

## The Effect of Annealing Temperature on Structural & Optical Properties of Nanocrystalline SnO<sub>2</sub> Thin Films Prepared by Sol-Gel Technique

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### ABSTRACT:

In this work, studying the structural and optical Nano crystalline SnO<sub>2</sub> thin films grown on cleaned glass substrates by using sol- gel (dip coating) technique. It is worthy to say that the thickness of the deposited film was of the order of (300-400)nm . The films are annealed in air at , 300°C, 400°C and 500°C temperatures for 60 minutes. The films that are analyses by X-ray diffraction (XRD), Scanning electron microscopy (SEM) , atomic force microscopy and optical absorption spectroscopy technique. The size of crystalline was observed, as well as, so as to increase with increasing annealing temperature . XRD analysis reveals that the whole films are polycrystalline with tetragonal structure with preferred orientation of (110),(101),(200) and (211) . The increase of annealing temperature leads to raise the diffraction peaks and decrease of FWHM. The atomic force microscopy (AFM) and Scanning electron microscopy (SEM) results showed that the average grain size was increase with the increase in annealing temperature. Spectra of transmittance and absorbance was recorded at wavelengths range (300-1000)nm .The optical properties showed high transmission at visible regions. The optical band gap energy was found to be (3.5 , 3.75 , 3,87) eV at annealing temperature (300,400,500 )°C respectively.

**Keywords:** SnO<sub>2</sub> thin film, annealing temperature, sol-gel.

### INTRODUCTION

**A** (SnO<sub>2</sub>) is an n-type semiconductor also known by the systematic name tin (IV) <sup>[1]</sup>. Tin oxide (SnO<sub>2</sub>) films that are used in widely manner such as transparent conducting electrodes in many optoelectronic devices such as a flat panel displays<sup>[2]</sup> . Furthermore, SnO<sub>2</sub> has a large band gap of 3.6–4.0eV <sup>[3–5]</sup> as well as great advantages like a low increasing temperature besides high chemical stability compared with other materials. SnO<sub>2</sub> used in a different and various applications including heat mirrors and solar energy conversion devices<sup>[3]</sup>. Thin films of transparent oxide semiconductors such as SnO<sub>2</sub>, SnO<sub>2</sub>:F, SnO<sub>2</sub>:Sb, SnO<sub>2</sub>:In and CdSnO<sub>4</sub> <sup>[4]</sup>. SnO<sub>2</sub> thin films were used as window layer in solar cells, and electrode to collect the charge in CdS/Cu<sub>2</sub>S <sup>[3]</sup>, CdS/CdTe, and other application of SnO<sub>2</sub> were used for gas sensors for CO, H<sub>2</sub>S, H, NO and CH<sub>4</sub> layers that can be deposited using different methods: sputtering <sup>[5]</sup>,

pulsed excimer laser ablation deposition (excimer) [6], chemical vapor deposition (CVD) [7], pyrolysis deposition [8], solvothermal [9] and, more recently by sol-gel process [10]. We have chosen the sol-gel method due to it is easy use and possible to deposit thin and even ultra-thin layers on various substrates of different shapes. The dip-coating technique has been grown during the last decade for the deposition several oxide compounds. So this method offers the following advantages of the possibility of high-purity starting materials additionally to be a low-cost one as well as simple with no vacuum equipment [11,12]. In this work, we study annealing temperature effect on structure and optical properties of SnO<sub>2</sub> thin films deposited by sol-gel(dip coating).

### **Experimental Procedure**

The sol-gel technique is chemical reaction depending on purities of materials and need certain time drying with temperature after the solution become gel. Then different annealing temperatures of the film are main process to get SnO<sub>2</sub> by dip coating technique.

The primary precursors for synthesis of SnO<sub>2</sub> include:

SnCl<sub>2</sub>.2H<sub>2</sub>O (chloride dehydrate (96%), FISON, ENGLAND), C<sub>2</sub>H<sub>5</sub>OH (ethanol (99%), Scharlau, Spain), C<sub>3</sub>H<sub>8</sub>O<sub>3</sub> (glycerin). These chemicals were used without further purifications.

