Annealing Effect on Structural and Optical Properties of SnO2 Thin Films

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الملخص

رسبت أغشية رقيقة من مادة SnO2 بطريقة الترسيب البخاري الكيميائي(CVD) على أرضيات زجاجية بدرجة حرارة 450°C ومعدل انسياب غاز 2.5L/min. . تم تلدين النماذج بدرجات حرارة (200,300,400,500)°C بالهواء لمدة 60 mins. . درست الخواص التركيبية بطريقة حيود الأشعة السينية (XRD) لجميع النماذج قبل وبعد التلدين . وجد بأن أغشية SnO2 المرسبة هي من نوع متعدد البلورات وان معدل قطر الحبيبة يزداد بازدياد درجة حرارة التلدين ويتراوح مابين (190-230)A° . أما ثوابت الشبيكة ذات التركيب الرباعي القائم فأنها تساوي(a=b=4.782,c=3.233)A° وهي لا تتأثر بالتلدين. درست أيضا الخواص البصرية باستخدام (UV-visible spectroscopy) ووجد بأن للأغشية الملدنة وغير الملدنة نفاذية عالية ضمن الطيف المرئي تتراوح أعلى قيمة لها ما بين %(85-95) تعتمد على درجة حرارة تلدين الغشاء ، وان الأغشية الملدنة بدرجة حرارة أعلى تمتلك قيمة أعلى للنفاذية . حسبت طاقات حافة الامتصاص ووجد بأنها تزداد بارتفاع درجة حرارة التلدين وتتراوح مابين eV(3.93-4.1) . أما فجوة الطاقة البصرية فإنها لاتتأثر كثيرا بالتلدين وتساوي تقريبا eV (4.17).

Abstract

Thin solid films of SnO2 were deposited by chemical vapor deposition (CVD) method on glass substrate at 450°C and 2.5L/min.air flow rate. Deposited films were annealed at different temperature (200,300,400,500) °C in air for 60 minutes.

Structural properties have been studied for annealed and unannealed films. It was found that the films have polycrystalline structure with grain diameter(190-230)A° depend on annealing temperature. And the crystal structure is tetragonal with lattice constants (a=b=4.782 ,c=3.233)A°.

Optical properties also studied for annealed and unannealed films using UV-visible spectroscopy. The transmission spectra showed higher transparency over the visible wave length region with maximum value (85-95)% depend on annealing temperature. Absorption edge energy is increased by annealing temperature from (3.93 to 4.1)eV while Optical energy gap is not affected by annealing and it is found to be (4.17)eV.

Introduction

Transparent, electrically conductive films have been prepared from a wide variety of materials. These include semiconducting oxides of tin, indium, zinc and cadmium; and metals such as silver, gold and titanium nitride .They have been used for many years as electrodes or resistive elements and applied to semiconductor devices as transparent gates on charge injection devices and charge coupled devices and as transparent barrier layers on solar cells[1]. The materials mostly used for such applications are tin oxide (SnO2), antimony-doped tin oxide and tin-doped indium oxide. These films have been deposited by chemical vapour deposition, sputtering, evaporation and spraying [2].

Tin oxide films is the most used material because of its cheap raw material and highly existing in nature. It is characterized by a wide band gap and high electrical conductivity through the existing of O2 vacancies and interestial tin atoms in the crystal structure of the films and that is depend on method of deposition. Also it is a good transparent anti-reflecting material.

Temperature stability and reproducibility of the film properties are important for device reliability. The films are exposed to heat during the preparation and operation of the device. This may cause structural changes which tend to either influence or degradation in most of the physical properties of the films. The effects of annealing are complex because of the variety of phenomenon that may observe. Many studies have been done on different transparent conducting oxides to find the effect of annealing on certain property of the films such as the refractive index (n), extinction index (k) and energy gap (Eg) for ZnO-SnO2 [3], resistivity and factor of merit for antimony-doped tin oxide[4], grain size, porosity and conductivity of tin-doped indium oxide[5] and many others [6,7,8,9].

In this study structural and optical properties of tin oxide films prepared by chemical vapour deposition are described. Also, the effect of annealing at different temperature in air on structural and optical properties of SnO2 thin films are studied including: grain size, lattice constant, transmission, optical energy gap and absorption edge.

Experimental Detail

The SnO2 thin films were prepared by CVD technique. Although this technique is well known and used by many workers[10], it still need some modification. We have modified and built this system in physics department, Education college, Mosul university, using the stannous chloride oxidation principle. The diagram of the experimental set-up used for SnO2 deposition is shown in Figure (1). Material used was SnCl2.2H2O (purity 99.99% supplied by Fluka Company). Films were

deposited on glass type (Gloim 1003/Italy) at 450°C substrate temperature and 2.5 L/min. gas flow rate.

