Study on Optical Properties of Tin Oxide Thin Film at Different Annealing Temperature

Saturi Baco[1,*], Abdullah Chik[2], Fouziah Md. Yassin[1]

[1]Physics with Electronic Programme,
School of Science & Technology, Universiti Malaysia Sabah,
Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia
[2]School of Material Engineering, Universiti Malaysia Perlis, Kampus Kubang Gajah,
02600 Arau Perlis, Malaysia.

*Corresponding email: saturi@ums.edu.my

Abstract

Tin Oxide (SnO_2) thin film is one of the important transparent conducting oxides (TCOs) and applied in various fields such as in solar cells, optoelectronic devices, heat mirror, gas sensors, etc due to its electrical and optical transparency in visible light spectrum. In this paper, we presented the optical properties of tin oxide thin film at four different annealing temperatures (373 K, 437 K, 573 K and 673 K) prepared by radio frequency sputtering technique. The optical characteristic of these films was investigated using the UV-VIS 3101-PC Spectrophotometer. From this study, all samples exhibit high transmittance more than 70% in the visible light spectrum. Sample annealed at 473 K shows the maximum transmittance which is 87%. Refractive index, n were in the range of 2.33 – 2.80 at λ = 550 nm and enhanced with the annealing temperature. However the extinction of coefficient, k was found to be very small. The optical band-edge absorption coefficients were found in the range of 10^4 – $10^5 cm^{-1}$. The energy gap value was decreased with increasing annealing temperature and the type of photon transition was allowed direct transition.

Keywords: tin oxide; radio frequency sputtering; energy band gap; annealing

1.   INTRODUCTION

Tin Oxide (SnO_2) is a n-type semiconductor with wide energy band gap (3.7 eV). The undoped SnO_2 [1] has low electrical resistance and high optical transparency in the visible range of the electromagnetic spectrum. These properties make tin oxide suitable for many applications, particularly as an electrode material in solar cell, light emitting diodes, transparent electromagnetic shielding materials, etc [2].

Numerous works have been reported concerning doped and undoped tin oxide thin films using various preparation techniques such as chemical vapor deposition [3], thermal beam evaporation [4], spray pyrolysis [5], pulse laser deposition [6], and sputtering techniques [7]. Sputtering technique has advantages among other methods, since film deposition can be carried out at low temperature, whilst yielding the preferred orientation and uniform properties [8]. Furthermore, sputtering technique is known to reproduce thin films of various types of materials especially the oxides [9]. Studies on effect of substrate type and temperature, deposition rate, oxygen partial pressure and annealing temperature are widely performed by many researchers to improve the structural, electrical and optical properties of the sputtered thin film. The annealing processes, for instance, are usually performed to reduce the intrinsic stress, to improve the lattice mismatch and create longer mean paths for the free electrons in getting better electrical conductivity [10].

In this work, tin oxide thin films were deposited by using radio frequency sputtering technique and later annealed at four different temperatures. The optical properties of SnO_2 films at different annealing temperatures were analyzed to determine their four optical parameters which are refractive index, extinction coefficient, absorption coefficient, and energy gap values.

2.   MATERIALS AND METHODS

In this study, the SnO_2 films were deposited onto soda lime glass substrate (7.6 cm x 2.6 cm x 0.1 cm) via radio frequency sputtering technique. First, before the deposition of thin films, the substrates were cleaned using an Ultrasonic Branson 3200 Cleaner by immersing the substrate in chromic acid and distilled water solution for 30 minutes at temperature of 45 ^{o}C. Next, the substrates were washed using distilled water and soaked in the beaker that also contained the distilled water for 30 minutes. The working pressure and RF power used in this study were 10 mTorr and 50 Watt respectively and the substrate temperature was kept at room temperature as listed in Table 1. After deposition of SnO_2, the films were annealed at four different temperatures which are 373 K, 473 K, 573 K and 673 K for two hours in air. The optical properties of films afterward were characterized using UV-VIS 3101-PC Spectrophotometer. The transmission spectrum in the visible light (300nm – 800nm)

was analyzed to determine the refractive index, extinction coefficient, optical band-edge absorption coefficient and energy gap value for each sample.

