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Preparation and Characterization of Nanostructured ITO Thin Films by Spray Pyrolysis Technique: Dependence on Annealing Temperature

Salam Amir Yousif

Department of Physics, College of Education, Mustansiriyah University, Baghdad – Iraq

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ABSTRACT

Transparent conducting oxides (TCOs) like Indium tin oxide (ITO) have wide attention from all scientists which have low resistance and high visible light transmittance, used as transparent electrodes in many optoelectronic devices such as liquid crystal displays, touch screens, light emitting diodes, and solar cells. In this research, the relationship between the crystallization, optical transmittance, and surface roughness of nanostructured ITO thin films and the change in annealing temperature was investigated. To enhance the efficiency of this material in optoelectronic applications, both the optical transmittance in the visible region and the crystallite size must be increased. These results can be obtained by the heat treatment of the films. Nanostructured ITO thin layer films have been successfully prepared at a substrate temperature equal to $(350)°\mathrm{C}$ *by chemical spray pyrolysis (CSP) technique. The physical characterizations of nanostructured ITO thin layer films were investigated at different annealing temperatures* $(400, 450\ and\ 500)°\mathrm{C}$. *The presence of diffraction peaks indicates that the as-deposited and post annealed films are polycrystalline cubic structure and the peak (400) is a preferred growth orientation. For all samples the value of intensity of diffraction peaks increases with increasing substrate temperature. The crystallite size of nanostructured ITO thin films is strongly related to the annealing temperature. The crystallite size estimated from XRD was found to rise with rising annealing temperature. The surface roughness of nanostructured ITO thin layer films increases with rising annealing temperature. High values of transmittance have been measured in the visible region 550 nm equal to (70, 82, 84 and 88)% corresponding to annealing temperature* $(350, 400, 450\ and\ 500)°\mathrm{C}$ *respectively.*

Keywords: Thin films, structural properties, optical properties, spray pyrolysis, nanostructure, annealing temperature.

1. INTRODUCTION

In the last few decades, more of transparent conducting oxides (TCO) like indium tin oxide (ITO) have been widely utilized in various optoelectronic devices because it has high optical transmittance in the visible wavelength area $(80-95\,\%)$, low value of resistivity $(10^{-3}-10^{-4}\ \Omega.cm)$, good mechanical strength and a wide bandgap $(3.5-4.2\ eV)$ degenerate n-type semiconductor [1]. Examples of these devices are solar energy cells [2], flat screen displays [3], photo diodes [4] and antireflection coatings [5]. Previously, many techniques have been used to synthesis nanostructured ITO thin layer films such as; ion beam assisted deposition (ISD) [6], pulsed laser ablation (PLA) [7], radio frequency magnetron sputtering [8] and chemical spray pyrolysis (CSP) [9]. From all of methods utilized, the results show that the chemical spray pyrolysis (CSP) is the most credible, simplest and cheapest method of prepare high quality of nanostructured ITO thin layer films [10, 11, 12]. The effect of post annealing treatment on the structural, optical and electrical properties of ITO thin films prepared on glass substrate using RF

* salammomica@uomustansiriyah.edu.iq

sputtering technique has been studied by Ahmed et al. [13]. These properties were investigated at $250, 350, 450$, and $500°C$. They had showed that the grain size, transmittance and morphology of ITO thin films increase with increasing annealing temperature and the highest quantity of grain size, transmittance and electrical conductivity has been obtained at 450°C. Wang et al. [14] deposited ITO thin films on a substrate of glass using electron-beam evaporating method. The influence of post preparation annealing treatment and the rate of deposition of ITO thin films was investigated for optical characterizations. They concluded that the optical transmittance of ITO thin films increases greatly with increasing annealing treatment. Hamzah et al. [15] had prepared ITO thin films on a glass substrate using RF magnetron sputtering. The influence of post deposition annealing temperature on the structural, optical and electrical properties of ITO thin films has been investigated in the range of 300°C to 600°C in oxygen environment. They showed that the crystallinity (grain size), optical transmittance and electrical conductivity of ITO thin films improved and enhanced by increasing the annealing temperature.

