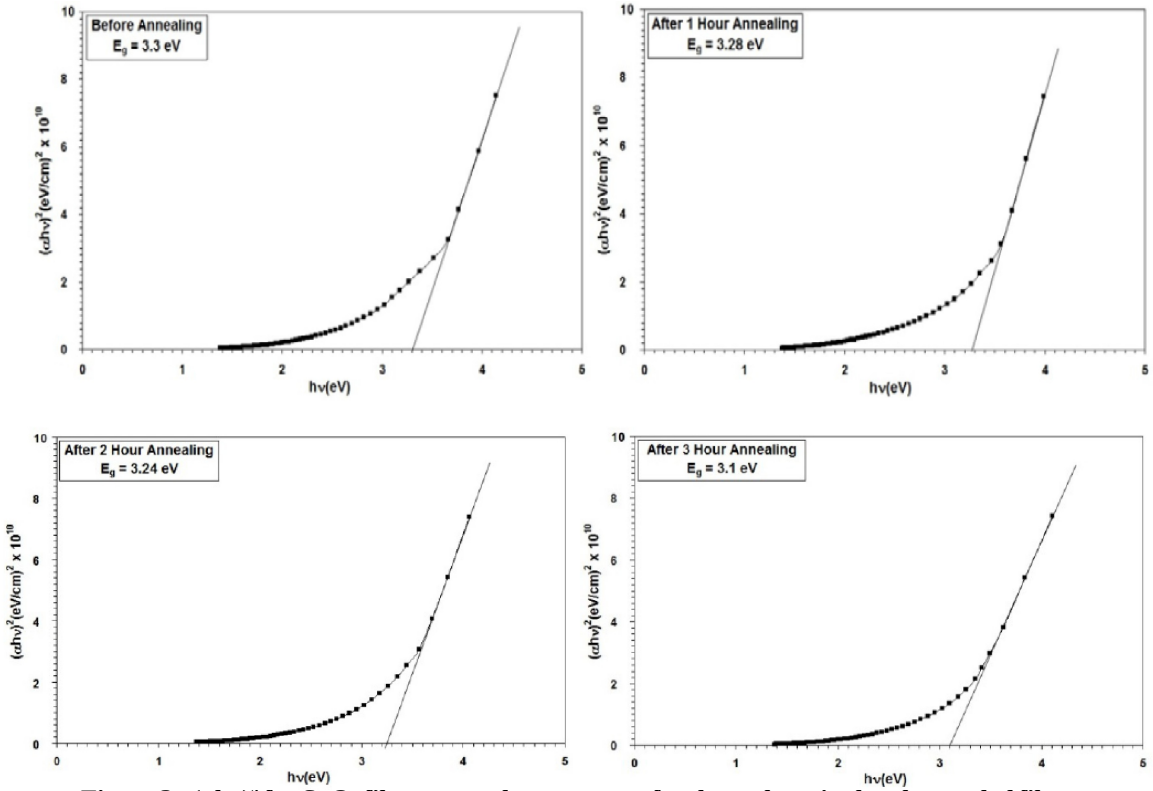

Figure 3 : $(\alpha h\upsilon)^2$ for SnO_2 film versus photon energy for the as deposited and annealed films

an indirect band gap.

The value E_g corresponding to the indirect band gap transition was calculated from the curve of $(\alpha h\upsilon)^2$ versus $h\upsilon$, using the formula:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \quad (4)$$

The extrapolation of the linear part of the curve $(\alpha h\upsilon)^2$ to the energy axis is shown in Figure 3. The indirect band-gap energy for the as deposited film is equal to 3.3eV, which is quite comparable with the reported values[26,31,32]. It can be seen that the energy band gap of the films tends to decrease with increasing annealing time to 3 hrs. The decrease in the optical band gap with increasing annealing time can be attributed to a decrease in crystallinity disorder of the films. The optical band gap of SnO_2 films is obviously affected by the defects and the crystallinity.

Wemple and Didomenico[33,34] use a single-oscillator description to define dispersion energy parameters E_d and E_o. The refractive index dispersion plays an important role in the optical communication and designing of the optical devices. Therefore, it is a significant factor. The relation between the refractive index n, and the single oscillator strength below the band gap is given by the expression:

$$n^2 = 1 + [E_d E_o / E_o^{2TM} E^2] \quad (5)$$

Where E_d and E_o are single oscillator constants, E_o is the energy of the effective dispersion oscillator, E_d the so-called dispersion energy, which measures the intensity of the inter band optical transitions. The oscillator energy E_o is an average of the optical band gap, E_{opt}, can be obtained from the Wemple–Didomenico model. This model describes the dielectric response for transitions below the optical gap. Experimental verification of Eq. (4) can be obtained by plotting $(n^{2TM}1)^{TM1}$ versus $(h\upsilon)^2$as illustrated in Figure 4 which yields a straight line for normal behavior having the slope $(E_oE_d)^{-1}$ and the intercept with the vertical axis equal to E_o/E_d. E_o and E_d values were determined from the slope, $(E_oE_d)^{TM1}$ and intercept (E_o/E_d) on the vertical axis. E_o values decreased as the optical band gap decreases. According to the single-oscillator model, the single oscillator parameters E_o and E_d are related to the imaginary part of the complex dielectric constant, the moments of the imaginary part of the optical spectrum M_{TM1} and M_{TM3} moments can be derived from the following relations[35]:

$$E_o^2 = M_{-1} / M_{-3} \quad (6)$$

$$E_d^2 = M^3_{-1} / M_{-3} \quad (7)$$

The values obtained for the dispersion parameters E_o, E_d, M_{-1} and M_{-3} are listed in TABLE 1. The obtained M_{-1} and M_{-3} moments have decreased with increasing annealing time. For the definition of the dependence of the refractive index (n) on the light wavelength (λ), the single-term Sellmeier relation can be used[33]:

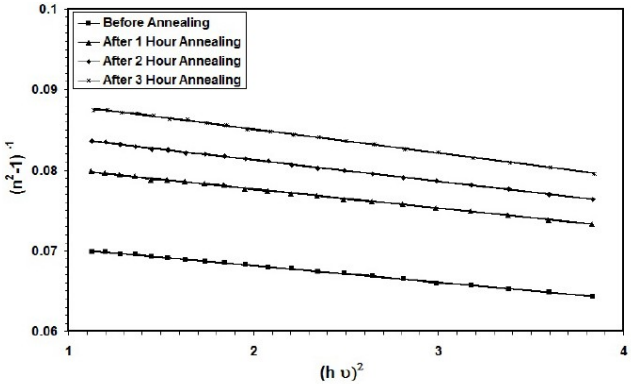

Figure 4 : Variation in $(n^2 - 1)^{-1}$ as a function of $(h\upsilon)^2$ for SnO_2 films

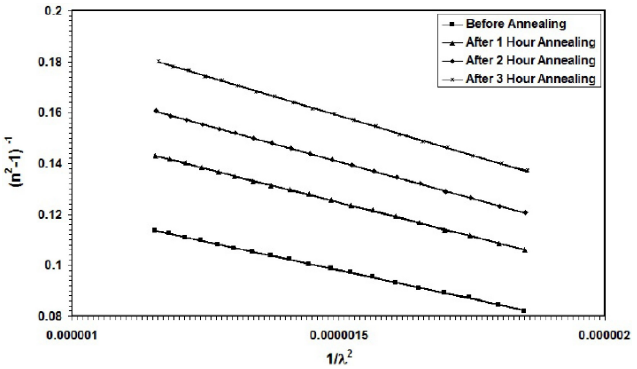

Figure 5 : Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for SnO_2 films

$$n^2(\lambda) - 1 = S_o\lambda_o^2 / 1 - (\lambda_o/\lambda)^2 \quad (8)$$

Where λ_o is the average oscillator position and S_o is the average oscillator strength. The parameters S_o and λ_o in Eq. (7) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ versus λ^{-2} as shown in Figure 5, the slope of the resulting straight line gives $1/S_o$, and the infinite-wavelength intercept gives $1/ S_o \lambda_o^2$. The results show a decrease in the band gap which may be attributed to the presence of unstructured defects, that increase the density of localized states and cause an expanding in the Urbach tail and consequently decrease the energy gap.

CONCLUSION

Tin Oxide SnO_2 thin films have been successfully deposited onto a glass substrate by the spray pyrolysis technique. The type of optical transition responsible for optical absorption was indirect allowed transitions. The E_g^{WD} values obtained from Wemple–Didomenico model are in agreement with those determined from the Tauc model and found to be decreasing with the increasing of annealing time and have the values of 3.3, 3.28, 3.24 and 3.1eV for the as deposited, annealed films for 1, 2 and 3 hrs respectively. The optical dispersion parameters were characterized and found to be obeying the single oscillator model. The single oscillator parameters were determined, the change in dispersion was investigated and its value decreased from 6.6 to 6.18eV with increasing annealing time to 3 hrs.

REFERENCES

[1] Claes G..Granqvist; Transparent conductors as solar energy materials: A panoramic review, Solar Energy Materials & Solar Cells, **91**, 1529–1598 **(2007)**.

[2] E.Elangovan, K.Ramamurthi; A study on low cost-high conducting fluorine and antimony-doped tin oxide thin films, Appl.Surf.Sci., **249**, 183-196 **(2005)**.

[3] K.L.Chopra, S.Major, D.K.Pandya; Transparent conductors-A status review, Thin Solid Films, **102**, 1-46 **(1983)**.

[4] C.G.Granqvist; Handbook of Inorganic Electrochromic Materials, Elsevier Publication, The Netherlands, **(1995)**.

[5] Bo-Huei Liao, Chien-Cheng Kuo, Pin-Jen Chen, Cheng-Chung Lee; Fluorine-doped tin oxide films grown by pulsed direct current magnetron sputtering with an Sn target, Applied Optics, **50**, C106-C110 **(2011)**.