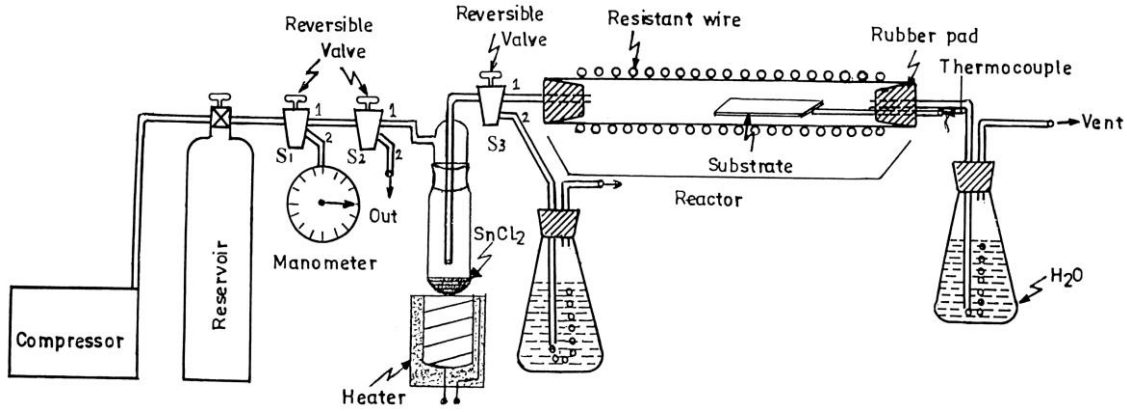


Fig.(1)Schematic Diagram of CVD System for SnO2 Films Deposition

When the desired deposition factors were attained and stabilized the tin chloride was melted (melting point 247°C) using coil heater (≈350°C). The tin chloride vapour was driven through the reactor by maintaining an air flow. Air carries the SnCl2 vapour to form SnO2 film deposited on the hot substrate and the reaction takes place as follows:

$SnCl2 + O2 \rightarrow SnO2 + Cl2$

After finishing the deposition the substrates were brought to room temperature inside the reactor. The deposition systems as well as the method have been described briefly in reference [11].

Some of the films were annealed in air by controllable electric oven type (Heraeus) at temperature (200,300,400,500)°C for 60 minutes, while the others were left without annealing.

Structural properties were studied for annealed and unannealed films by X-ray diffraction (XRD) using a Philips X-ray diffractometer model (PW 1130). Source of radiation was Cu Kα (λ=1.5405 A°) and the scanning range of 2θ was restricted to range (10-60)°. Perpendicular distance between adjacent crystal layers(dhkl) for each grain, Lattice constants (a=b, c) and grain diameter (D) of SnO2 film were calculated using the XRD pattern data and the following equations [12] :

$$2d_{hkl} \sin\theta = n\lambda \quad \text{- - - - - - - - - - - - - - -} \quad (1)$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{- - - - - - - - - - - - -} \quad (2)$$

$$K\lambda$$

$$D = \frac{K\lambda}{B\cos\theta} \quad \text{- - - - - - - - - - - - - - - - (3)}$$

Where λ is x-ray wave length, n: is reflection order (equal one), h,k,l: are miller indices, K is correction factor (≈1), B is the full band width in the middle of the peak (in radian).

Optical properties were also studied by recording transmission spectrum over the range (200-1100) nm using Shimadzu UV-visible spectrophotometer model (1650 PC). The thicknesses of the films were determined by optical interference technique using wavelengths at maxima and minima and applying the following equations[13]:-

$$m = \frac{\lambda_{m-1}}{\lambda_{m-1}-\lambda_m} \quad \text{- - - - - - - - - - - - - - - - (4)}$$

$$m = \frac{\lambda_{m+1}}{\lambda_m - \lambda_{m+1}} \quad \text{- - - - - - - - - - - - - - - - - (5)}$$

$$m = \frac{\lambda_{m-1}+\lambda_{m+1}}{\lambda_{m-1}-\lambda_{m+1}} \quad \text{- - - - - - - - - - - - - - - - (6)}$$

$$t = n_{SnO2}\, d = \frac{m\lambda_m}{4} \quad \text{- - - - - - - - - - - - - - - (7)}$$

Where $\lambda_{m+1}<\lambda_m<\lambda_{m-1}$, t : is the optical thickness ,d : is the geometrical thickness, n_{SnO2} : is the refractive index (≈2), m: is the interference order.

The effects of annealing on the transmission, absorption coefficient, optical energy gap and absorption edge were also discussed.