The aim of this work is to study the effect of annealing temperature on the physical properties like structural, morphological and optical properties of nanostructured ITO thin layer films produced by simple spray pyrolysis technique, to improve the performance of optoelectronics applications.

2. EXPERIMENTAL PART

A homemade chemical spray pyrolysis technique (as shown in Figure 1) was utilized to prepare nanostructure ITO thin layer films of (5 wt%) tin doping at a substrate temperature of (350)°C. The optimum percentage of (5 wt%) tin doping has been studied and published previously [9]. Indium Chloride ($InCl_3$), Stannic Chloride ($SnCl_4.5H_2O$) and distilled water were used to prepare the spray solution and two drops of hydrochloric acid were added to rise the solubility of the compounds. The deposition conditions of nanostructured ITO thin films deposited on glass substrate at (350)°C by spray pyrolysis (SP) technique are shown in the Table 1.

Table 1 Deposition conditions of nanostructured ITO thin films

Gas pressure	(3 bar)
Carrier gas	Nitrogen (N_2), under ambient atmosphere
Spraying rate	($5-6$ ml/min)
Molarity of solution	(5% $mole/litre$)
The nozzle distance from the substrate	(40 cm)
Substrate temperature	(350)°C

The molarities of the solution were calculated using Equation (1) as follows:

$$M = \frac{W_t}{M_{wt} \times \frac{V}{1000}} \qquad (1)$$

where; M is the concentration of molarities, M_{wt} is the molecular weight of ($SnCl_4.5H_2O$) or ($InCl_3$), V is the volume of distilled water (100 ml) and W_t is the weight of ($SnCl_4.5H_2O$) or ($InCl_3$).

The nanostructured ITO thin films were annealed under ambient atmosphere for (1 hour) at temperatures equal to $(400, 450\ and\ 500)$°C. The crystal structure of nanostructured ITO thin layer films was examined by SHIMADZU instrument (x-ray diffraction 6000). Shimadzu ultraviolet – visible - 1650 PC spectrophotometer was used to study the optical properties of ITO films in the wavelength range of (300 - 1000) nm.

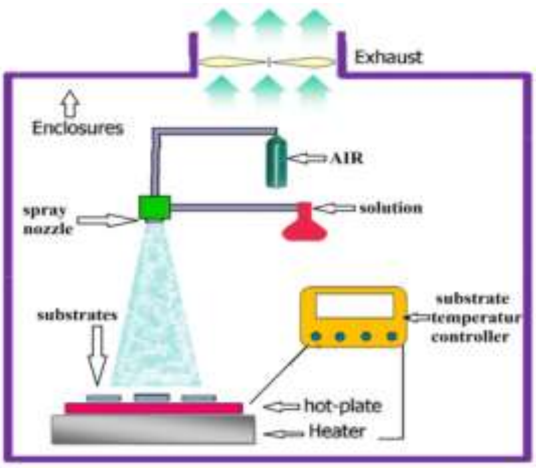

Figure 1. Setup of spray pyrolysis technique.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

The crystal structure of nanostructure ITO thin films was examined by X-ray diffraction analysis. XRD patterns were recorded for different films deposited onto a glass substrate kept at different annealing temperatures in (2θ) range of $(20^0 - 80^0)$. Figure 2 illustrates the XRD patterns of nanostructured ITO thin films deposited at different annealing temperatures and have been indexed with JCPDS (card 06-0416 $In_2O_3, cubic$). The presence of diffraction peaks indicates that the samples have a polycrystalline cubic structure. For all samples, the texture coefficient measurements showed that the peak (400) is a preferred growth orientation and the intensity of diffraction peaks increases with increasing annealing temperature. There are a large number of oxygen (interstitial atoms) in nanostructured ITO samples with a growth direction along (400) plane due to the irregular allocation of the vacancies of oxygen [16].

