Structural and Optical characterization of Nanocrystalline SnO_2 thin film prepared by spray pyrolysis technique

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Abstract

Nanocrystalline Tin Oxide SnO_2 thin films have been grown on cleaned glass substrates at 450 C° using spray pyrolysis deposition technique, prepared from two precursor solutions $SnCl_2.2H_2O$ and $SnCl_4.5H_2O$.The XRD analyses showed that these films have polycrystalline in nature with tetragonal rutile structure with preferred orientation of (110),(200),(211) and the crystalline size (grain size) of thin films are found to vary from 32.6 to 56.98 nm .

UV -VIS spectra of the films were studied using the optical absorbance measurements which were taken in the spectral region from 190 nm to 1100 nm. The transmittance and ref1ectance spectra of the films in the UV -VIS region were also studied. Optical Constants such as optical band gap, absorption coefficient and extinction coefficient, were evaluated from these spectra. All the films were found to exhibit high transmittance greater than (~ 85 %), and high absorbance values at ultraviolet region which they decrease rapidly in the visible / near infrared region. The optical band gap energy was found 3.98 eV for sample A and 3.97 eV for sample B.

Keywords: SnO_2 thin film, Nanocrystalline, TCO spray pyrolysis, structural and optical properties.

الخصائص التركيبية والبصرية لأغشية SnO_2 نانوية التبلورالمحضرة بتقنية الرش الحراري

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الخلاصة

حضّرت اغشية اوكسيد القصدير SnO_2 نانوية التبلورعلى قواعد زجاجية نظيفة مسخنة بدرجة حرارة 450 C° بأستعمال طريقة الرش الكيميائي الحراري. أذ حضرت من محلولين أوليين هما محلول $SnCl_2{\cdot}2H_2O$ لنموذج A ومحلول $SnCl_4{\cdot}5H_2O$ لنموذج B . وقد بينت نتائج فحوصات الاشعة السينية XRD ان كافة الاغشية المحضرة ذات تركيب متعدد التبلور polycrystalline من نوع رباعي قائم tetragonal وباتجاهية سائدة (211),(200),(110) والحجم البلوري (الحجم الحبيبي) للأغشية المحضره يتراوح من 32.6 الى 56.98 nm. درست اطياف الاشعة المرئية- فوق البنفسجية للاغشية بأستخدام حسابات الامتصاص البصري والتي اخذت في المنطقة الطيفية 190 nm- 1100 nm . كما درست ايضاً النفاذية والانعكاسية للاغشية في المنطقة المرئية فوق البنفسجية UV -VIS ومن هذه الاطياف حسبت الثوابت البصرية مثل فجوة الطاقة البصرية ومعامل الامتصاص ومعامل الخمود ،واظهرت جميع الاغشية نفاذية عالية اكثر من (% 85 ~) وامتصاصية عالية في المنطقة فوق البنفسجية وتقل بالتدريج في المنطقة المرئية/تحت الحمراء القريبة . وجدت قيمة فجوة الطاقة البصرية تساوي 3.98 eV بالنسبة للنموذج A و3.97 eV بالنسبة للنموذج B .

1. Introduction

Semiconductors nanomaterials are of current interest due to their unique optical and electronic properties which are different from that of the materials in the bulk form. Transparent conducting oxide (TCO) films consist of degenerate wide band gap semiconductors with low resistance and high transparency in the visible region, tin oxide (SnO_2) has emerged as one of the most used transparent conducting oxide films [1]. Tin oxide is a crystalline solid with a tetragonal crystal lattice, Tin oxide can exist in two structures belonging to direct and indirect optical transitions ,with different band gaps ; a direct band gap that ranges from 3.6 to 4.6 eV at room temperature and indirect bandgap of about 2.6 eV[2,3] .Tin oxide has been extensively investigated for gas sensors[4] , electrocatalytic anodes[5], and optical-conductive coatings for solar cells[6], glass coatings for furnace windows as well as transparent electrodes for liquid crystal displays[7] , flat-panel displays[8]and defrosting windows[9]. SnO_2 films have been fabricated using various technologies, including sputtering, chemical vapor deposition CVD [10], spray pyrolysis [11], atomic layer deposition (ALD) [12], pulsed laser deposition (PLD)[13], physical vapor deposition (PVD)[14], sol-gel [15] and Chemical bath deposition (CBD) [16]. In this study tin oxide thin films were prepared by the spray pyrolysis technique, the spray pyrolysis technique is particularly attractive because of its simplicity. It is fast, inexpensive, vacuumless and suitable for mass production [17]. In this work, we have investigated the structure and optical properties of SnO2 films deposited onto glass substrates using the spray pyrolysis technique.