Dissolved (4) g. of (SnCl<sub>2</sub>.H<sub>2</sub>O) in (30) ml of ethanol. The solution was stirred by a magnetic stirring apparatus for 1 hour at a temperature of (75-80) °C. After that the sol was mixed with (2) ml of glycerin as a dispersion stabilizer to obtain the sol-gel for dip coating.

Actually, it was preferred to rely on and using of the films from the solution (sol) so as to applied in using dip-coating technique. The substrates (slides glass with dimension ((25.4x76.2) mm) were cleaned by emerged in ultrasonic bath during 5 minutes and finally rinsed by ethanol. Thus, as all of them were dipped into the sol then they were slowly withdrawn from the bath at a fixed speed that equal to 80 mm/min. Firstly, all films were applied to be dried at low temperature reaches to (100 °C) during 30 minutes after that, the films subject to heated treatment at (300, 400, 500) °C during just one hour.

The crystal structure of SnO<sub>2</sub> films was analyzed by relying on and using x-ray diffraction system (Shimadzu XRD diffraction) with CuK<sub>α</sub> radiation with λ=1.541 Å. The crystalline size was calculated by Scherer equation:-<sup>[13]</sup>

$$D = 0.9\lambda / \beta \cos\theta \quad \dots(1)$$

where λ, β, and θ are represented the X-ray wavelength, full width at half maximum (FWHM) and Bragg angle respectively.

The morphologies were investigated on scanning electron microscope (SEM) (IRFANVIEW Li CENCE, INSPECT S500). Atomic Force microscope (AFM) (Csp M- 5000 instrument, USA, 2008)

The optical transmittance and absorbance measurement were performed with a double beam UV/ VIS Spectrophotometer (UV-1800 SHMADZU) in the wavelengths range of (300-1000) nm.

### **Results and Discussion:-**

fig (1) shows X-ray diffraction patterns of SnO<sub>2</sub> thin films prepared and being annealed at 300, 400 and 500°C. It can be noted that these prepared SnO<sub>2</sub> films are polycrystalline with tetragonal structures, the polycrystalline film with preferred growth direction along (110). Other peaks corresponding to the direction (101) (200) (211) and (220) compatible with the standard JCPDS(41-1445) data. The increase of annealing temperature (Ta) will improve the crystal structure by increasing the intensity of the planes. In such improvement in crystal structure could be in accordance to the increasing in crystallite size as the small crystallites that join each other's in the planes with increasing annealing temperature as shown in Table (1). Thin film which annealing at temperature 500°C shows a strong preferential growth orientation

along (110) plane and the diffraction peaks of the film becoming sharper, in turn, leads to increase in the crystallites, cause the enhancement of crystallinity of the films. The full width at half maxima (FWHM) decrease with increasing annealing temperature. This result is in agreement with the previous results [13,14,15]. The crystalline size was calculated by Scherrer formula was (8, 14, 22.34) nm at (300,400,500) °C respectively, the results is shown in fig (2).