Results and Discussions

X-ray diffraction pattern for SnO2 film deposited on glass substrate at 450 °C and air flow rate of 2.5L/min. is shown in Fig.(2). The pattern shows only five peaks namely (110),(101),(200),(211) and (220). Since all peaks are sharp, it is evident that the film is polycrystalline in nature. Comparing the intensities of the peaks and angles of diffractions with the data of (JCPDS)[14] international diffraction standard card for SnO2 powder, it was concluded that the deposited film is a tetragonal SnO2 film. The values of dhkl calculated from the values of 2θ at maximum intensities using equation (1), followed by lattice constants and grain diameters using equations (2)&(3) respectively were agreed perfectly

with JCPDS. All calculated values and constants were listed on table (1). The figure also shows a maximum intensity for (110) plane. This can be explained in term of a preferential orientation of the plane. As the deposition takes place, some of the plane orient themselves to give maximum reflection. This type of behavior for SnO2 film have been reported by Bartholomew and Garfinkel [15].

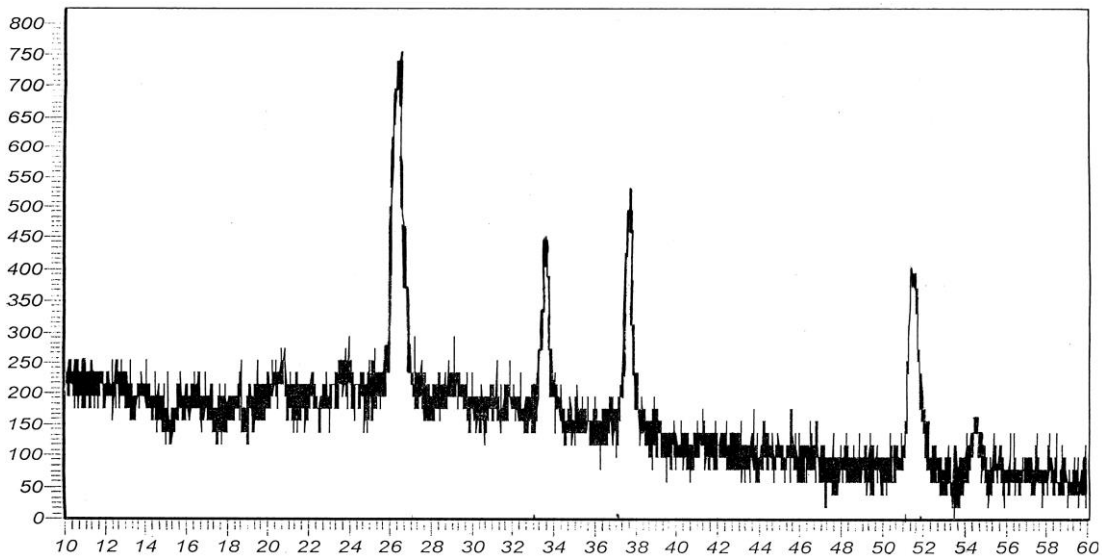


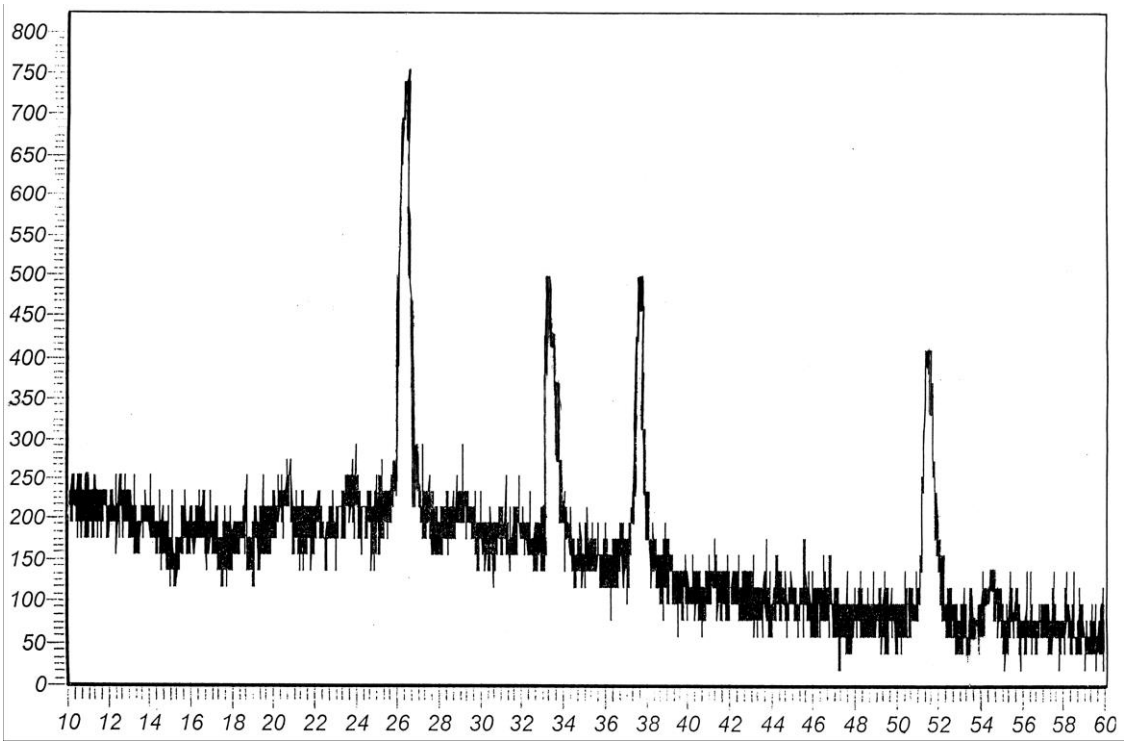
Fig.(2) X-Ray Diffraction Pattern for SnO2 Thin Film

