The Influence of Annealing Temperature on Optical Properties of Tin Oxide (SnO₂) Thin Films Prepared by Thermal Evaporation Process

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Abstract: The research paper reveals study of influence of annealing temperature on optical properties of Tin Oxide (SnO_2) thin films prepared by Thermal Evaporation process. Tin Oxide thin films were synthesized on glass substrate (corning 7059) by Thermal Evaporation unit (model 12A 4D) and annealed at different temperatures $(100^{\circ}c, 200^{\circ}c, 300^{\circ}c & 400^{\circ}c)$ for different durations (1hr, 2hr, 3hr). Optical characteristics were analyzed from the transmission spectrum data which was obtained from UV/VIS spectrophotometer (model ELICO-159). From the study of optical properties it was observed that all the samples exhibited maximum transmittance above 70%, average transmittance was maximum at 100°c for each annealing time. Refractive index of the films was varied with respect to annealing time & temperature, it was maximum 2.26 at 200°c annealed for 1 hr and minimum with value 1.93 at 100°c for 3hr annealing. The energy gap was calculated as maximum at 300°c temperature for all annealing durations. The optical absorption coefficient α was found in the order of 10^4 cm^{-1} to 10^5 cm^{-1} .

Keywords: Annealing temperature, transmittance, refractive index, energy gap

1. Introduction

Tin Oxide (SnO₂) is also known as Stannic Oxide which is an inorganic substance and generally an n-type semiconductor. It has energy band gap of 3.6 eV which is generally high. In visible spectrum the film is more transparent due to high band gap. These properties make tin oxide suitable for many applications, such as in Gas sensors [1-3], transistors [4], photo voltaic cells [5], transparent conductive electrode for solar cells [6], Protective and wear-resistant coating on glass containers [7], Photochemical and photoconductive devices in liquid crystal display [8], etc. The properties of SnO₂ that influence its potential applications depend on the different phases of its fabrication history. Tin oxide thin films can be synthesized by various methods, such as R.F. Magnetron Cosputtering [9], Vapor deposition technique [10], Chemical Vapor Deposition [11-12], Thermal Evaporation [13 -14], Sol-Gel [15-17], Spray Pyrolysis [18-20], ultrasonic spray pyrolysis [21], Laser Pulse Evaporation [22-23], etc. Thermal evaporation has advantages for synthesis of non doped thin films as concern for uniform deposition and cost effect.

2. Experimental Details

In this present paperwork, we prepared tin oxide thin films on coring 7059 glass substrates by thermal evaporation process and studied the effect of annealing temperature and annealing time on optical properties of tin oxide thin films such as refractive index, absorption $coefficient(\alpha)$ and transmittance and energy band gap.

3. Fabrication of Thin Film

In thermal evaporation method thin films were prepared on glass substrates (corning7059, 7.6cm/2.6cm/0.1cm) before deposition, glass plates were cleaned thoroughly with cleaning liquid soap and then with acetone using ultrasonic

cleaner which can remove organic particles on the surface of the glass plate. Finally washed with distilled water and dried. The above cleaned substrates were placed inside the vacuum chamber of Thermal Evaporation unit (model 12A 4D). The pressure of the chamber was maintained at 2.5×10^{-5} torr and rate of deposition fixed at 6-10 A⁰/sec at substrate temperature 35-40°C. During the process the target and source was maintained at 10 cm apart.

4. Annealing

After successful completion of deposition, the substrates were taken out from vacuum chamber and placed in an oven. Here the samples were annealed at 100°C temperature for 1hr, 2hr and 3hr. By following the above process thin films were prepared and annealed at different temperatures 200°C, 300°C & 400°C for 1hr, 2hr & 3hr time durations. Annealed sample thin films cooled down to room temperature. These samples are studied for optical properties.

5. Results and Analysis

5.1 Optical characterization

Optical properties of tin oxide thin films were analyzed from the transmission % vs. wavelength graph which was plotted from the data carried out by the equipment ELICO UV\VIS spectrophotometer (model SL-159) in the range 300nm to 1100nm.Refractive index [24] and thickness of the film [25] were measured from the following expressions.

$$\mathbf{n} = \left[\left\{ N + \left(N^2 - \mu^2 \right)^{\frac{1}{2}} \right\}^{\frac{1}{2}} \right]^{-1}$$
 (1)

Where

N=
$$2\mu \frac{(T_u - T_l)}{T_u T_l} + \frac{\mu^2 + 1}{2}$$
 ------(2)

Where n is the refractive index of thin film μ the refractive index of the substrate, T_u and T_l the transmission maximum at upper envelop and transmission minimum at lower envelop for a particular wavelength λ .