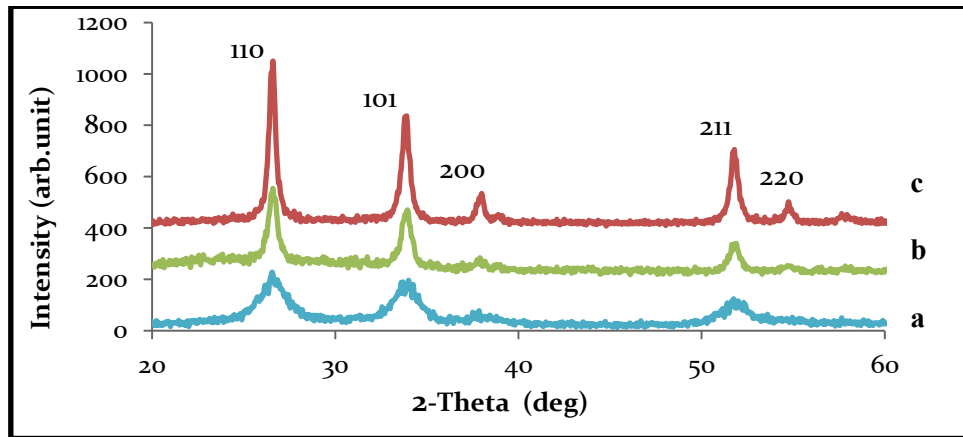


Figure (1) XRD pattern of SnO<sub>2</sub> thin films at different annealing temperatures (a) 300 °C (b) 400 °C (c) 500 °C

Table(1). XRD Measurement of SnO<sub>2</sub> thin films by Sol- gel (dip coating)method

Annealing temperatures (°C)	d <sub>stan</sub> (110)	d <sub>cal</sub> (110)	a (Å)	c (Å)	Crystalline size(nm) D
300	3.347	3.3363	4.738	3.18	8
400	3.347	3.3215	4.78	3.174	14
500	3.347	3.3470	4.763	3.2	22.34

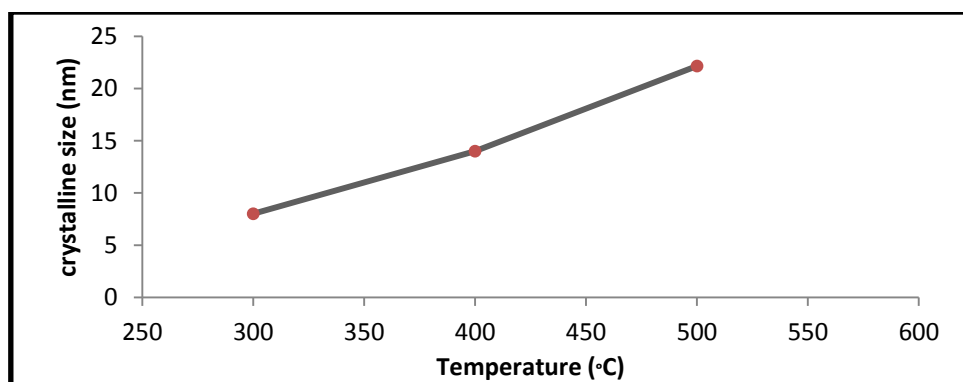
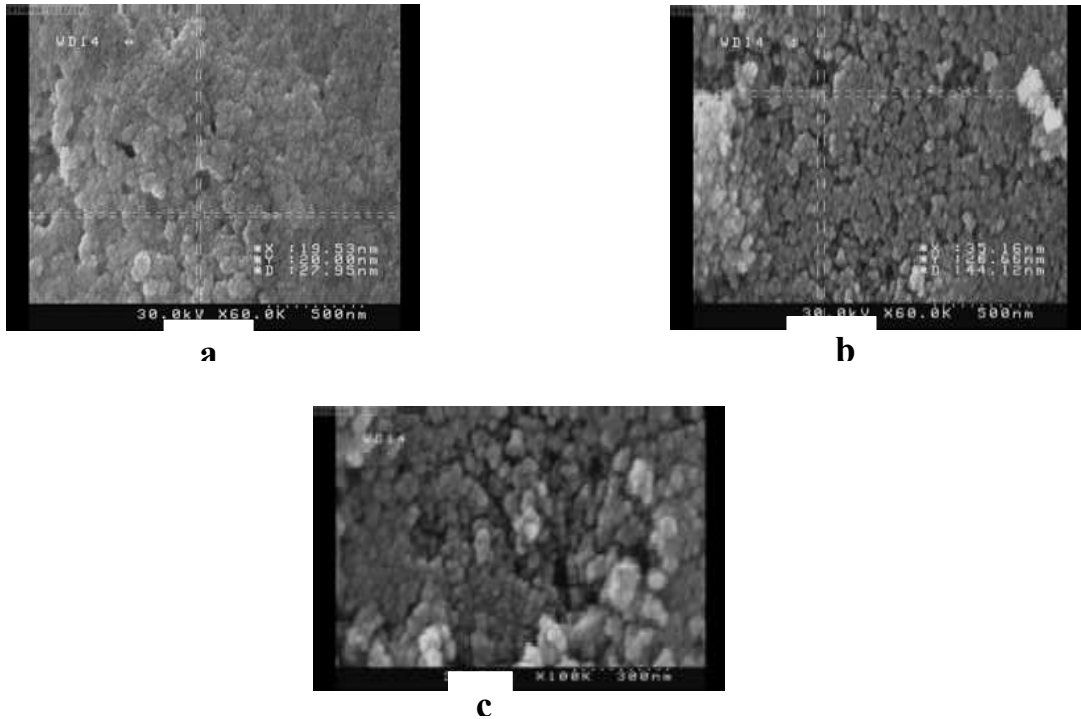


