Preparation and Characterization of Tin Oxide Thin Films by Using Spray Pyrolysis Technique

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ABSTRACT

In this work, tin oxide thin films have been prepared by Spray pyrolysis technique, using tin chloride over soda – lime glass. Structural and optical properties were studied under different conditions like substrate temperatures of 300, 350 and 400°C, and annealing in air at temperature 300°C for 1 hr. The films were characterized by XRD, SEM, AFM, and UV-VIS analysis. The optical spectra of the films were measured in the wavelength range of 300 –900 nm by UV-VIS Spectrometer device. The X-ray diffraction studies confirmed the films have the orthogonal structure at low substrate temperature change to a tetragonal structure at high substrate temperature. Films prepared with different substrate temperatures were correspond to preferential orientation along the plane (132) and (110) planes for structural orthogonal, tetragonal respectively. The grain size founded(25.2-9.77nm) for different substrate temperatures range (300- 400°C) after annealing , from the (SEM) images the grain size values of the SnO_2 thin films are found to be in the range of (32.3-24.2 nm) corresponding to the substrate temperature (350 and 400°C) after annealing and from the AFM the root mean square (RMS) values for the thin film at substrate temperature 350C was found to be 10.4 nm, the surface roughness 8.86 nm. The maximum value of transmittance was found to be 78 % around the wavelength of 900nm at substrate temperatures 300°C also have energy gap (2.9-3.4eV) at substrate temperatures range (300- 400°C) after annealing in air at temperature 300°C for 1 hr.

Keywords : Tin oxide , thin film , spray pyrolysis , structure and optical properties.

تحضير وخصائص أغشية ثنائي اوكسيد القصدير الرقيقة بواسطة استخدام تقنية الرش الحراري

الخلاصة :
في هذا العمل حضر ثنائي أوكسيد القصدير بطريقة الرش الحراري , باستخدام كلوريد القصدير على قاعدة زجاجية , درست الخصائص التركيبية والبصرية تحت شروط مختلفة مثل درجة حرارة القاعدة (400,350,300) درجة سيلزية ولدنت في الهواء عند درجة حرارة (300) درجة سيلزية ولمدة ساعة . شخصت خصائص الاغشية بواسطة فحص حيود الأشعة السينية والمجهر الالكتروني الماسح ومجهر القوة الذرية وقياسات الأطياف للأشعة المرئية وفوق البنفسجية , الأطياف البصرية للأغشية حسبت عند الطول الموجي (من 300الى900) نانومتر . أكدت دراسة حيود الأشعة السينية ان الاغشية تمتلك تركيب متعامد عند درجات الحرارة الواطئة للقاعدة وتتغير الى تركيب رباعي الزاوية عند درجات الحرارة العالية للقاعدة , وجدت قيمة الحجم الحبيبي تتغير (من 9.77 الى25.2) نانومتر عندما تتغير درجة حرارة القاعدة بين (300 الى 400) درجة سيلزية بعد التلدين , كذلك وجدت من صور المجهر الالكتروني الماسح قيمة الحجم الحبيبي لأغشية اوكسيد القصدير تساوي (24.2- 32.3) نانومتر الذي يقابل درجة حرارة القاعدة (350 و 400) درجة سيلزية بعد التلدين , اظهرت نتائج مجهر القوة الذرية ان قيمة مربع متوسط الجذر تساوي (10.4) نانومتر ومعدل الخشونة يساوي 8.86 نانومتر عندما تكون درجة حرارة القاعدة 350 درجة سيلزية . بالاضافة الى ذلك وجد ان أعلى قيمة للنفاذية تساوي 78% عند الطول الموجي (900) نانومتر عند درجة حراة القاعدة 350 درجة سلزية , وتمتلك فجوة طاقة (2.9-3.4) الكترون فولت لاغشية اوكسيد القصدير عندما درجة الحرارة تتغير بين (300- 400) درجة سليزية بعد التلدين لمدة ساعة.

INTRODUCTIONT

Tin oxide (SnO2) is one of the semiconducting oxides that has unique optical, electrical, transparent, conductive properties[1]. Tin oxide (SnO2) is wide band gap an n-type semiconductor of tetragonal structure [2] and can resist high temperature [3]. It has been widely used for various catalytic applications such as gas sensors[4] , photovoltic cells[5],transistors[6] ,lithium batteries[7] , and solar cells[8] ...etc.