Table (1) lattice constants and grain diameters for SnO2 films deposited on glass substrate and JCPDS card data.

Figures 3,4,5 and 6 are the x-ray diffraction patterns for SnO2 films

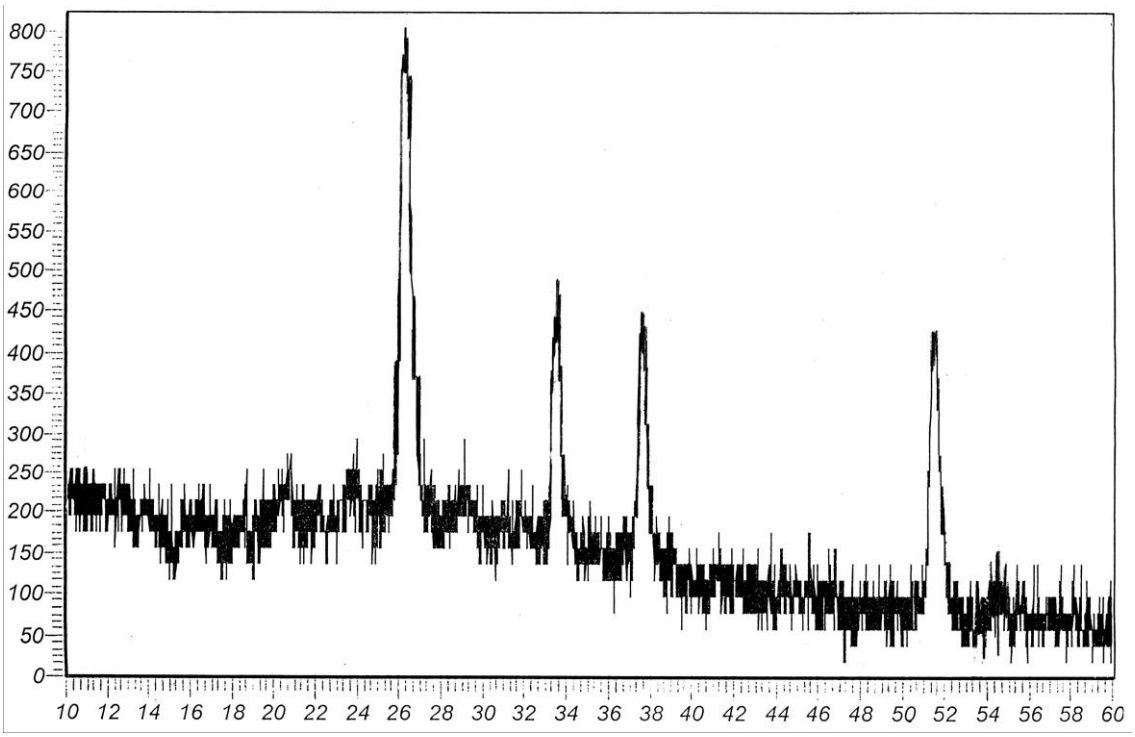
Data from Fig.(2)					Data from JCPDS card
a=4.782(A°) , c=3.233 (A°)					a=4.738 (A°),c=3.188(A°)
hkl	2θ	Sinθ	d(A°)	D(A°)	d (A°)
110	26.3	.2275	3.385	226.6	3.35
101	33.4	.2874	2.68	187	2.644
200	37.6	.322	2.39	233	2.369
211	51.3	.4328	1.779	190.09	1.765
220	54.5	.4579	1.682	185	1.675

annealed at (200,300,400,500)°C respectively. It is clear that the intensity of (221) plane and the preferred orientation (110) plane increased gradually with annealing temperature while (220) plane decreased by annealing until it vanished at 400°C. This is due to the crystallization occur by heating which increase the arrangement of small crystals in preferred plane rather than other planes.