Figure (2) Variation grain size of SnO<sub>2</sub> thin films at different annealing temperatures.

**Morphological analysis**

Figure (3) shows the scanning electron microscopy SEM images that is featured by surface morphology of the SnO<sub>2</sub> thin films on glass substrate at different annealing temperatures. The SEM photograph clearly illustrates the tightly packed grains. Furthermore, we can see that all the films have a more smooth and homogeneous surface morphology, all the films are dense

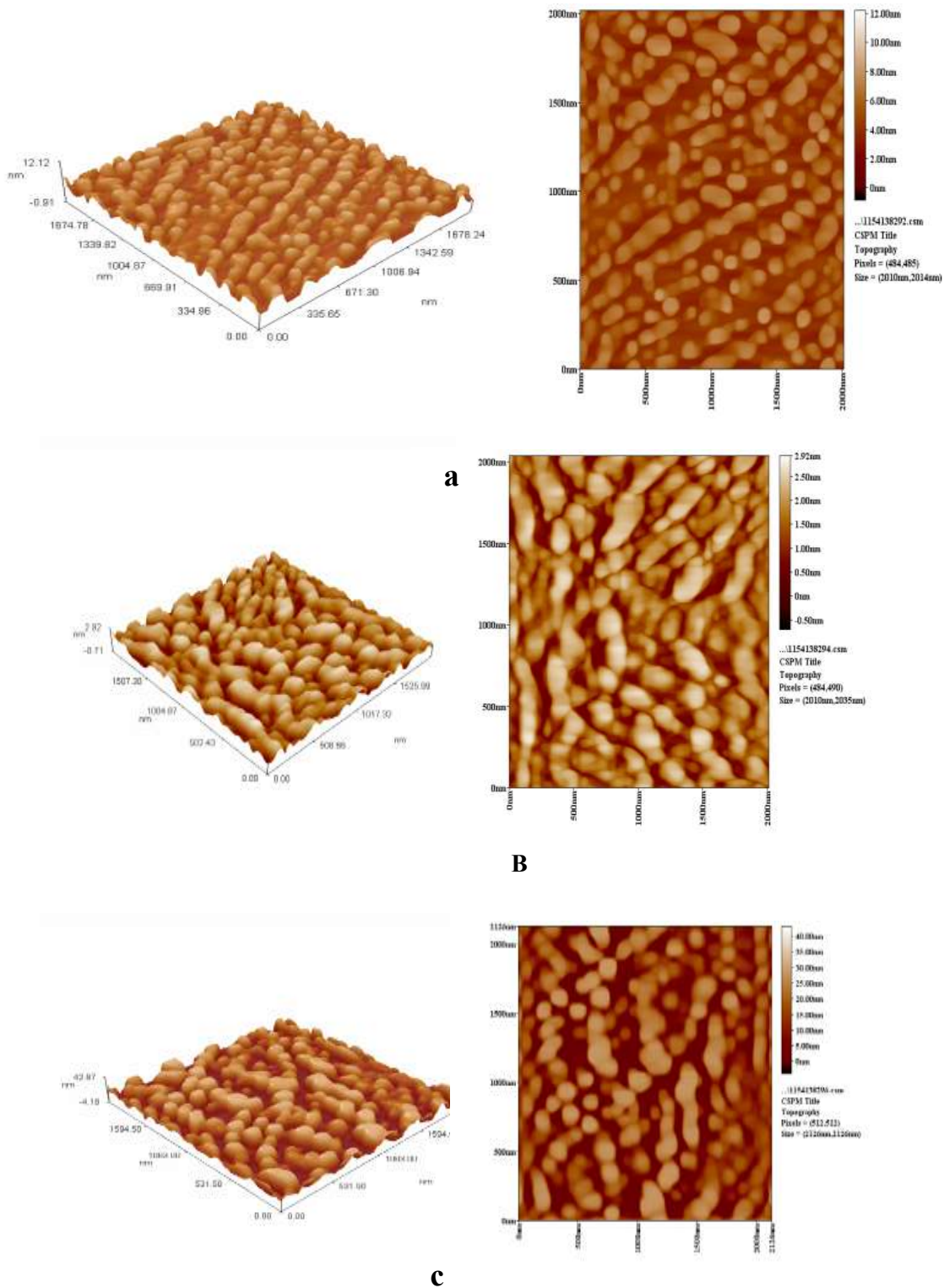
and adherence well to the substrate without any cracks. The grains size obtained from SEM images are (27.95 ,44.12 and 79.22 nm) at (300 , 400 and 500)°C respectively ,the SEM images noted increase of particle size with increasing annealing temperature, due to reduction of grain boundaries in SnO<sub>2</sub> thin film, these results agreement with XRD results .