SnO2 films can be prepared by different techniques such as sputtering [9] ,evaporating tin grains in air[10] ,chemical vapor deposition[11] , thermal evaporation of oxide powders[12] , rapid oxidation of elemental tin[13],the sol–gel method[14],ion beam assisted deposition[15] and spray pyrolysis[16 . [

The Spray pyrolysis is one of the most cost-effective methods to prepare SnO2 films due to its ability to deposit large uniform area with low fabrication cost, simplicity and low deposition temperature.

In this work we study the effect of substrate temperature on the Structural and optical properties of SnO2 thin films .

Experimental

Figure (1) shows a typical spraying system. In this technique the films produced by using

- The SnO_2 was prepared by means of dissolving of (0.1M) tin Chloride prepared by using the dissolving in distilled water.
- The solution was made to 100ml with distilled water.
- The solution was stirred with a magnetic stirrer type (LMS-1003) for 15 minute.

- The substrates were heated to (300,350 and 400°C) temperature for film deposition by an electrical heater.
- The nozzle was kept at a distance of 30cm from the substrate during deposition.
- The glass substrate were cleaned with ethanol in ultrasonically cleaner and then dried.
- The solution was sprayed by means of a nozzle, assisted by a carrier gas, over a hot substrate .

When aerosol droplets came close to the substrates, the compounds reacted to become a new chemical compound. SnO_2 formulation can be represented as:

$$SnCl_2.2H_2O \rightarrow SnO_2+2H_2\uparrow+Cl_2\uparrow \qquad \ldots (1)$$

Table(1) process parameters for the spray deposition of SnO_2 thin films.

Substrate temperature (°C)	300, 350, 400°C
Nozzle to substrate distance	30cm
Deposition time (minutes)	5 (minutes)
$SnO_2.2H_2O$ solution concentration	0.1 M
Temperature annealing	300°C
Time annealing	60 (minutes)
Solvent	Distilled water

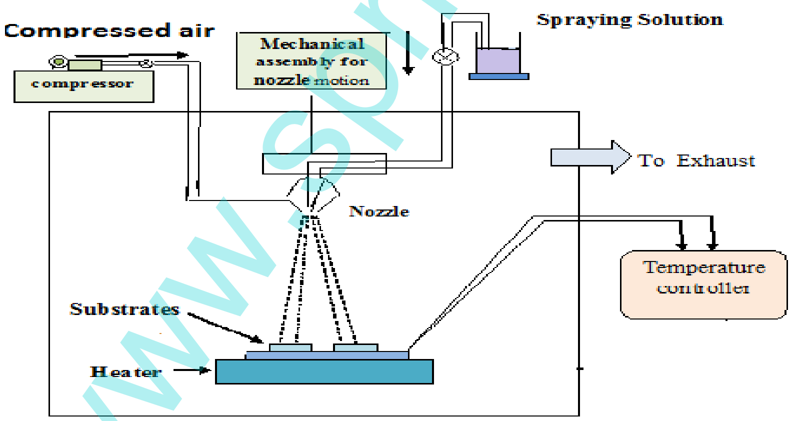

Figure (1) Schematic set-up for spray pyrolysis technique.

The X-ray diffraction (XRD) data of the prepared films were taken using: (Source CuKα with radiation of wavelength λ =1.5406Å , target: Cu, Current =30mA , Voltage = 40 kV, scanning speed = 5 deg /min) over the diffraction angle range 2θ=20-60° at room temperature .The average crystallite size (D) was estimated using the Scherrer equation as follows[17] :

$$D=0.9\lambda/\beta \cos\theta \qquad \ldots(2)$$

Where
λ, β, and θ are the x-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak, and Bragg's diffraction angle, respectively. Morphology studies of the SnO_2 films on the glass substrate were carried out with scanning electron microscope (SEM) type Inspect S50, and magnification over 100000.
The surface distribution of SnO_2 thin films were measured using atomic force microscopy (AFM) using a scanning probe microscopy (CSPM-5000) instrument.
UV-VIS, Phoenix-2000V device was used to record the optical transmission for SnO_2 thin films after annealing in air at temperatures 300°C for 1 h. Using furnace type S302AU England.