X-ray diffraction measurements with Cu-K_α (λ = 1.5405 Å)□□ Shimadzu 6000 diffractometer , operating at 30 mA and 40 kV. The transmittance and absorbance of the films were measured using UV-VIS spectrophotometer Shimadzu UV-1650 in the spectral range 190-1100 nm.

2. Experimental

Two samples of nanocrystalline SnO_2 thin films were prepared by spray pyrolysis technique using different precursor materials. Sample(A) an amount of 11g of $SnCl_2.2H_2O$ was dissolved in 5 ml of concentrated hydrochloric acid (HCl) by heating at 90°C for 10 minutes. The addition of HCl rendered the solution transparent [18], mostly, the transparent solution thus obtained and subsequently diluted by methanol the amount of spray solution was made together 50 ml, microscope glass slides, cleaned with organic solvents, were used as substrates. The substrate temperature was fixed at 450□C^o. Sample (B) by addition 8.76 gm of $SnCl_4.5H_2O$ was dissolved in 250 ml of distilled water with some drops of HCl [19] with the same substrates temperature. The structure of the films was determined by

3. Results and Discussion

3.1 structural properties:

The crystal structures of the films were identified by XRD measurements. The diffraction data were collected at width over a 2θ range from 0 to 60°.The prominent peaks for sample A at 2θ = 26.510° ,38.00° ,51.960° and for sample B at 2θ = 27.375° ,38.7° ,52.50° belongs to (110) , (200) , (211) planes . (Fig.1-A,B) shows all the peaks presents in consideration with (110) as preferential orientation for both samples. The X-ray diffraction studies showed that the films are polycrystalline in nature having nanosize

scale with tetragonal rutile structure as confirmed by standard JCPDS data (card no.46-1088) .The structural properties as shown in (table 1). The crystallite size (grain diameter), *D*, of the deposit was determined using the Debye-Scherer's equation [20,21]:

$$D = \frac{K\lambda}{\omega \cos\theta} \text{.....(1)}$$

where λ is the wavelength of X-rays, θ the Bragg angle and ω the full width at half maximum(FWHM) in radian. *K* varies with (*h k l*) and crystallite shape but usually nearly equal to 0.9 [22], values of the grain size are given in Table1. The Crystallite size was found to be varying between 32-56 nm for both samples. The lattice constant of the spray coated Tin oxide films calculated using the formula [22, 23]:

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

Where'd' is the interplanar distance, (h k l) are the Miller indices, 'a' and 'c' are the lattice constant for the tetragonal structure, they are evaluated as in table 1 which is well in agreement with the standard values of JCPDS data.

3.2 Optical properties:

Fig.(2) shows the optical transmission spectra of the two films (A) and (B).This film shows more than 85% transmission in the wavelength range between 300 and 1100 nm for both films, this behavior is similar to the behavior in the transmission spectra of SnO_2 films prepared by chemical spray pyrolysis [24].

The absorbance spectra of SnO_2 films is shown in fig.(3). It can be noticed high absorbance at ultraviolet region, then it decrease rapidly in the visible near infrared region from 400 nm to 1100nm.