3.1 Refractive Index

Refractive index of tin oxide thin films was increased by increasing annealing temperature and maximum at 200° c for different annealing time durations as 1, 2 & 3 hrs. Refractive index was maximum 2.26 at 200° c annealed for 1 hr and minimum with value 1.93 at 100° c for 3hr annealing durations.



3.2 Transmittance

By using the transmission spectra data from ELICO UV/VIS spectrophotometer (model SL-159), we noticed that in all the concerned annealing cases tin oxide thin films exhibited maximum transmittance above 71% and maximum average T% was at 100°c for three annealing time periods 1hr, 2hr and 3hr with values 67.7%, 58.9% and 63.2% respectively when compared with other annealing conditions.

 Table 1: Average transmission % for different annealing temperatures & time

S. No	Annealing	Average T %
1	No annealing	67.83
2	1-hr at 100°c	67.71
3	2-hr at 100°c	58.99
4	3-hr at 100°c	63.23
5	1-hr at 200°c	50.24
6	2-hr at 200°c	54.21
7	3-hr at 200°c	55.37
8	1-hr at 300°c	62.94
9	2-hr at 300°c	52.03
10	3-hr at 300°c	52.02
11	1-hr at 400°c	55.81
12	2-hr at 400°c	49.08
13	3-hr at 400°c	52.83

We observed the films were very transparent which may be attributed by the formation of the Fermi level in the conduction band. 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



T% vs wavelength







Figure 5: Transmission vs. wavelength graph for annealing at 400°c

3.3 Thickness of the film

Thickness of the film can also calculate from transmission spectra data. Thickness of the film d is given by,

$$\mathbf{d} = \left| \frac{\lambda_1 \lambda_2}{4 \left(n_1 \lambda_2 - n_2 \lambda_1 \right)} \right| \quad (3)$$

Where n_1 and n_2 be the refractive index of thin film at maxima (for wavelength λ_1) and corresponding minima (for wavelength λ_2). Here λ_1 and λ_2 are taken from the minima and subsequent maxima.



Figure 6: Wavelength vs transmission % for 3 hr annealing at 200°c

From above graph T_u and T_l the transmission maximum at upper envelop and transmission minimum at lower envelop for a particular wavelength λ can be noticed. By substituting these valves in equation (3) we can get the thickness of the film.

3.4 Absorption coefficient α_a

According to Lambert-Beer-Bouguer Law

$$\mathbf{I} = \mathbf{I}_0 \ e^{-\alpha_a d}$$

Where I_0 is the intensity of incident light on the sample with thickness d and I be the intensity of transmitted light. f the

light with intensity I. α_a is the absorption co-efficient. The above equation can be simplified and the absorption coefficient can be obtained from the measured transmission spectra, T according to the following formula [26],

$$\alpha_a = \frac{1}{d} \ln \left(\frac{1}{T} \right)$$
(4)

By substituting the value of thickness of the film and optical transmission, absorption coefficient was calculated with equation (4) for the prepared thin films. For different annealing conditions absorption coefficient α_a values were tabled below.

Table 2: A	Absorption	coefficient α_a	for	different	annealing
		conditions			

S no	Annealing	Absorption coefficient α_a cm ⁻¹
1	No annealing	124660
2	1-hr at 100°c	138437
3	2-hr at 100°c	149651
4	3-hr at 100°c	130665
5	1-hr at 200°c	116266
6	2-hr at 200°c	65364
7.	3-hr at 200°c	59876
8	1-hr at 300°c	147314
9	2-hr at 300°c	58638
10	3-hr at 300°c	122033
11	1-hr at 400°c	247245
12	2-hr at 400°c	119388
13	3-hr at 400°c	190508

From the above data it was observed that the absorption coefficient α_a varying between 10^4 cm⁻¹ to 10^5 cm⁻¹.

3.5 Estimation of band gap energy

The excitation of electron from valence band to conduction band by absorption of photon energy can occur in two ways, either in direct or indirect transitions. The energy band gap of the film can roughly determine by the transmittance spectra. The energy band gap was calculated from the graph $(\alpha h\nu)^2 vs. (h\nu)$. It was observed that band gap of the tin oxide thin films maximum at 300°c for all durations of annealing.



Figure 7: Photon energy (hv) vs. $(\alpha hv)^2 \text{ cm}^2 \text{ eV}^2$ for SnO₂ thin film without annealing.