Results and Discussion
Structural Properties
X – Ray Diffraction (XRD) for SnO_2thin films
X-ray diffraction(XRD) of SnO_2 thin film prepared by spray pyrolysis technique at substrate temperatures of (300,350 and 400°C) after annealing in air at temperature 300°C for 1h, have been shown in Figure (2). The peaks of the XRD were observed in the range of 2ɵ (20° - 60°) .

The presence of diffraction peaks indicates that the film is have the orthogonal structure in the low substrate temperature and change to a tetragonal structure in the high substrate temperature . It is revealed that the sprayed film has peaks corresponding to (132) and (110) which is corresponding to the positions $2q$ = 28.24° and 26.57° for orthogonal and tetragonal structure respectively, for the films which depend on the substrate temperature after annealing , the intensity increases as the substrate temperature increases after annealing, due to the improvement of the films crystallinity, while decreases at substrate temperature 400°C .

The crystallite size of SnO_2 films prepared at different substrate temperature was calculated using the full width at half maximum (FWHM) for SnO_2 films using Scherrer formula. The highest crystallite size of (25.2nm) and this value decreases with the increases substrate temperature and after annealing in air at temperatures 300°C for 1 h as shown in Table (2). The values of full width at half maximum (FWHM) are increase with increasing substrate temperature of the films, this indicates that the grain size decreases with increasing substrate temperature. The main calculations of the structural properties have been listed in the Table (2).

Table (2) the structural properties of SnO_2 thin films at various substrate temperature 2θ - Theta (deg), Full width at half maximum (FWHM) and Grain size (D).

substrate temperatures ºC	2θ (deg)	hklplanes	FWHM	Grain Size (nm)
After annealing 300	26.5761	113	0.31930	12.83
	28.2448	132	0.16860	25.2
	34.0388	330	0.20000	20.86
After annealing 350	22.9263	220	0.21400	18.99
	28.2305	132	0.18620	22.11
	58.3027	113	0.26940	16.93