Absorption Coefficient

From the absorbance data, the absorption coefficient α. was calculated in the fundamental absorption region .using Lambert law [25,26]:

$$Ln(I_\circ / I) = 2.303A = \alpha d$$

$$\alpha = 2.303A / d \text{.....(3)}$$

Where $I_\circ$ and I are the intensity of incident and transmitted light respectively ,A the optical absorbance and d the film thickness. Fig.(4) shows the variation of absorption coefficient with photon energy for both SnO_2 thin film ,the figure also shows the variation of absorption coefficient in the low energy range then its value increase rapidly beyond absorption edge region . It can be seen that SnO_2 thin film has high value of absorption coefficient (a > 10^4 cm^{-1}) which is conducive to increasing the probability of occurrence direct transitions.

Extinction Coefficient

Extinction coefficient (k) of prepared films was calculated by .using the relation[27,28]:

$$K = \frac{\alpha\lambda}{4\pi} \text{.....(4)}$$

Where λ is the wavelength of the incident photon. Variation of extinction coefficient as a function of photon energy is shown in fig. (5),the extinction coefficient of prepared film has values in the range (0.0076 - 0.1671) for sample A and in the range (0.0281- 0.134) for sample B. The_rise and fall in the extinction coefficient are directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries [24].This leads to non-~zero value of k for photon energies smaller than the fundamental absorption edge.

Reflectance

Fig.(6) shows the optical reflectance spectra for SnO_2 thin films. The reflectance has been found by using the relationship [25, 28]:

$$R+T+A=1 \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

The figure also shows that the film reflectance decreases rapidly at low energies and then increases at photon energy less than the energy band gap, and then makes peaks at the energies which are corresponding to the energy gap of the film.

Refractive Index

From the reflectance data, the refractive index (n) was calculated by using the following relationship [25,29]:

$$n=\frac{1+\sqrt{R}}{1-\sqrt{R}} \quad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Fig.(7) shows the variation of refractive index with photon energy of SnO2 thin film. The behavior of this figure is similar to the behavior of reflectance spectra in fig (5), because of the strong dependence calculation of the refractive index values on the reflectance values as above relationship, the results show that the refractive index values of prepared film are in the range(1.639-2.64)eV for sample A and in the range (1.685-2.60)ev for sample B.

Optical Conductivity

From the below relation we can calculate the optical conductivity σ[30,31]:

$$\sigma=\frac{\alpha n c}{4\pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Where c is the velocity of light. The optical conductivity versus photon energy curve is shown in figure (8). It can be noticed from the fig. the slow variation of optical conductivity in the low energy range then its value increases rapidly beyond absorption edge region, because of the high increase of the absorbance in this region.

Energy Gap

Study of material by means of optical absorption provides a simple method for explaining some features concerning the band structure of material. In the present investigation, optical absorption (fig.2) in SnO_2 films were studied in the wavelength (190-1100) nm.

The nature of transition (direct or indirect) is determined by using the relation[31,32]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Where hv is the photon energy, Eg the band gap energy, A and n are constants. For allowed direct transition, n = 1/2 and for allowed indirect transition, n =3/ 2. The plots of $(\alpha h\nu)^2$ vs. hv are shown in figures (9&10), for SnO_2 films. The linear nature of the plots indicates the existence of direct transitions. In fig. (9) from the straight line obtained at high photon energy the direct allowed energy gap could be determined which was equal(3.98 eV) for the sample A, while fig.s (10) shows that the direct allowed energy gap equal (3.97 eV) for sample B. This result was in good agreement with the results in reference [2], which is from (3.6-4.6)eV.

4. Conclusion

Nanocrystalline SnO_2 thin film with different precursor materials have been prepared by spray pyrolysis technique using a different solution of $SnCl_2.2H_2O$ and $SnCl_4{\cdot}5H_2O$, the two films A and B were deposited on a glass substrate at temperature (450°C) which thickness(167.50,126.56)nm. The film exhibits high transmittance (~85%) and high absorbance values at ultraviolet region which they decrease rapidly in the visible / near infrared region, the film shows a direct transition which was (3.984eV) for allowed energy gap for sample (A) and (3.97eV) for allowed

energy gap for sample (B). In conclusion, spray pyrolysis method for the production of thin solid films is a good method for the preparation of thin films which are suitable for scientific studies and for many applications in technology and industry.

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Table 1: Structural parameters of SnO_2 thin films sample A and B.