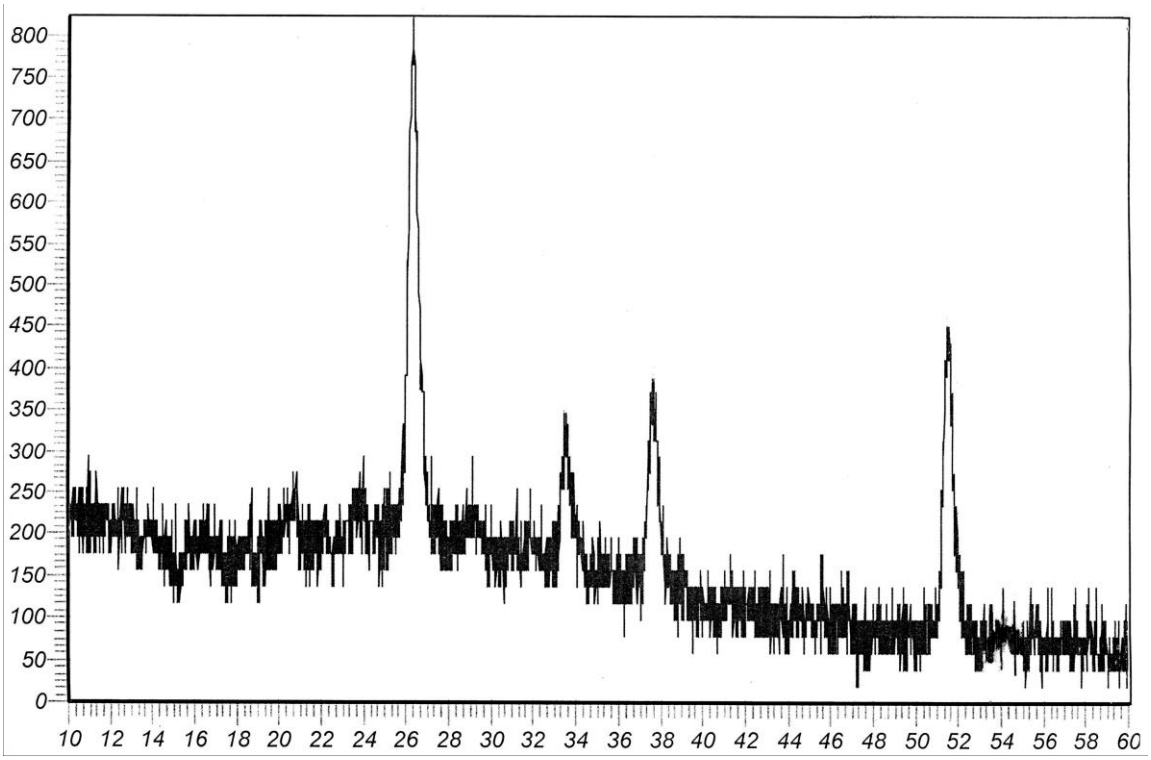
(2θ)

Fig.(3) XRD Pattern for SnO2 Thin Film Annealed at 200°C



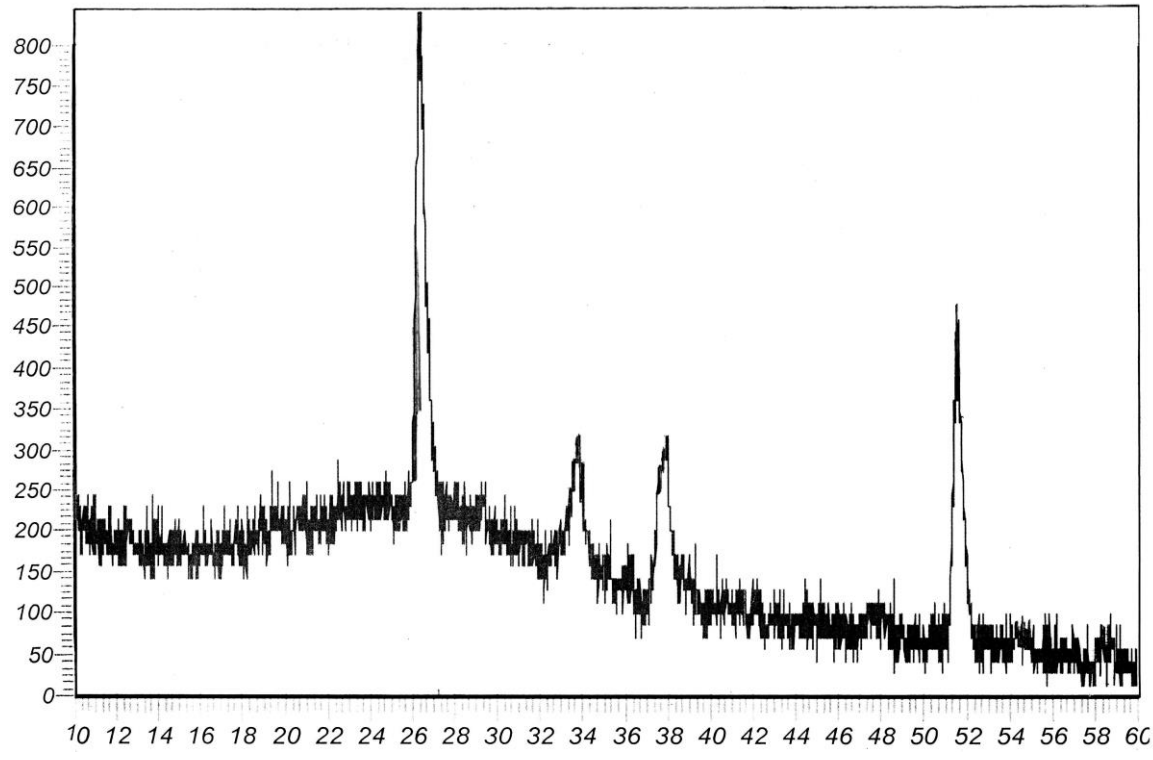
(2θ)