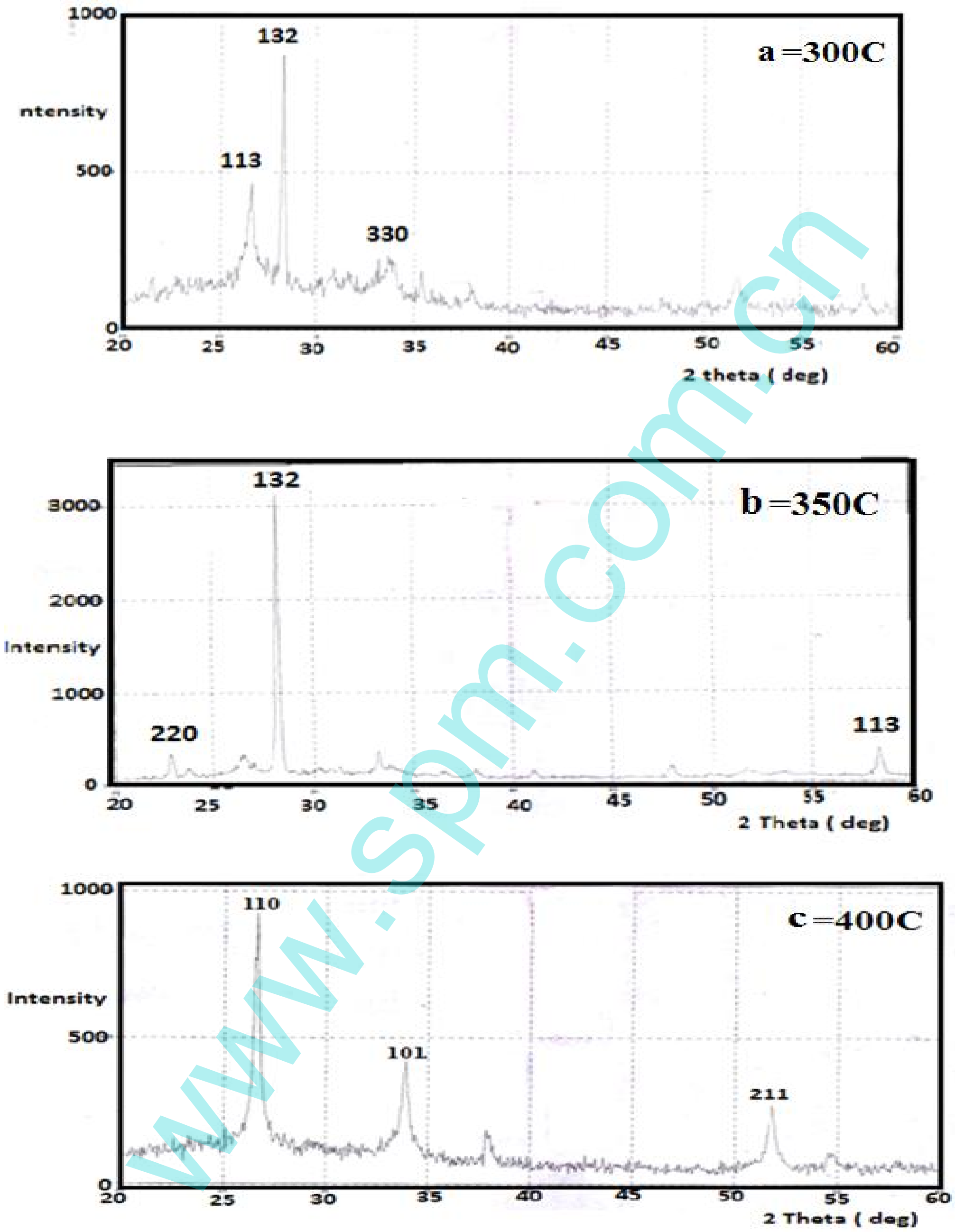

Figure (2) XRD of SnO_2 films for substrates temperatures (a=300°C,b=350°C, c=400°C) after annealing.

Surface Morphology

Scanning Electron Microscope (SEM) for SnO2 thin films

The surface morphology of the SnO_2 thin films deposited on a glass substrate at substrate temperatures (350 and 400°C) by spray pyrolysis technique was examined by Scanning Electron Microscope (SEM) are shown in Figures [(3-a)-(3-b)] for different magnification after annealing in air at temperatures 300°C for 1 hr. As can be seen from the Figures the SnO_2 thin films at different substrate temperature are quite similar except for a small decreasing in particle size, besides that, there are some crystal shapes structures, agglomeration of grains. Clearly, we found the films deposited at higher substrate temperature have the grain size less of the films deposited at low substrate temperature. From the (SEM) images the grain size values of the SnO_2 thin films are found to be in the range of (32.3-24.2) nm corresponding to the substrate temperature (350 and 400°C) after annealing respectively. These values are comparable with that estimated from XRD results as shown in Table (3).

Table (3) comparison between the grain size estimated from (XRD) and (SEM) analysis.

substrates temperatures °C	Grain size estimated from (XRD) (nm)	Grain size estimated from (SEM) images (nm)
350	22.11	32.3
400	11.07	24.2