Table 1: Process Parameters used in this study

Target	SnO_2 (99.99% purity)
Substrate	Soda lime glass
Substrate Temperature	Room Temperature
Working Pressure	10 mTorr
RF Power	50 Watt
Film Thickness	49 nm

3. RESULTS AND DISCUSSION

3.1 Optical Transmittance

SnO_2 thin films were successfully deposited onto glass substrate and the films were very transparent. This may be attributed by the formation of the Fermi level in the conduction band [11]. Fig. 1 shows the optical transmittance spectra in the visible light region (300 nm- 800nm) for samples annealed at different temperature. From the graph, the film annealed at 473 K exhibits highest transmittance in the range of 500nm – 700nm which maximum transmittance is 87%. This is in a good agreement with the results obtained by [12] where the SnO_2 films annealed at 473 K shows high transmittance above 80%. Conversely at the wavelength between 300 nm- 450 nm, the film at 473 K initially shows the lowest transmittance and gradually increases. On the other hand film annealed at 673 K shows the lowest transmittance. Nevertheless, all samples exhibit more than 70% of transmittance in the visible light region. The transmittance for all annealed samples rises with increasing wavelength and this also approved as in [13]. The ripples as shown in the transmittance spectra may resulted from the interference of light, since they show wave forms that are characteristic of the interference light [14].
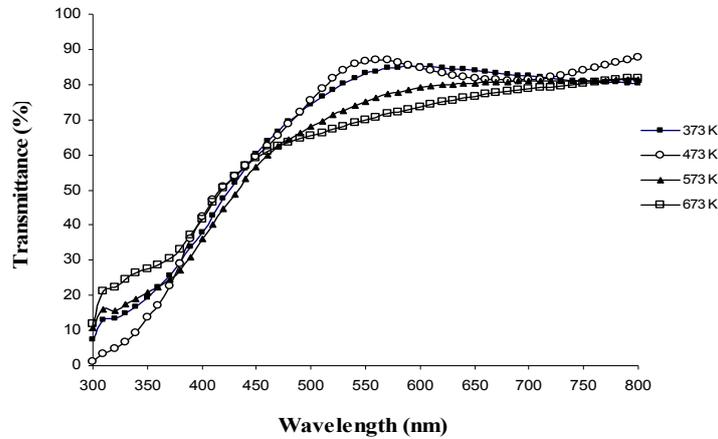
Figure 1: Optical Transmittance against wavelength in visible light spectra at different annealing temperature (373 K, 473 K, 573 K and 673 K)

3.2 **Refractive Index, *n* and Extinction Coefficient, *k***

Optical constants of SnO_2 films which are refractive index, *n* and the extinction coefficient, *k* were calculated from transmission and reflectance spectra. The refractive index of SnO_2 films can be obtained with the following equation [15]:

$$n = n_s \left(\frac{1 + \sqrt{R}}{1 - \sqrt{R}} \right)^{1/2} \tag{1}$$

with n_s is the refractive index of substrate and R is the reflectance. Refractive index for soda lime glass substrate used in this study is 1.51. The extinction coefficient, *k* is given by [9]:

$$k = \frac{\alpha \lambda}{4\pi} \tag{2}$$

where α is the absorption coefficient of the film, and λ is the wavelength of light. Fig.2 shows the variation of refractive index and the extinction coefficient with wavelength. It can be seen that, the refractive index were decrease with the wavelength according to the behavior of reflectance spectrum. At $\lambda = 550$ nm, the values of *n* were in the range of 2.33 – 2.80 and enhanced with the annealing temperature. As reported in [1] the refractive index of SnO_2 at 550 nm was 2.00 and the extinction coefficient was 0.03. However the extinction of coefficient in this study was found very small and this similar behavior also found as in [16] that showing the SnO_2 is transparent in the visible light spectrum.
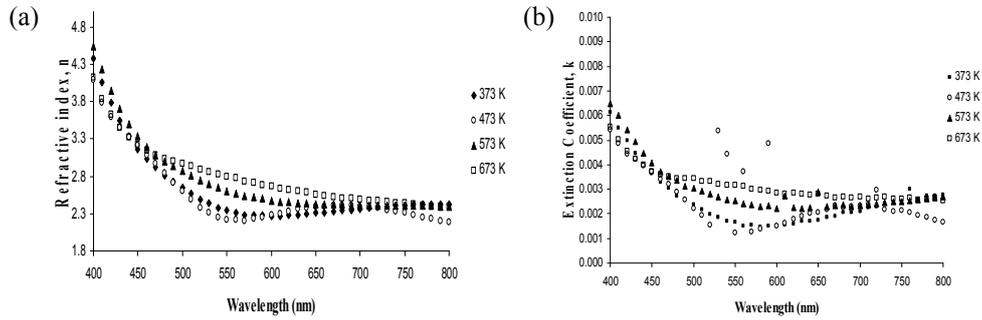
Figure 2: (a) Dispersion of refractive index, n (b) Dispersion of extinction coefficient, k with wavelength for SnO$_2$ films annealed at different temperature.

3.3 Analysis on Optical Band-Edge Absorption Coefficient

If the light with intensity I_o incident on the sample with thickness d, the intensity that is transmitted is expressed as the Lambert-Beer-Bouguer Law [17]:

$$I = I_o \exp(-\alpha d) \tag{3}$$

where I is transmitted intensity; I_o is incident intensity; α is absorption coefficient (cm^{-1}) and d is a sample thickness. The equation (3) can be simplified and the absorption coefficient can be obtained from the measured transmission spectra, T according to the following equation:

$$\alpha = \frac{1}{d} In\left(\frac{1}{T}\right) \tag{4}$$

The graph of absorption coefficient as a function of photon energy was plotted in Fig.3. The graph shows the absorption coefficient is related to the photon energy, since as the photon energy increases, the absorption edge shifted and broadened to high energy. At very low wavelength (high energy) absorption is observed due to the domination of fundamental band-gap, and for higher wavelength, high reflection is observed due to the released of free electrons in SnO$_2$ [18]. Based on the graph, the absorption coefficient values in this study are in the range of 10^4-10^5 cm^{-1} and similar to previous study [7].
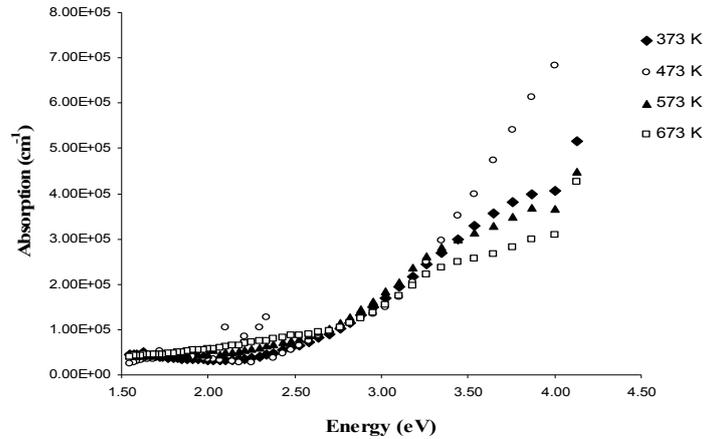
Figure 3: Optical absorption coefficient as a function of photon energy at different annealing temperature.