Fig.(4) XRD Pattern for SnO2 Thin Film Annealed at 300°C



(2θ)

Fig.(5) XRD Pattern for SnO2 Thin Film Annealed at 400°C



(2θ)

Fig.(6) XRD Pattern for SnO2 Thin Film Annealed at 500°C

The effect of annealing on grain diameter also studied by calculating D for(110) and (220)planes.Data for this study was displayed on table (2).

Table (2) Effect of annealing on the grain diameter of SnO2 film in crystallization .

	D(A°)				
hkl	25°C	200°C	300°C	400°C	500°C
110	226.6	259	302	362.58	453.2
211	190.09	193	190.79	195.74	217.49

A study by group of researchers [16] has been done using computer program to calculate the structural factor F(hkl). They found an increase in $|F(200)|2$ and $|F(101)|2$ in case of the present of oxygen vacancies in the crystal structure and tin atoms inserted in the interstitial sites respectively. This results explained the high intensity of those tow plains in Fig.(2). Annealing SnO2 films in air at 200°C reduces the number of tin atoms through the oxidation process so the intensity of (200) plane in Fig.(3) is lowered compared to that in Fig.(2). This was happed again in films annealed at 300oC in Fig.(4). By increasing annealing temperature to 400°C and 500°C, oxygen from air has been absorbed gradually to fill the oxygen vacancies and to oxidized tin atoms. So the intensities of planes (200) and (101) faced more decrements. This was noticed before by several researchers in thermal aging and heat treatment of SnO2 films[17,18].

The transmission spectrum for SnO2 film was shown in Fig.(7). It is clear that the transmission increases sharply at the beginning of the visible region to reach the average maximum value of (90%) at the end of this region near the IR. The curve oscillations in this wave length region are due to interference effects on thin film. SnO2 film thickness was calculated using interferometer technique mentioned in experimental detail. Its value is about 365nm.

Figure (8) shows the transmission spectra of SnO2 films annealed for 60 minutes at (200,300,400,500)°C. It is clear that the transmission increases by increasing annealing temperature started from 300 °C specially at (400-500) nm. This increment was reported by several researchers [17,19,20]. We thought that this was attributed to the decrease in free charges in SnO2 films by annealing through oxidation and removing oxygen vacancies.