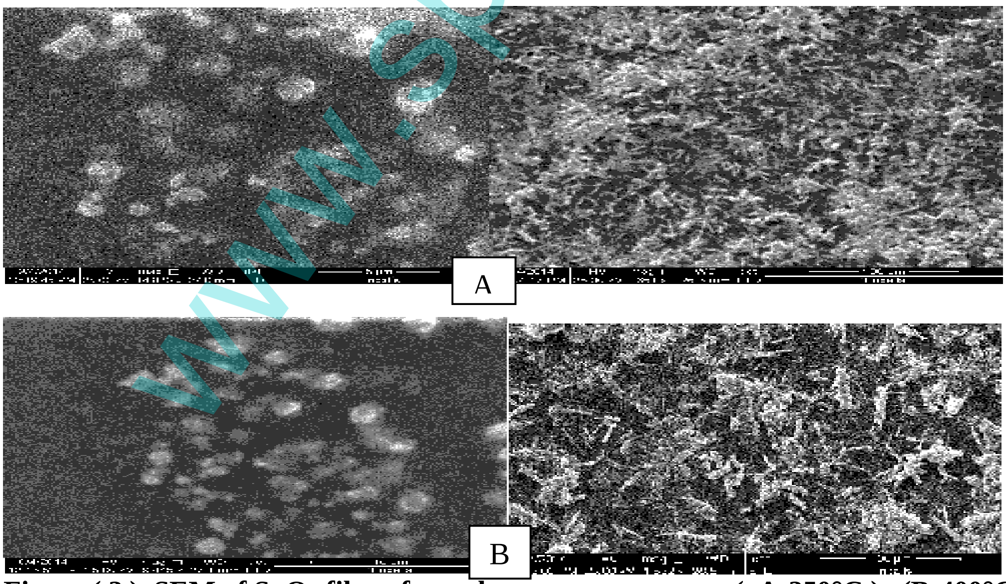

Figure (3) SEM of SnO_2 films for substrate temperatures(A-350°C) , (B-400°C) After annealing

Atomic force microscopes (AFM) for SnO_2 thin film

The surface morphology of the SnO_2 thin film was studied also by AFM . Figure (4) shows the typical two- dimensional and three - dimensional AFM image of SnO_2 thin film deposited on a glass substrate at substrate temperature 350°C after annealing in air at temperature 300°C for 1 h using spray pyrolysis technique. AFM surface 3D (three-dimensional) it was observed that the distribution of grains is uniformly on the substrate surface. The root mean square (RMS) values of surface roughness are found to be 10.4 nm, the surface roughness was observed to 8.86 nm.

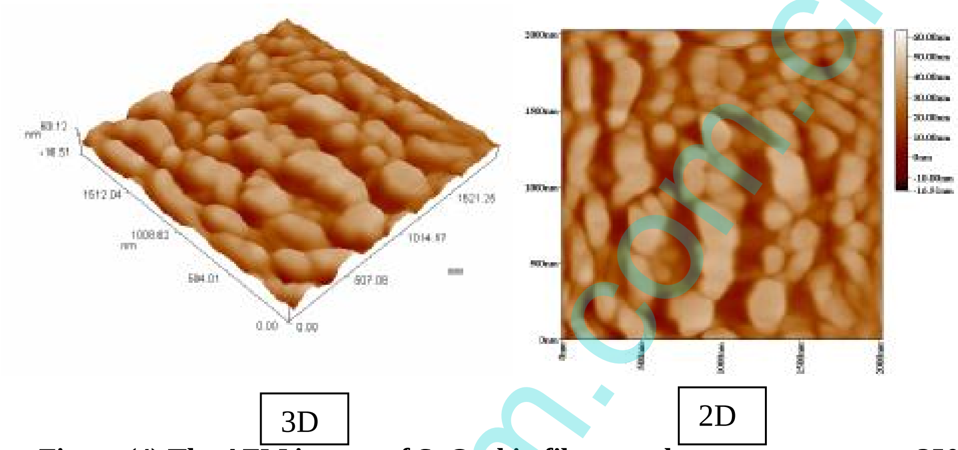

Figure (4) The AFM images of SnO_2 thin film at substrate temperature 350°C and annealing in air at temperatures 300°C

Optical characterization

The knowledge of optical constants of the thin films is very significant since they can determine the exact application of the films. The optical properties of SnO_2 thin films prepared by spray pyrolysis technique on soda – lime glass substrate with different substrate temperature of 300, 350 and 400°C after annealing have been investigated. The absorption and transmittance spectra were measured in the wavelength range of 300–900nm by UV-VIS Spectrometer device .The film thickness was determined by using the following formula:-

$$d = \frac{\Delta x}{x} * \frac{\lambda}{2} \qquad \text{…..(3)}$$

Where

(x) is the fringe width,(Δx) is the distance between two fringes and (λ) is the wavelength of laser light.