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3.6

3.5

3.4

3.3

3.2

vithout annealing

0







Figure 9: Photon energy (hv) vs. $(\alpha hv)^2$ cm² ev² for SnO₂ thin film at 300°C for 2 hr annealing.



Figure 10: Photon energy (hv) vs. $(\alpha hv)^2 \text{ cm}^2 \text{ eV}^2$ for SnO₂ thin film at 300°C for 3 hr annealing.





200

annealing temp (°c)

300

400

100



S. No.	Annealing	Energy gap (ev)
1	No annealing	3.4597
2	1-hr at 100°c	3.7375
3	2-hr at 100°c	3.2403
4	3-hr at 100°c	3.4233
5	1-hr at 200°c	3.3770
6	2-hr at 200°c	3.6927
7	3-hr at 200°c	3.7956
8	1-hr at 300°c	3.8703
9	2-hr at 300°c	3.7845
10	3-hr at 300°c	3.9509
11	1-hr at 400°c	3.4353
12	2-hr at 400°c	3.3830
13	3-hr at 400°c	3.3315

From the above it was noticed that energy gap of the tin oxide thin films by increasing annealing temperature energy gap also increased and it was maximum at 300°c for three different durations of time periods.

Conclusion 6.

Effect of annealing temperature on optical properties of Tin oxide thin films which were prepared by the Thermal evaporation process has studied. The optical properties were analyzed under different annealing temperatures and time durations by using transmission spectrum data obtained by spectrophotometer (ELICO model SL-159) from this study of optical properties it was observed that all the samples exhibited maximum transmittance above 70%, average transmittance was maximum at 373 K for each annealing time. Refractive index of the films was varied with respect to annealing time & temperature, it was maximum 2.26 at 473 k annealed for 1 hr and minimum with value 1.93 at 373 K for 3hr annealing. The energy gap was calculated as maximum at 573K temperature for all annealing durations. The optical

absorption coefficient α was found varying in the order of 10^4 to 10^5 cm⁻¹.

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References

- [1] A. Sutti, C. Baratto, G. Calestani, C. Dionigi, M. Ferroni, G. Faglia, G. Sberveglieri, "Inverse opal gas Sensors: Zn(II)-doped tin dioxide system for low temperature detection of pollutant gases," Sens. Actuators B, 130, 567-573, (2008).
- [2] L. A. Patil, D.R. Patil, "Hetero contact type Cu Omodified SnO2 sensor for the detection of a pp m level H2S gas at room temperature," Sens. Actuators B, 120, 316-323, (2006).
- [3] H.J.Lim, D.Y. Lee, Y.J. Oh, "Gas sensing properties of ZnO thin films prepared by micro contact printing, "Sens. Actuators A, 125, 405-410, (2006).
- [4] M.S. Arnold, P. Avouris, Z.W.Pan, and ZL.Wang, "Field Effect transistors Based on single semiconducting oxide nanobelts", Journal of Physical Chemistry B, 107, pp. 659- 663, 2003.
- [5] Cachet, J.Bruneaux, G.Folcher, C. Levy- Clement, C.Vard and M. Neumann-Spallart, "n-Si/SnO2 junctions based on macro porous silicon for photo conversion," Solar Energy mater and Solar Cells, 46, 10-1141, (1997).
- [6] A.M. Gheidari, E.A. Soleimani, M. Mansorhoseini, S. Mohajerzadeh, N. Madani, W. Shams-Kolahi, "Structural properties of indium tin oxide thin films prepared for application in solar cells", Mater Res. Bulletin, 40, pp.1303-1307, 2005.
- [7] M.Nakagawa, T.Amano, and S.Yokokura, "Development of lightweight returnable bottles", J. Non-Cryst. Solids, 218, pp.100 -104, 1997. U.
- [8] U.Betz, M.K.Olsson, J. Marthy, M.F.Escola, and F.Atamny, "Thin films engineering of indium tin oxide: Large area flat panel displays application", Surf. Coat. Technol., 200, pp.5751-5759, 2006.
- [9] K.S. Yoo, S.H. Park and J.H. Karg," Nano-grained thinfilm indium tin oxide gas sensors for H2 detection," Sensors and Actuators B, 108, 159-164, (2005). P.M. Gorley, V.V. Khomyak, S.V. Bilichuk, I.G. Orletsky, P.P. Hovly, V.O. Grechko, Mater. Sci. Eng. B 118, 160(2005).
- [10] J. Joseph, V. Mathew, and K. E. Abraham, "Studies on Cu, Fe, and Mn Doped SnO2 Semi-Conducting Transparent Films Prepared by a Vapour Deposition Technique" Chinese Journal of Physics, 45, No.1, 84-97 (2007).