3.4 Estimation of SnO₂ Optical Energy Band Gap

Based on [19], the excitation of electron from valence band to conduction band by absorption of photon energy can occur in two ways usually either in direct or indirect transitions. The energy band gap of the film can roughly determined by the transmittance spectra. According to the Tauc relation [20], the absorption coefficient is given by:

$$\alpha h v = B\left(h v - E_g\right)^m \tag{5}$$

where B is constant and has different values for different transitions, E_g is the energy gap, hv is the photon energy and m is an exponent which assumes the values ½, 3/2, 2 and 3 depends on the electronic transition. In order to determine the optical energy band gap of films, the graph of $(\alpha h v)^n$ versus hv has been plotted by replacing n = 1/m which are n = 2 for allowed direct transition, n = ½ for allowed indirect, n = 1/3 for forbidden indirect and n = 2/3 for forbidden direct of optical transitions [21]. In this study, $(\alpha h v)^n$ versus hv for $n=2,1/2,1/3$ and 2/3 values respectively have been plotted.

In our case, the value of n was selected to be 2 (for allowed direct transition band gap) as illustrated in Fig.4 because it was most probable transition and by using n=2, the graph gave the best line fit [22][23]. By extrapolating the linear portion of the plot to $(\alpha h v)^2 = 0$ as plotted in Figure 5, the optical band gap was obtained. It was found that the energy gap decreased with annealing temperature. Reference [9] reported that apart from eliminating the oxygen vacancies, annealing process also localizes the oxygen atoms at interstitials. The induced oxygen interstitials form separate band defects in the band gap region, causing the reduction in E_g value with increasing annealing temperature [24]. The variation of direct band gap with annealing temperature was presented in Table 2 along with the comparisons

with the published values of energy band gap [24]. The highest optical band gap was obtained from the sample annealed at 473 K while the lowest energy band gap was from the sample annealed at 673 K with 3.39 *eV* and 2.85 *eV* respectively.
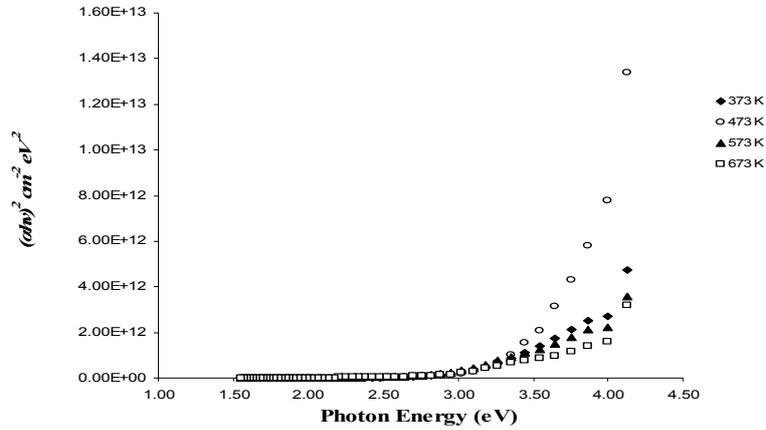
Figure 4: Plot of $(\alpha h v)^2$ vs. photon energy for SnO_2 films annealed at different temperature.

Table 2: Comparison of energy bad gap obtained with other researcher on tin oxide thin film at various annealing temperature.