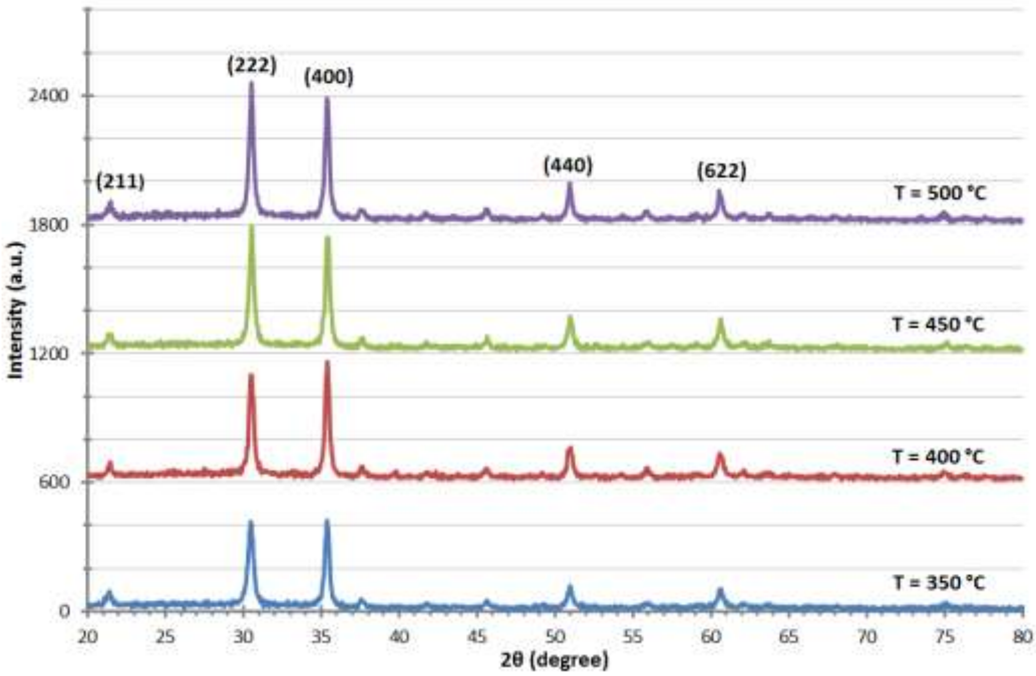

Figure 2. XRD patterns of nanostructured ITO samples at different annealing temperatures**.**

We can calculate the crystallite size (D) of ITO samples by using the following Debye-Scherrer equation [17].

$$Crystallite\ size\ (D) = \frac{0.9 \times wave\ length\ (\lambda)}{FWHM\ (\beta) \times cos\theta} \quad (2)$$

The calculated crystallite size is listed in Table 2. The incident x-ray beam used has a wavelength equal to $\lambda = 1.5406$ Å, β is given in radians and θ represents the Bragg's angle in degrees. Figure 3 shows the crystallite size of nanostructured ITO thin films is strongly dependent on annealing temperature. The crystallite size was found to increase with increasing annealing temperature which is in agreement with the report [13]. The optical bandgap decreases with increasing crystallite size or progressing the crystalline structure of ITO samples. The reduction of optical bandgap with rising annealing processes could be explained by the ability of oxidation, re-arranged and interaction the atoms of the samples with substrate [18].

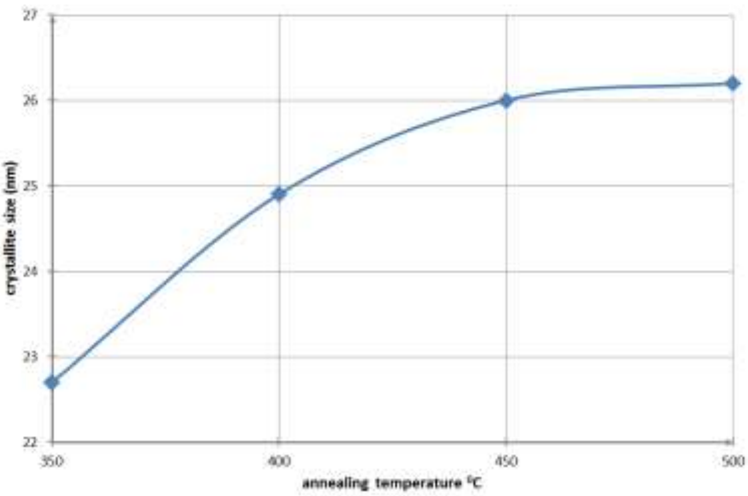

Figure 3. Crystallite size vs annealing temperature**.**

The lattice constant a of cubic structure is given the following relation and listed in Table 2:

$$a = d/\sqrt{h^2 + k^2 + l^2} \quad (3)$$

Here, d is the planes spacing and hkl are miller indices of that plane.