Figure (5) shows the thickness of SnO_2 thin films with different substrate temperatures and after annealing in air at temperature 300°C for 1 h . It is seen that the film thickness increased with increasing substrate temperature from 300°C to 350°C and then decreased with increasing substrate temperature (400°C). Initially, at lower substrate temperatures 300°C,the temperature may not be sufficient to decompose the sprayed droplets from the solution and this results in a low thickness. At substrate temperature of 350°C, decomposition occurs at the optimum rate resulting in the terminal thickness being attained. A noticeable decrease of the film thickness with increasing the substrate temperature is observed after substrate temperature 350°C. This decrease may be attributed to re-evaporation of film material after deposition or to thermal convection of the sprayed droplet during the deposition process or both [18].

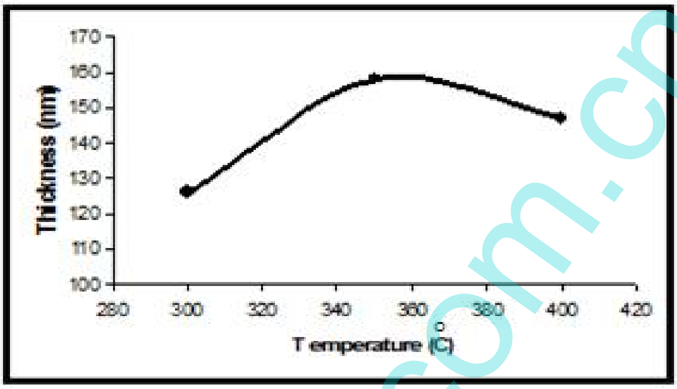

Figure (5) SnO2 film thickness with substrate temperature

Transmittance for SnO_2 thin film

Figure (6) shows the optical transmittance spectra obtained for the SnO_2 thin films in the wavelength range 300-900nm. The substrate temperature and the annealing play an important role in the films formation. The transmission improves as the substrate temperature increases .The transmittance value of the films found increased to 75 % after annealing in air at temperatures 300°C for 1 h, maximum transmittance in case of the film having a thickness of 120 nm is slightly more than the film with thickness 145 nm.

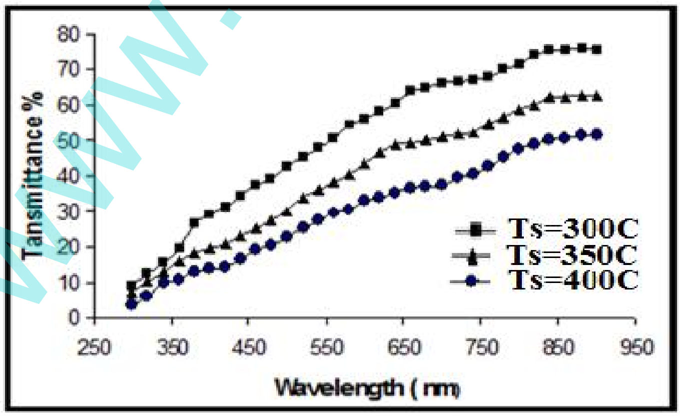

Figure (6) The optical transmittance spectra of the SnO_2 thin films after annealing at temperature 300°C for 1 h at different substrate temperature

Absorption Coefficient (α) for SnO_2 thin film

The Absorption Coefficient (α) for SnO_2 films, is calculated according to the following equation:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \qquad ...(4)$$

Where

(d) is the thickness of thin film and (T) is the transmission.

Figure (7) shows the optical absorption spectra for the SnO_2 thin films with different substrate temperature (300 - 400°C) after annealing in 300ºC for 1h .The absorption coefficient decreases with increasing substrate temperature and a weak change in the absorption edge is observed towards lower wavelengths as substrate temperature increases, this attributed to the effect of the thickness which was thicker for higher substrate temperature.

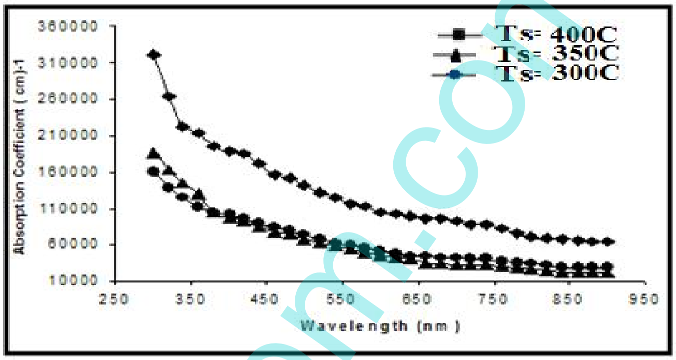

Figure (7) the Absorption Coefficient (α) of the SnO_2 thin films after annealing in 300ºC for 1h at different substrate temperature