- [11] P.M. Gorley, V.V. Khomyak , S.V. Bilichuk, I.G. Orletsky, P.P. Hovly and V.O. Grechko, SnO2 films: formation, electrical and optical properties," Mater. Sci. and Engg. B, 118, 160, (2005).
- [12] R. Mamazza Jr., D.L. Morel and C.S. Ferekider, "Transparent conducting oxide thin films of Cd2SnO4 prepared by RF magnetron co-sputtering of the constituent binary oxides", Thin Solid Films, 484, 26-33, (2005).
- [13] E. Comini, G.Faglia, G. Sberveglieri, Z. Pon and Z. L. Wang, "Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts", Appl. Physics lett., 81, 1869-1871, (2002).
- [14] V.S. Vaishnav, P.D. Patel and N.G. Patel, "Indium Tin Oxide thin film gas sensors for detection of ethanol vapours," Thin solid films, 490, 94-100, (2005).
- [15] O. Culha, M.F. Ebeoglugil, I. Birlik, E. Celik, and M. Toparli, "Synthesis and characterization of semiconductor tin oxide thin films on glass substrate by sol-gel technique," J.Sol-Gel Sci. Technol, 51, 32-41 (2009).
- [16] J.P. Chatelon, C. Tenier, E. Bemstein, R. Berjoan and J.A. Roger, "technique," Thin Solid Films, 247, 162-168, (1994)..
- [17] B. Oreal, U. Lavrencic-Stangar, Cmjak-Olel, P. Bukovea and M. Kosec, "Structural and FTIR spectroscopic studies of gel-xerogel-oxide transitions of SnO2 and SnO2: Sb powders and dip-coated films prepared via inorganic sol-gel route", J. Non-Cryst. Solids, 167, 272-288, (1994). Oreal, U. Lavrencic-Stangar, Cmjak-Olel, P. Bukovea, M. Kosec, J. Non-Cryst. Solids 167, 272 (1994).
- [18] A.A.Yadav, E.U. Masumdar, A.V. Moholkar, K. Y. Rajpure, C.H. Bhosale, "Gas Sensing of Fluorine Doped Tin Oxide Thin Films Prepared by Spray Pyrolysis," Sensors & Transducers Journal, 92(5) 55-60, (2008). S.K.Tripathy, P.V.Rajeswari, and B.P.Hota, "Study of Optical Characteristics of Tin oxide thin film prepared by Sol-Gel Method" Bull. Mater. Sci., 36, pp.1231-1237, 2013.
- [19] D.W. Lane, J.A. Coath, K.D. Rogers, B.J. Hunnikin and H.S. Beldon," Optical properties and structure of thermally evaporated tin oxide films", Thin Solid Films, 221, 262-266, (1992).
- [20] F. Paraguay, D.W. Estrada, L.D.R. Acosta, N.E. Andradeb and M. Miki-Yoshida, "Growth, structure and optical characterization of high quality ZnO thin films obtained by spray pyrolysis", Thin Solid Films, 350 192-202, (1999).
- [21] G. Blandenet, M. Court and Y. Lagarde, "Thin layers deposited by the pyrosol process", Thin Solid Films, 77, 81-90, (1981).
- [22] H.T.Yang and J.T.Cheung, "Pulsed laser evaporated SnO2 films," J.Crystal Growth, 56, 429-432, (1982).
- [23] Hui Fang, T.M. Miller, Robert H, M. Magruder and R.A. Weller, "The effect of strain on the resistivity of indium tin oxide films prepared by pulsed laser deposition, J.Appl.Phys" 91, 6194-6196, (2002).

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- [24] J.C. Manifacier, J. Gasiot, J.P. Fillard, " A simple method for the determination of the optical constants n,k and the thickness of a weakly absorbing thin film," Journal of Physics E: Sci. Instrum., 9, 1002-1004, (1976).
- [25] S.K.Tripathy, P.V.Rajeswari, and B.P.Hota, "Study of Optical Characteristics of Tin oxide thin film prepared by Sol-Gel Method" Bull. Mater. Sci., 36, pp.1231-1237, 2013
- [26] R.D. Tarey and T.A. Raju, "A method for the deposition of transparent conducting thin films of Tin Oxide," Thin Solid Films, 128, 181-189, (1985).