**Figure (3) SEM image (top view) of SnO<sub>2</sub> film at annealing ( a) 300 °C (b) 400 °C(c) 500°C**

**AFM Analyses:**

Figure (4) shows the Atomic force microscopy (AFM) scan image of SnO<sub>2</sub> films with different annealing temperatures. AFM images show that the all films are well faceted crystallites, uniform packed and small grain . AFM is shown two and three dimensions surface the grain size increases due to increase annealing temperature and the histogram of size distance show the particle size ranging from(70 -91.67) nm . the surface roughness decrease with increasing annealing temperature as shown in Table 2, we note from this table there is a difference between the values of size particle obtained through the use of (Scherrer) equation and obtained from measurements (SEM) and (AFM) this is a natural variation of the different measurement mechanism where the intervention of several factors, including the expansion device is called ((Instrumental broadening as arising from optical components is ideal used in the device, such as slit width (Slit width) (exit hole X-rays) and display waveforms ((Wavelength widths user, as it is added to the widening curve (XRD) shall be displayed diffraction curve in the middle of the Great intensity (FWHM) of more than widening resulting from grains. These result agrees with Khan et al [13] .



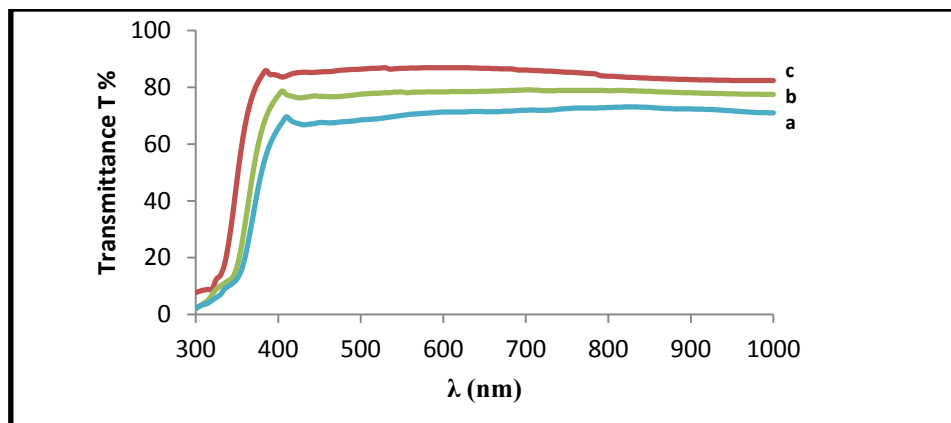
**Figure (4):** two and three dimension AFM images of SnO<sub>2</sub> thin films at different annealing temperatures (a) 300 °C (b) 400 °C, and (c) 500 °C.