[6] V.Vasu, A.Subrahmanyam; Electrical and optical properties of sprayed SnO_2 films: Dependence on the oxiding agent in the starting material, Thin Solid Films, **193–194**, 973-980 **(1990)**.

[7] Chunzhong Li, Bin Hua; Preparation of nanocrystalline SnO_2 thin film coated Al_2O_3 ultrafine particles by fluidized chemical vapor deposition, Thin Solid Films, **310**, 238-243 **(1997)**.

[8] B.Thangaraju; Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped SnO_2 thin films from $SnCl_2$ precursor, Thin Solid Films, **402**, 71-78 **(2002)**.

[9] H.Kim, R.C.Y.Auyeung, A.Pique; Transparent conducting F-doped SnO_2 thin films grown by pulsed laser deposition, Thin Solid Films, **516**, 5052-5056 **(2008)**.

[10] Arturo I.Martinez, Dwight R.Acosta; Effect of the fluorine content on the structural and electrical properties of SnO_2 and ZnO–SnO_2 thin films prepared by spray pyrolysis, Thin Solid Films, **483**, 107-113 **(2005)**.

[11] A.V.Moholkar, S.M.Pawar, K.Y.Rajpure, C.H.Bhosale; Effect of solvent ratio on the properties of highly oriented sprayed fluorine-doped tin oxide thin films, Mater.Lett., **61**, 3030-3036 **(2007)**.

[12] Sung-Sik Chang, M.S.Jo; Luminescence properties of Eu-doped SnO_2, Ceram.Int., **33**, 511-514 **(2007)**.

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

[14] J.R.Brown, P.W.Haycock, L.M.Smith, A.C.Jones, E.W.Williams; Response behaviour of tin oxide thin film gas sensors grown by MOCVD, Sensors and Actuators B, **63**, 109-114 **(2000)**.

[15] S.K.Tripathy, B.Nagarjun, V.S.Jahnavy; Optical and Structural Characteristics of Copper Doped Tin Oxide Thin Film Prepared by Thermal Evaporation Method, Int.J.of Eng.and Inn.Tech. (IJEIT), **3**, 296-300 **(2013)**.

[16] 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)**.

[17] 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)**.

[18] 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)**.

[19] 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)**.

[20] 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)**.

[21] 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)**.

[22] 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)**.

[23] 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)**.

[24] H.Tabet-Derraz, N.Benramdane, D.Nacer, A.Bouzidi, M.Medles; Investigations on $Zn_xCd_{1™x}O$ thin films obtained by spray pyrolysis, Sol.Energy Mater.Sol.Cells., **73**, 249-259 **(2002)**.

[25] M.Medles, N.Benramdane, A.Bouzidi, A.Nakrela, H.Tabet-Derraz, Z.Kebbab, C.Mathieu, B.Khelifa, R.Desfeux; Optical and electrical properties of Bi_2S_3 films deposited by spray pyrolysis, Thin Solid Films, **497,** 58-64 **(2006)**.

[26] G.E.Patil, D.D.Kajale, D.N.Chavan, N.K.Pawar, P.T.Ahire, S.D.Shinde, V.B.Gaikwad, G.H.Jain; Synthesis, characterization and gas sensing performance of SnO2 thin films prepared by spray pyrolysis, Bull.Mater.Sci., **34(1)**, 1–9 **(2011)**.

[27] F.Urbach; The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids, Phys.Rev., **92**, 1324-1325 **(1953)**.

[28] J.Tauc; Amorphous and Liquid Semiconductors, Plenum Press, New York, **(1974)**.

[29] J.Tauc, R.Grigorovici, A.Vancu; Optical Properties and Electronic Structure of Amorphous Germanium, Phys.Status Solidi, **15**, 627-637 **(1966)**.

[30] M.Hemissi, H.Amardjia-Adnani, J.C.Plenet, B.Canut, J.M.Pelletier; Influence of annealing time on structural and electrical properties of Sb doped SnO_2 films, Revue des Energies Renouvelables, **10**, 273-279 **(2007)**.

[31] Yuhua Xiao, Shihui Ge, Li Xi, Yalu Zuo, Xueyun Zhou, Li Zhang, Guowei Wang, Xiufeng Han, Zhenchao Wen; Structure, optical, and magnetic properties of rutile $Sn_{1-x}Mn_xO_2$ thin films, Applied Surface Science, **255**, 7981–7984 **(2009)**.

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

[33] S.H.Wemple, DiDomenico; Oxygen – Octahedra Ferroelectrics I. Theory of Electro-Optical and Non Linear Optical Effects, J.Appl.Phys., **40(2)**, 720-734 **(1969)**.

[34] S.H.Wemple, DiDomenico; Behavior of the Electronic Dielectric Constant in Covalent and Ionic Materials, Phys.Rev., **B3**, 1338-1351 **(1971)**.

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