The direction of preferential growth of the samples (Texture coefficient) is given by [19] and listed in Table 2:

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{N_r^{-1}\sum I(hkl)/I_0(hkl)} \quad (4)$$

where $I(hkl)$ is the measured intensity, $I_0(hkl)$ is the standard intensity according to the JCPDS (card 06- 0416 $In_2O_3, cubic$) and N_r is the number of diffraction peaks presented.

We can calculate the dislocation density δ and the strain $\varepsilon_\circ$ by using equations 5 and 6 respectively [20] as listed in Table 2 :

$$\delta = \frac{1}{D^2} \quad (5)$$

$$\varepsilon_\circ = \frac{\beta \, COS\theta}{4} \quad (6)$$

Table 2 Structural properties of ITO thin films

Substrate temperature °C	(hkl)	FWHM (deg)	Crystallite size (nm)	Dislocation Density δ $\times 10^{15}$ line/m^2	Strain $\varepsilon_\circ \times 10^{-3}$	Lattice Constant (Å)	Texture coefficient TC
350	211	0.4100	19.7	2.569	1.75	10.156	**0.8174**
	222	0.4096	20.1	2.471	1.72	10.145	**0.7152**
	400	0.3672	22.7	1.937	1.52	10.140	**2.3841**
	440	0.3880	22.6	1.942	1.52	10.132	**0.5108**
	622	0.4120	22.3	2.003	1.55	10.128	**0.5722**
400	211	0.3600	22.4	1.980	1.54	10.146	**0.5676**
	222	0.3616	22.7	1.926	1.52	10.128	**0.7152**
	400	0.3349	24.9	1.611	1.39	10.129	**2.4083**
	440	0.3564	24.7	1.638	1.40	10.127	**0.5573**
	622	0.3194	28.8	1.203	1.20	10.125	**0.7513**
450	211	0.2711	29.8	1.122	1.16	10.127	**0.5460**
	222	0.3519	23.4	1.824	1.48	10.134	**0.6650**
	400	0.3163	26.0	1.437	1.31	10.137	**2.5482**

	440	0.3885	22.6	1.947	1.52	10.131	**0.5678**
	622	0.3553	25.9	1.489	1.33	10.130	**0.6727**
500	211	0.3307	24.4	1.671	1.41	10.126	**0.5774**
	222	0.3306	24.9	1.610	1.39	10.134	**0.7349**
	400	0.3174	26.2	1.447	1.31	10.137	**2.3519**
	440	0.2584	34	0.861	1.01	10.133	**0.6299**
	622	0.2680	34.3	0.847	1.00	10.132	**0.7055**

3.2 Topography Properties

Three-dimensional Atomic Force Microscopy (AFM) images of nanostructured ITO thin films are shown in Figure 4. It was seen that the root mean square (RMS) values of surface roughness of as-deposited (350)°C and annealed films (400, 450 and 500)°C were (12, 13.3, 14.1, 15.9) nm, respectively. The (RMS) roughness and Grain size of nanostructured ITO thin films estimated from AFM images are shown in Table 3. The surface roughness of nanostructured ITO thin films increases with increasing annealing temperature due to increase of kinetic energy of the atoms causing to rise of mobility which in turn risen the roughness, which is in agreement with the report [21]. The values of grain size estimated from AFM examination confirm the nature of nanostructure films and the values grain size of ITO films increase with rising annealing processes.