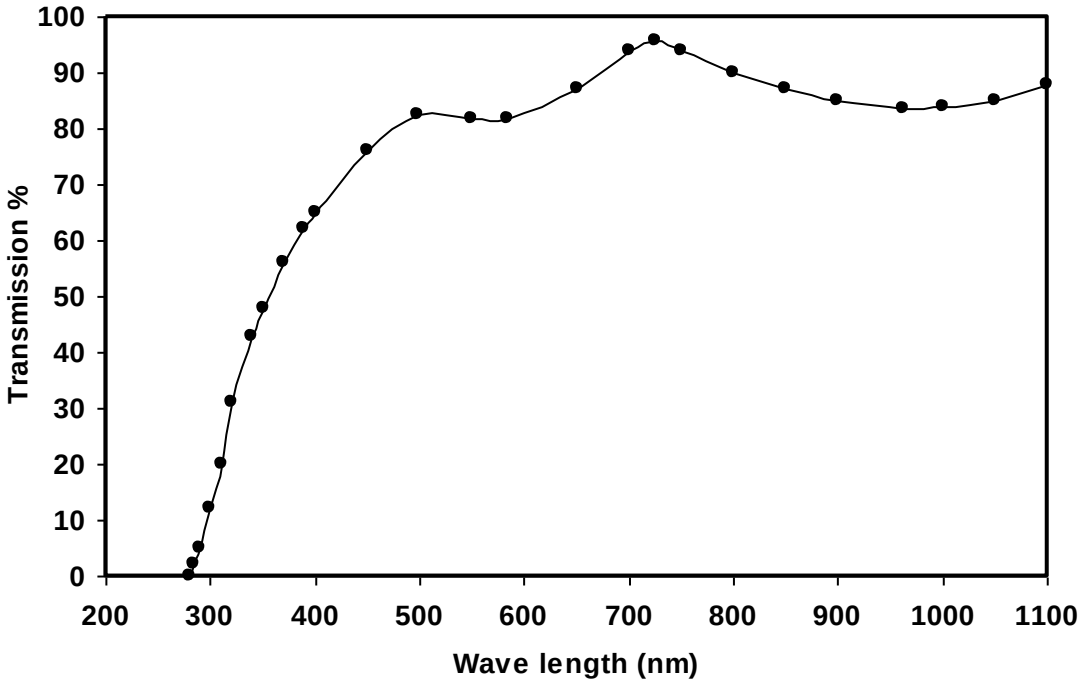


Fig.(7) Transmission Spectrum for SnO2 Thin Film

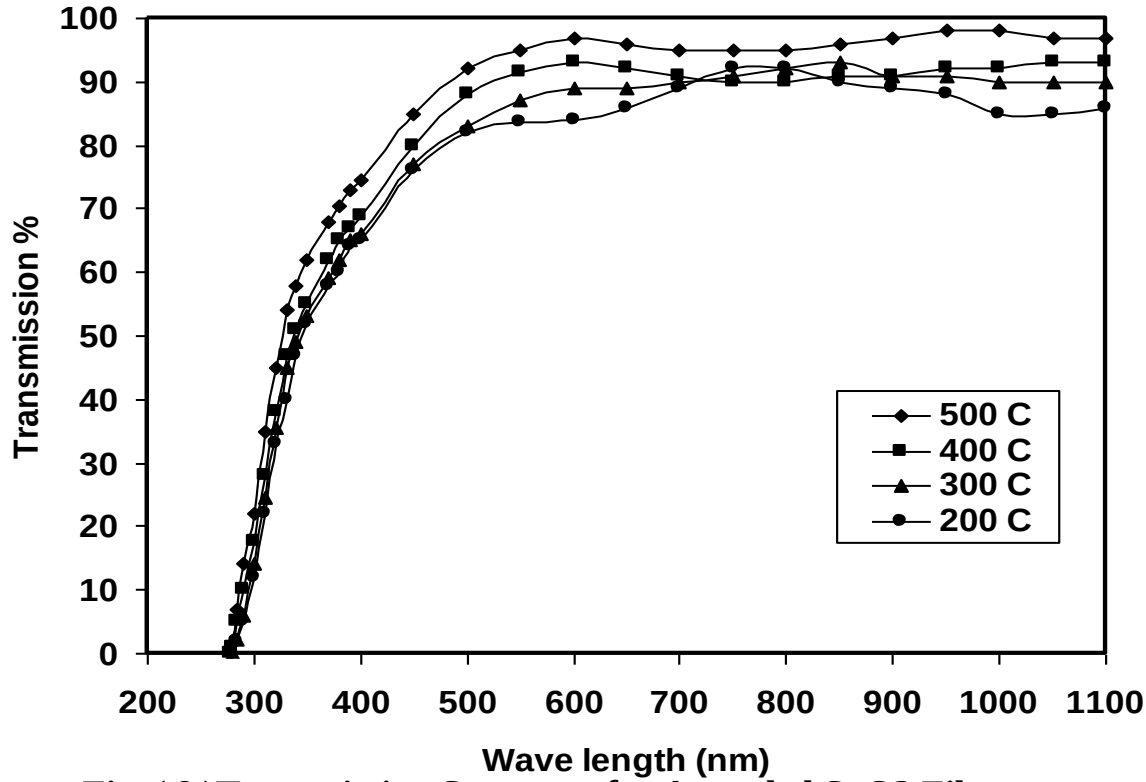


Fig. (8)Transmission Spectrum for Annealed SnO2 Film

Figure (9) displays the absorption coefficient (α) as a function of the photon energy (Eph) for annealed and unannealed SnO2 films. It is clear that α increases by Eph increment. The linear portion are extrapolated at zero absorption to give absorption edge energies (Eab). The values of Eab lie between (3.93-4.1) eV. And the film annealed at highest annealing temperature has the highest Eab and vice versa.