Optical Energy Gap (Eg) for SnO_2 thin film

The optical Energy Gap (Eg) of the thin films was calculated from the allowed direct transition given by[19] :

$$\alpha h v = A(hv - Eg)^n \qquad ....(5)$$

Where

α (cm-1) is the absorption coefficient, h (J.s) is Planck's constant, υ(Hz) is the photon frequency, A is constant , and Eg (eV) is the band gap energy.

Figure (8) shows the energy gap (Eg) for the SnO_2 thin film with different substrate temperature of 300, 350 and 400°C (after annealing in 300ºC for 1 h) . The results show that the substrate temperature and the annealing influence is very important in the band gap assignment; it found the energy gap increase with increase the substrate temperature after annealing. The optical energy gap of the films varied significantly with the increase of substrate temperature, which was attributed to the presence of various phases in the films . The films formed at substrate temperature 300, 350ºC showed orthogonal structure with an energy band gap of (2.9, 3.4eV) and the films formed at substrate temperature

400ºC showed tetragonal structure with an energy gap of (3.1eV), these results imply that the deposited films can be used in photovoltaic devices.

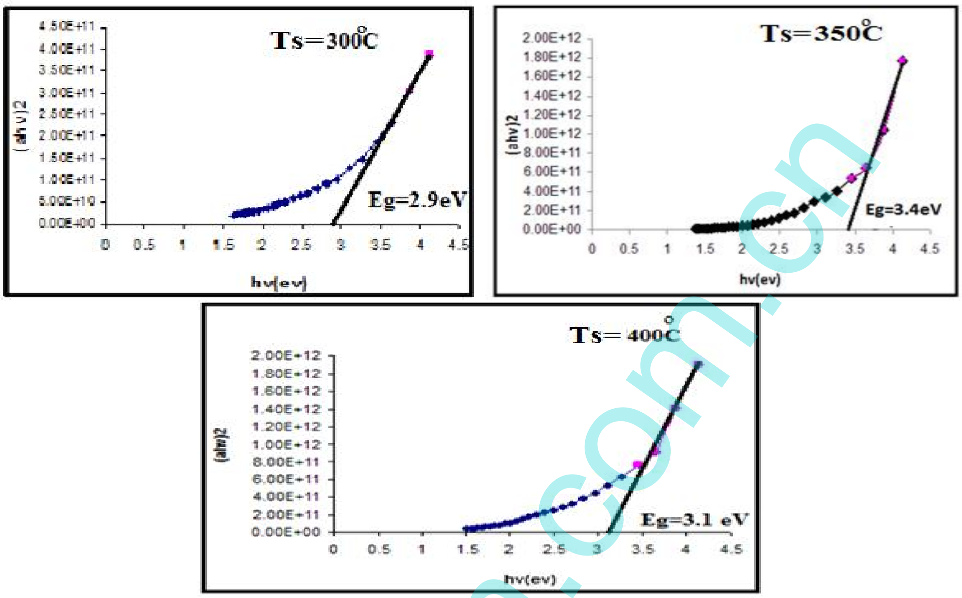

Figure (8) The Energy gap (Eg) for the SnO_2 thin film with different substrate temperatures after annealing in300ºC for 1h .

CONCLUSIONS

SnO_2 thin film deposited by spray pyrolysis technique at different substrate temperatures. The XRD studies showed that have orthogonal structure in low substrate temperature and change to a tetragonal structure in the high substrate temperature after annealing the films. The grain size decreases with increasing substrate temperature after annealing. The film thickness and the values of energy gap, are increasing with increasing substrate temperature to 350ºC and decreases in the 400ºC substrate temperature, while the transmittance decreases with increasing substrate temperature. (SEM) images are found the grain size values to be in the range of (32.3-24.2 nm) corresponding to the substrate temperature (350 and 400°C) after annealing and AFM the root mean square (RMS) values for the thin film at substrate temperature 350C was found to be 10.4 nm, the surface roughness 8.86 nm.

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