Sample	Precursor	Structure	Lattice constant (A°)		2θ (degrees)	*h k l*	*d* spacing		Grian size nm
			a	c			Obtained value	JCPDS value	
A	$SnCl_2 \cdot 2H_2O$	Tetragonal	4.754	3.1833	26.510 38.00 51.690	110 200 211	3.362 2.367 1.768	3.3510 2.3799 1.7648	32.67 56.18 44.13
B	$SnCl_4 \cdot 5H_2O$	Tetragonal	4.600	3.280	27.375 38.700 52.50	110 200 211	3.253 2.320 1.7429	3.3510 2.3799 1.7648	33.10 56.31 44.31

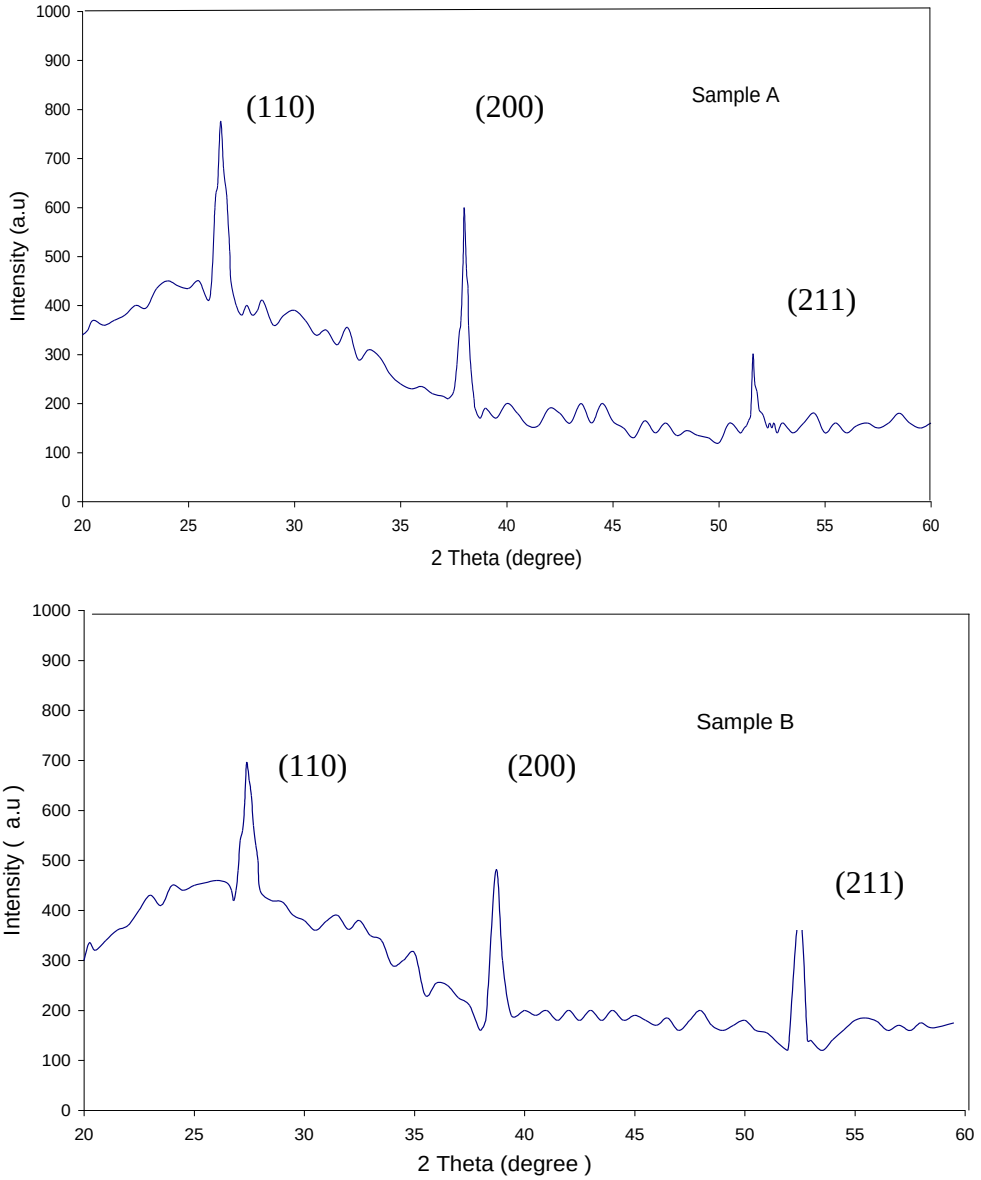

Fig.1 XRD patterns of SnO_2 thin films sample (A) from $SnCl_2.2H_2O$ precursor and sample (B) from $SnCl_4.5H_2O$ precursor.

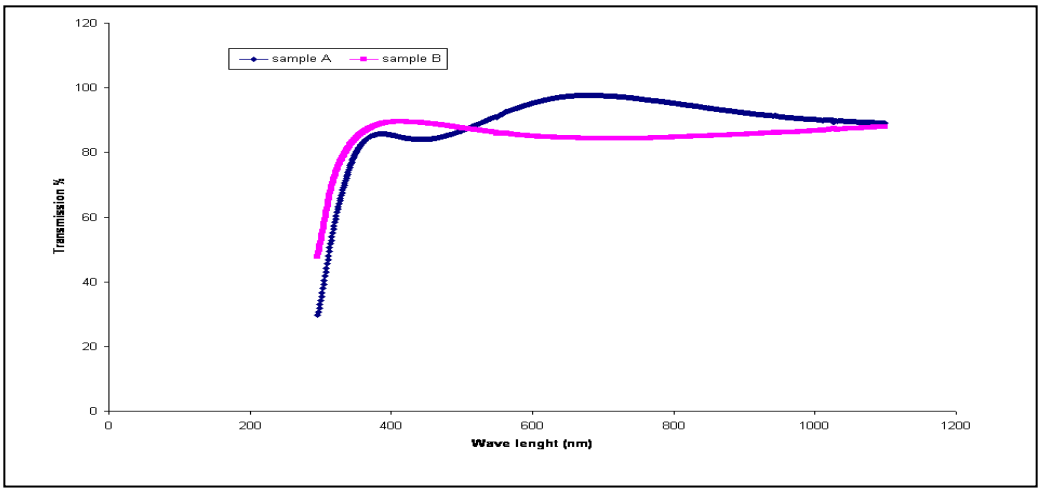

Fig. (2) Transmission spectra of SnO_2 thin films.

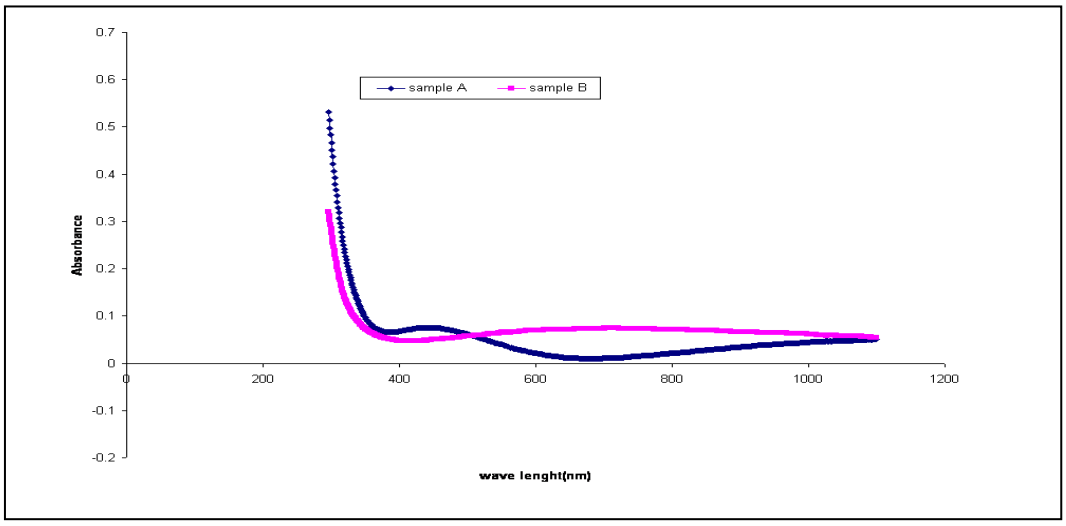

Fig. (3) Absorbance spectra of SnO_2 thin films.