	Method	Annealing Temperature (K)				
		373	473	573	672	673
Energy Gap (*eV*) (In present study)	RF Sputtering	3.00	3.39	2.95	-	2.85
Energy Gap (*eV*) [24]	Chemical Bath Deposition	3.20	2.60	2.40	1.60	-
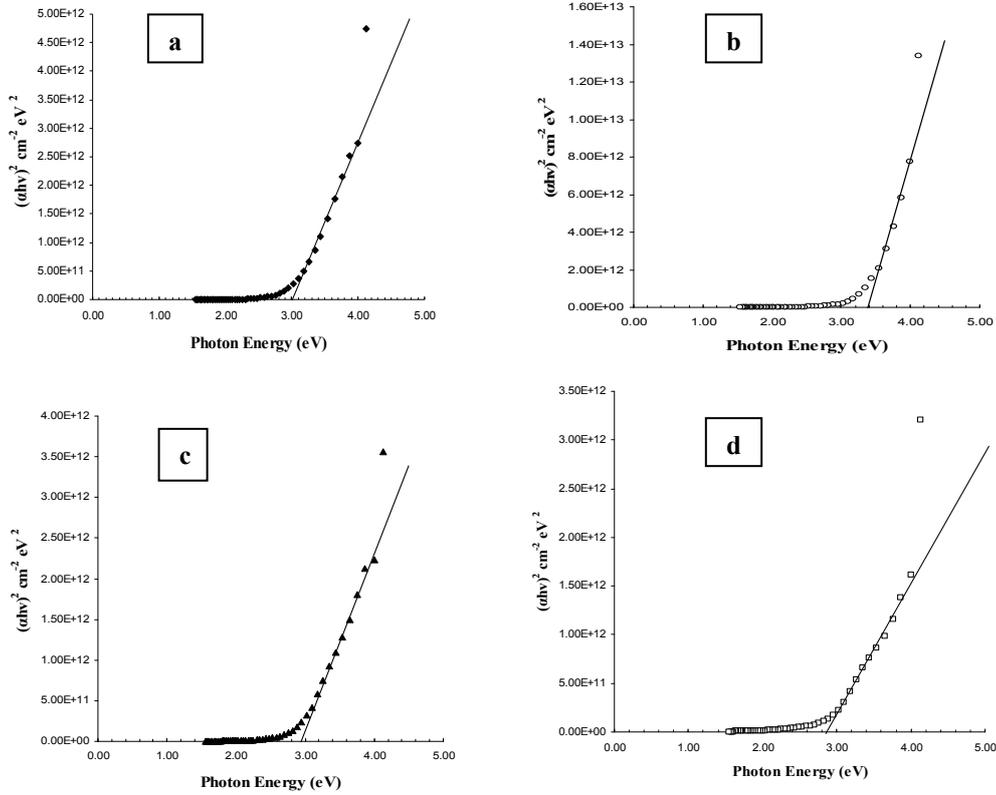
Figure 5: Graph of extrapolation on $(\alpha h v)^2 = 0$ at photon energy for SnO_2 film at (a) 373 K, (b) 473 K, (c) 573 K and (d) 673 K

4. CONCLUSIONS

Tin Oxide (SnO_2) thin films have been successfully deposited using radio frequency sputtering and the four optical parameters of films at different annealing temperature were successfully measured. All samples exhibit high transmittance more than 70% in the visible light spectrum.. Refractive index were in the range of 2.33 – 2.80 at $\lambda =$ 550 nm and the absorption coefficients were in the range of $10^4 – 10^5 cm^{-1}$. Energy gap of SnO_2 was found to be decreased with increasing in annealing temperature with the photon transition was allowed direct transition.

REFERENCES

[1]   J.C. Manifacier, M. De Murcia, J.P. Fillard, E. Vicario. (1977). Optical and electrical properties of SnO_2 thin films in relation to their stoichiometric deviation and their crystalline structure. *Thin Solid Films*.41: 127-144.

[2]   H.L. Hartnagel.(1995). Semiconducting Transparent Thin Films, 1a ed. Institute of Physics Publishing, Philadelphia.

[3]   S. Geetha, R. Rup, A. Mansingh. (1991). Band-gap narrowing and band structure in degenerate tin oxide (SnO_2) films. *Journals of Physics Review B*.44: p.5672–5680.

[4]   Debajyoti Das & Ratnabali Banerjee. (1987). Properties of tin oxide films prepared by reactive electron beam evaporation. *Thin Solid Films*.:149(3): 291-301.

[5]   K.S, Shamala, L.C.S, Murthy & K. Narasimha Rao. (2004). Studies on tin oxide films prepared by electron beam evaporation and spray pyrolysis methods. Bull. Mater. Sci., 27(3). pp. 295–301.

[6]   R.Dolbec, M.A.El Khakani, A.M.Serventi, M.T rudeau, R.G.Saint-Jacques. (2002). Microstructure and physical properties of nanostructured tin oxide thin films grown by means of pulsed laser deposition. *Thin Solid Films*. 419:p. 230–236.