**Table (2): Grain size from , SEM, AFM and XRD and roughness from AFM for SnO<sub>2</sub> thin films**

Annealing temperature (°C)	Grain size (nm) AFM	Grain size (nm) SEM	Grain size (nm) XRD	Roughness (nm)	RMS (nm)
300	70.	27.95	8	8.93	10.3
400	80.38	44.12	14	2.77	3.21
500	91.67	79.22	22.16	1.01	1.17

**The optical studies:  
Optical transmittance spectrum**

Figure (5) shows the optical transmittance of SnO<sub>2</sub> thin films deposited with various annealing temperature . The transmittance of all samples was more than 71.1% up to 82.4% in the whole visible region (*i.e.*, above 400 nm) . As annealing temperature increases, optical transmission increase too , this due to the increase in film homogeneity and degree of crystallinity of the film , in addition there was a shift in absorption edges to shorter wavelength(blue shift) with annealing temperature equal 500 °C which was due to the Burstien–Moss shift<sup>[14]</sup>, these results are in agreement with previous results [14,15,16,17].



**Figure (5) Variation of transmittance with wavelength of SnO<sub>2</sub> thin films at different annealing temperatures (a=300 °C, b=400 °C, c=500 °C).**

**The absorption coefficient (α)**

The absorption coefficient (α) has been calculated from equation (2)

$$\alpha = 2.303 A/t \quad \dots(2)$$

Where α is the absorption coefficient , A is the absorbance , t is the thickness of film Figure (6) shows the absorption coefficient (α) versus, wavelength at different annealing temperatures of SnO<sub>2</sub> films, it's clear from this figure that the absorption edge shifts towards higher energies (shorter wavelength) these results are in agreement with previous results [16,18,19]. The figure shows increase in annealing temperature which lead to decrease in absorption coefficient values.

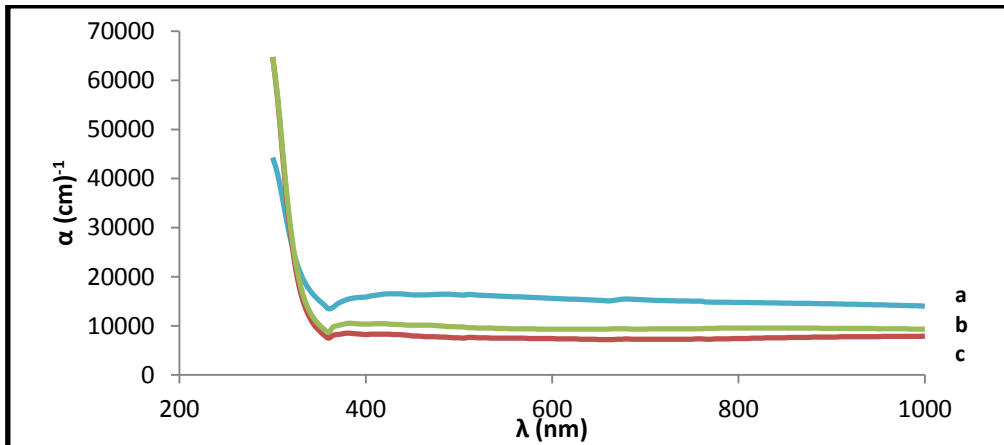


Figure (6) (α) absorption coefficient versus. wavelength plot of SnO<sub>2</sub> thin films at different annealing temperatures (a) 300 °C, (b) 400°C and (c) 500 °C .