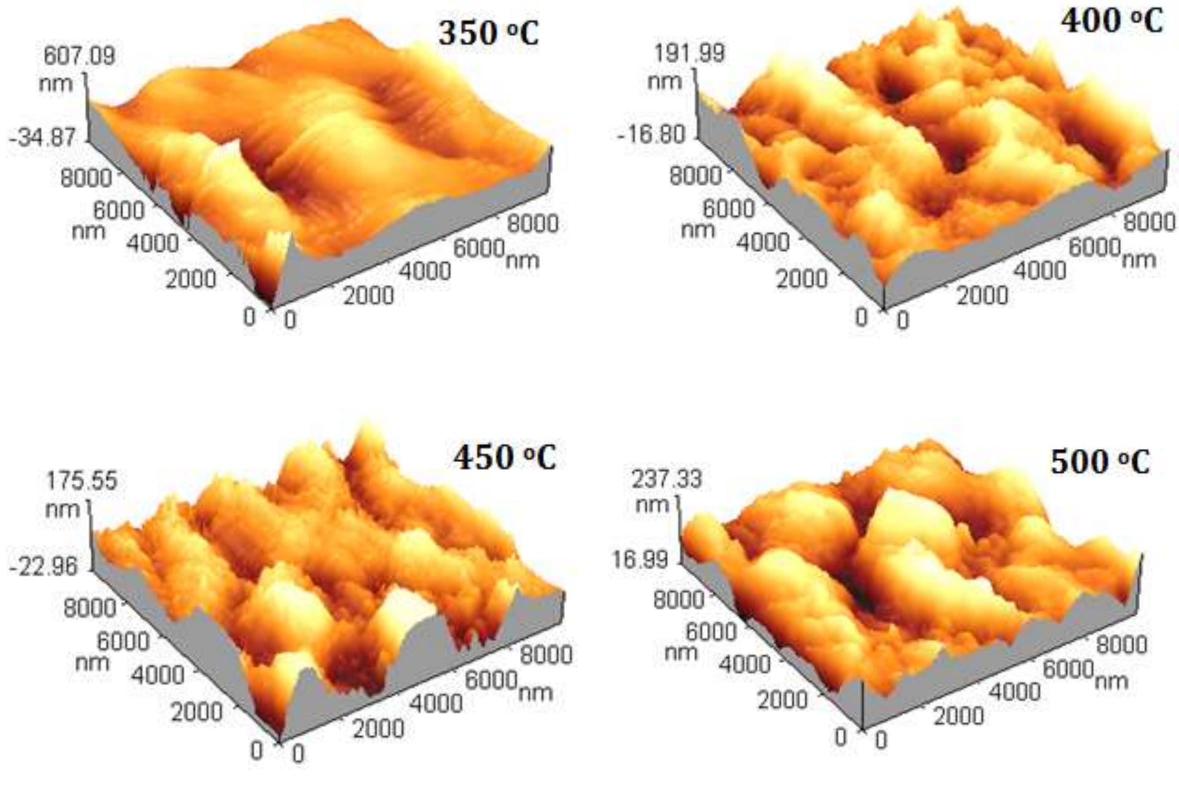

Figure 4. AFM images of ITO samples at different annealing temperatures.

Table 3 RMS roughness and Grain size of ITO thin films

Annealing temperature (°C)	**RMS (nm)**	**Average Grain size (nm)**
as-deposited (350)	12.0	30
400	13.3	41
450	14.1	60
500	15.9	64

3.3 Optical Properties

Figure 5 shows the optical transmittance spectra of nanostructured ITO thin films measured at room temperature in the wavelength range from 300 to 900 nm. The as-deposited and annealed ITO films have sharp absorption edge in the ultraviolet area and highly transparent in the visible area from 450 to 700 nm. The transmittance of ITO films increases with increasing annealing temperature due to improvement in crystalline structure. High values of transmittance have been measured in the visible region 550 nm equal to 70, 82, 84, and 88% corresponding to annealing temperature 350,400,450 and 500$^{\circ}C$, respectively. According to the progression of crystallization of nanostructured ITO thin layer films, the density and the mobility of the carriers improved with rising heat treatment, which in turn, reduce the resistance of the surface. The increase of the density of the carriers leads to decrease in black indium oxide molecules, which in turn leads to the progressing of transmittance in the visible region. The absorbance spectra of nanostructured ITO films are shown in Figure 6. The absorbance of ITO films decreases with rising of annealing temperature.