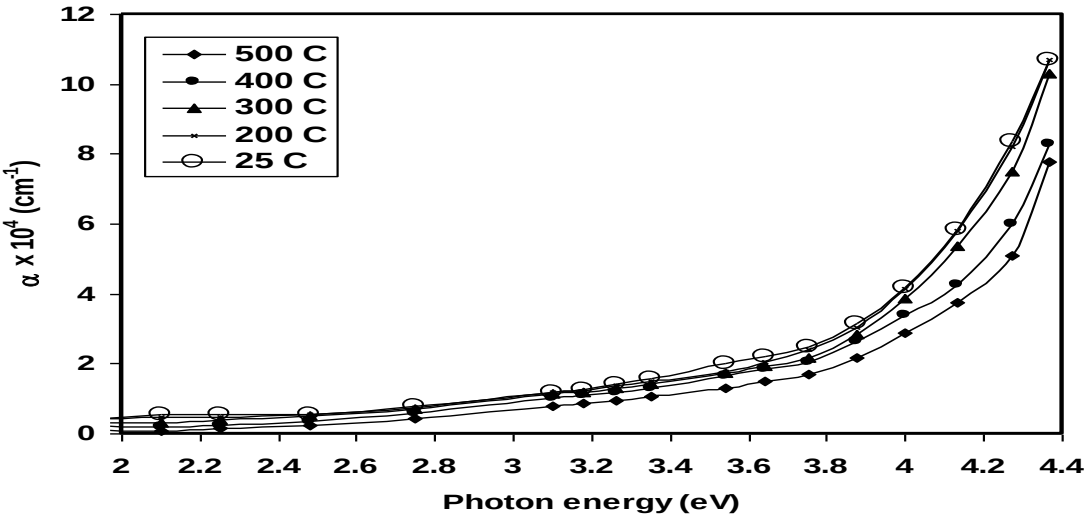


Fig.(9) α Versus Eph for Annealed and Unannealed SnO2 Films

A plot of α2 versus photon energy for annealed and unannealed SnO2 films was shown in Fig.(10). The linear portions are extrapolated to zero absorption at energies of optical energy gap (Eg). The average values of Eg is 4.17eV and it dose not affected by annealing.

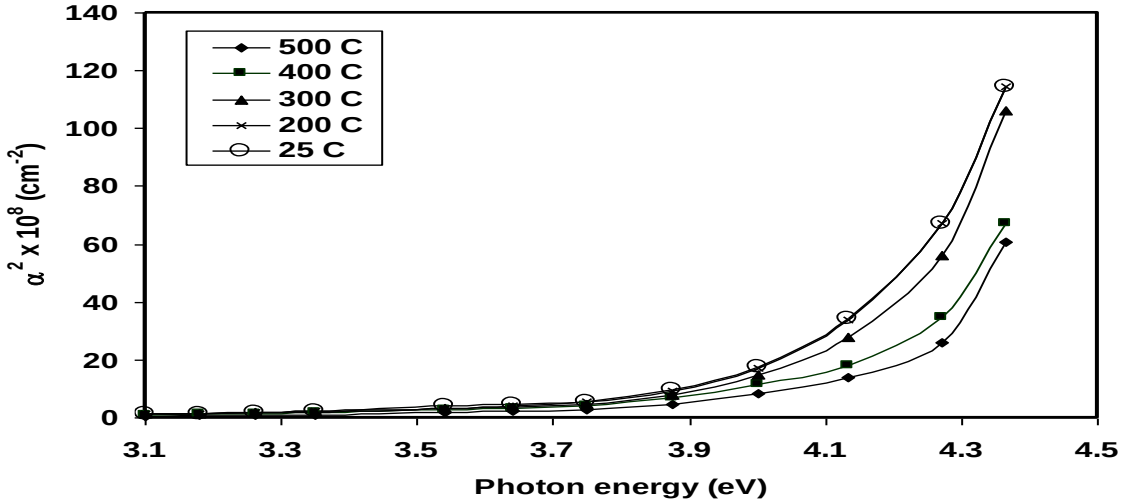


Fig.(10) α2 Versus Eph for Annealed and Unannealed SnO2 Films

Conclusions

1- SnO_2 films deposited by chemical vapor deposition is a tetragonal polycrystalline structure with (110) plane as preferred crystal plane orientation.
2- Annealing SnO_2 film in air increases the grain size in the preferred orientation plain.
3- Absorbed oxygen from air during annealing fill the oxygen vacancies and oxidize the interestial tin atom in the crystal structure.
4- SnO2 films are transitive in the visible region. Its transmission percent increases by annealing specially at (400-600) nm .

5- The absorption edge energy for SnO_2 film increases by annealing. The values of Eab for SnO_2 film annealed at (200,300,400,500)°C are between (3.93-4.1)eV.
6- The energy gap dose not affected by annealing and its average value equal to (4.17)eV.

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