### Optical energy gap

The band gaps of these films were calculated from the formula <sup>[18]</sup>.

$$\alpha h\nu = A (h\nu - E_g)^r \quad \dots(3)$$

where  $\alpha$  = Absorption coefficient,  $h$  = Planck's constant,  $\nu$  = frequency of incident light,  $E_g$  = optical energy gap of the material,  $r$  is 2 or 1/2 depending on presence of the allowed direct and indirect transitions. The ( $E_g$ ) can be determined by extrapolations of the linear portion of the curve to the  $h\nu$  axis. Where  $A$  constant,  $h\nu$  is the photon energy and  $E_g$  is the optical band gap . Fig (7) shows the relationship between  $(\alpha h\nu)^2$  and photon energy ( $h\nu$ ) for the SnO<sub>2</sub> thin films . It observed, by increasing the annealing temperature, energy gap gradually increases from 3.5eV to 3.87eV which is related to increase the degree of crystallinity, this is due to the increase in grain size and the decrease in defect states near the bands and this is turn increased the value of  $E_g$  <sup>[18]</sup>. The value of the energy band gap for each sample is shown in table 3. These results are in agreement with previous results [18,119,20,21].

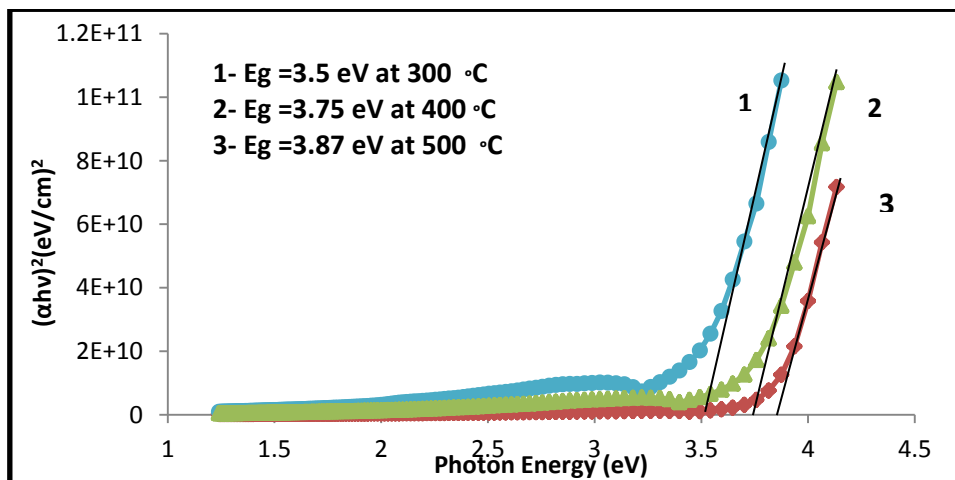


Figure (7)  $(\alpha h\nu)^2$  versus. Photon energy plot of SnO<sub>2</sub> thin films at different annealing temperatures

**Table (3) : Energy band gap of SnO<sub>2</sub> thin films annealed at different temperatures**

Temperature (°C)	Energy Band Gap, Eg (eV)
300	3.5
400	3.75
500	3.87

## CONCLUSIONS

SnO<sub>2</sub> thin films were deposited on glass substrates by used sol–gel (dip-coating) technique . The structural, morphological and optical properties of the films were studied as a function of annealing temperature. The structural by XRD analysis shows that all the samples are polycrystalline and increase in crystallinity at 500 °C , This result agreement with the SEM and AFM images showed that the crystallinity of the films was increased by annealing temperature . All films have high transmittance in the visible region, which increased with increasing of annealing temperature, this may be due to reduce of grain boundary scattering . The optical band gap values were found to increase with annealing temperature from 3.5 to 3.87 eV for direct transitions. SEM& AFM results show that the grain size increase with increasing of annealing temperature. In conclude , sol- gel (dip coating) technique for the production of thin films is a good method for the preparation of thin films which are suitable for scientific studies and for variety applications in technology and industry.

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