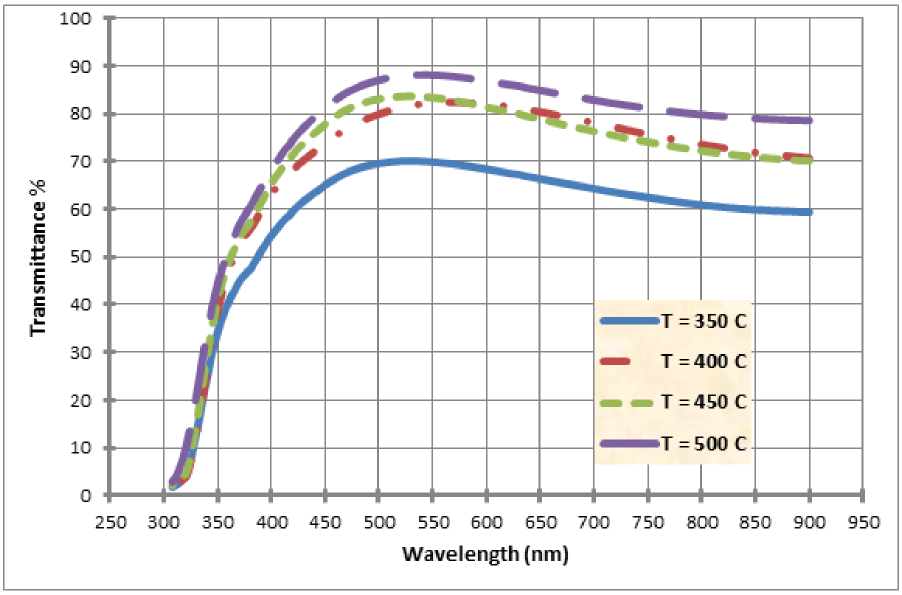

Figure 5. Transmittance spectra of ITO samples at different annealing temperatures.

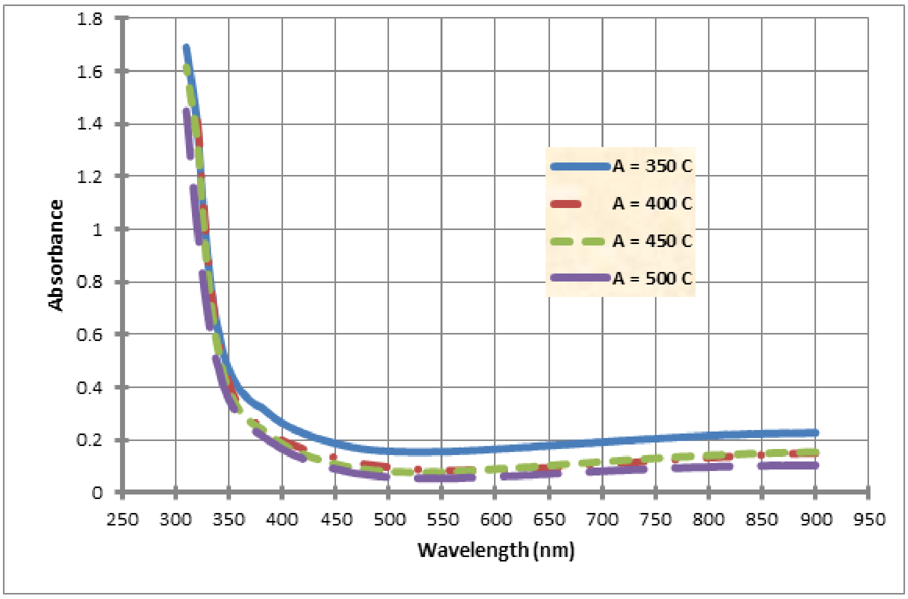

Figure 6. Absorbance spectra of ITO samples at different annealing temperature.