[7]   Saad Hamzaoui & Mohamed Adnane. (2000). Effects of temperature and r.f. power sputtering on electrical and optical properties of SnO2. *Applied Energy* 65:p.19-28.

[8]   Sung Uk Lee, Jin-Hyo Boo & Byungyou Hong. (2011). Structural, electrical and optical properties of SnO_2 : Sb films prepared on flexible substrate at room temperature. *Japanese Journal of Applied Physics*.50

[9]   S. Saipriya, M. Sultan, R. Singh. (2011). Effect of environment and heat treatment on the optical properties of RF-sputtered SnO_2 thin films. *Physica B*: 406. P.812-817.

[10]   Abdul Faheem Khan, M. Mehmood, A.M. Rana, M.T. Bhatti. (2009). Effect of annealing on electrical resistivity of rf-magnetron sputtered nanostructured SnO_2 thin films. *Applied Surface Science*. 255 : 8562–8565.

[11]   C.Kilic & A.Zunger. (2002). Origins of coexistence of conductivity and transparency in SnO_2*Physics Review Letters:* 88. 095501.

[12]   M.O, Nwodo, S.C, Ezugwu, F.I, Ezema, P.U, Asogwa & R.U, Osuji. (2010). Chemical Bath deposition and characterization of PVP cappetin oxide tin films. *Journal of Optoelectronics and Biomedical Materials Vol.2 Issue 4, October-December 2010,* p. 267 – 272.

[13]   H.U. Igwe, O.E. Ekpe and E.I.Ugwu (2010). Effects of thermal annealing on optical properties of titanium oxide thin films prepared by chemical bath deposition techniques. *Research Journal of Applied Science,Engineering and Technology* 2(5):447-451,2010.

[14]   H. Lin, S. Kumon, H. Kozuka and T. Yoko. (1998)**.** Electrical properties of sol–gel-derived transparent titania films doped with ruthenium and tantalum. *Thin Solid Films*: 315 (1-2).p:266-272.

[15]   D. E. Morton. (2001). Characterizing Optical Thin Films (I). *Vacuum Technology and Coating* :2, No. 9. p. 24-31.

[16]   Raul J. Martín-Palma, J. M. Martínez-Duart, and Angus Macleod. (2000). Determination of the Optical Constants of a Semiconductor Thin Film Employing the Matrix Method. *IEEE Transaction on Education Vol 43,No.1*

[17]   Chopra, K.L., R.C. Kainthla, D.K. Pnadya. (1982). *Physics of Thin Films*. Academic Press: New York. p 169-235

[18]   F, Abeles. (1972). Optical Properties of Solid. North-Holland Publishing, Amsterdam.

[19]   Bardeen, J., Blatt, F.J. & Hall, L.H. (1965). Indirect transition from the valence to the conduction bands. Proceeding of Conference on Photoconductivity: 149-154.

[20]   J.C Tauc. (1972). In 'Optical Properties of Solid.' in (F.Abeles, ed). North-Holland Publishing, Amsterdam. p 279.

[21]   J.I Pankove. (1971). Optical Processes in Semiconductor. Dover Publlication, Inc. New York.Chapter 3,p.34.

[22]   Shanthi, E., Dutta, V., Banerjee, A., Chopra, K. L. (1980). Electrical and optical properties of undoped and antimony-doped tin oxide films. *Journal of Applied Physics*. 51:p. 6243-6251.

[23]   H H Afify, R S Momtaz, W A Badawy, S A Nasser. (1991). Some physical properties of fluorine-doped SnO_2 films prepared by spray pyrolysis. *Journal of Materials Science Materials in Electronics* :2(1).p: 40-45.

[24]   H.U. Igwe and E.I. Ugwu. (2010). Optical Characteristics of Nanocrystaline Thermal 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.

Journal of Science and Technology