We can calculate the optical bandgap energy of the samples by applying the following relation [22].

$$Ah\gamma = A(h\gamma - E_g)^x \quad (7)$$

The values of direct bandgap were 3.71, 3.7, 3.72, 3.76 eV for the as-deposited and annealed film $350, 400, 450$, and $500°C$, respectively. Figure 7 shows that the bandgap of ITO film rises with rising annealing temperature from 3.71 eV to 3.76 eV, which is in agreement with the report [22]. The change of oxygen sites in the ITO crystal leads to change of energy bandgap. The rise in annealing temperature leads to increase of energy bandgap which is associated with the decrease of oxygen sites in the ITO thin films. The oxygen content in the nanostructured ITO thin films was reduced with increase of annealing temperature due to the evaporation process that took place to the oxygen. The increase of energy bandgap leads the shift of absorption edge to a larger frequency as shown in Figure 5. According to Burstein-Moss effect, the shift of Fermi level to the conduction band leads to the broadening of energy bandgap which in turn, increases the carrier concentration. The increase of crystallinity (grain size) with increasing annealing temperature of nanostructured ITO thin films is associated with the blue shift of the absorption edge, which is in agreement with the report [21].

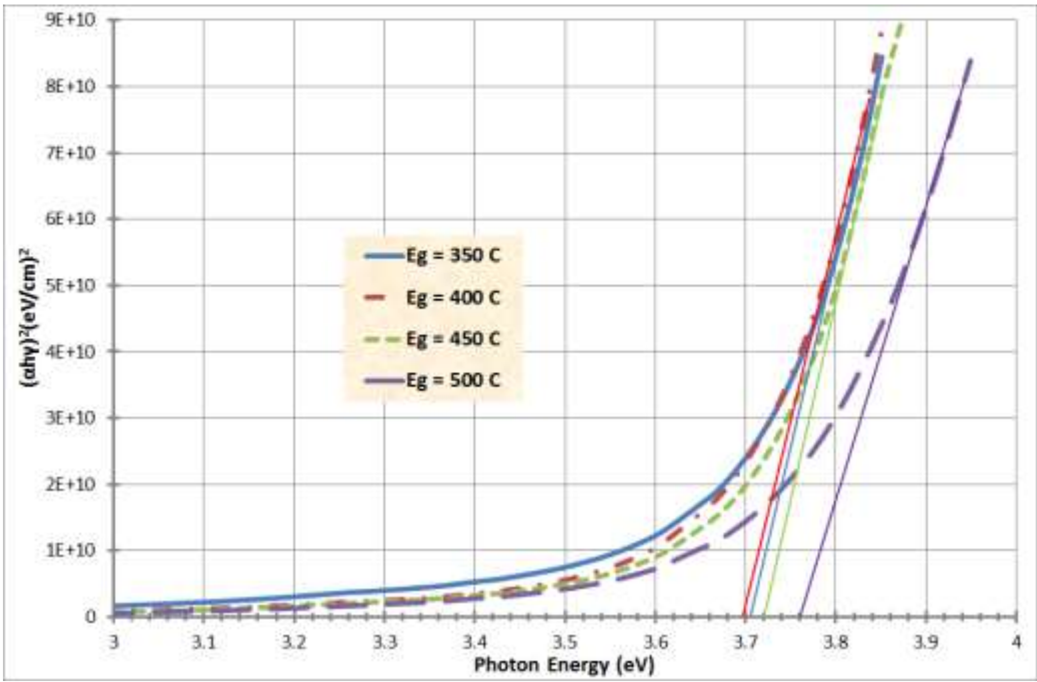

Figure 7. Energy bandgap of ITO samples at different annealing temperature.

4. CONCLUSIONS

Nanostructured (ITO) thin layer films were accurately prepared on glazier slides by CSP method. The dependence of crystallization, optical transmittance and surface roughness of nanostructured ITO thin films on the heat treatment have been proved. The significance of this work when the annealing temperature is risen, is to enhancement the efficiency of ITO thin films in optoelectronic devices when used as transparent conducting electrodes by enlarging both the optical transmittance in the visible region and the grain size which increase the electrical conductivity. The films are nanostructure in nature and the grain size of nanostructured ITO thin films increase with rising annealing temperature. High values of transmittance have been measured in the visible region 550 nm which can be used in many optoelectronics applications like a window in solar cells. Also, the increase of annealing temperature caused the increase of surface roughness, transmittance and the values of energy bandgap of nanostructured ITO thin films.

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