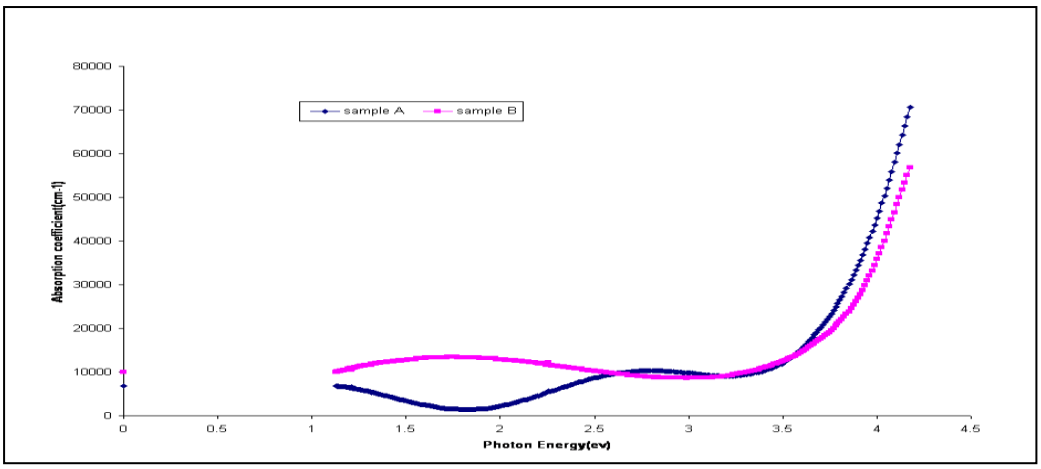

Fig. (4) Absorption coefficient vs. photon energy of SnO_2 thin films.

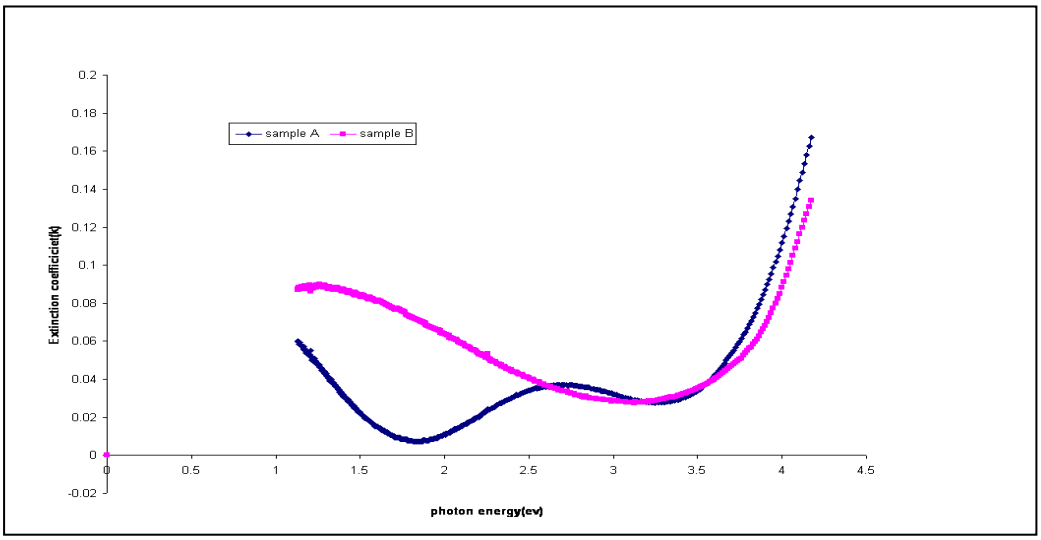

Fig. (5) Extinction coefficient vs. photon energy of SnO_2 thin films.

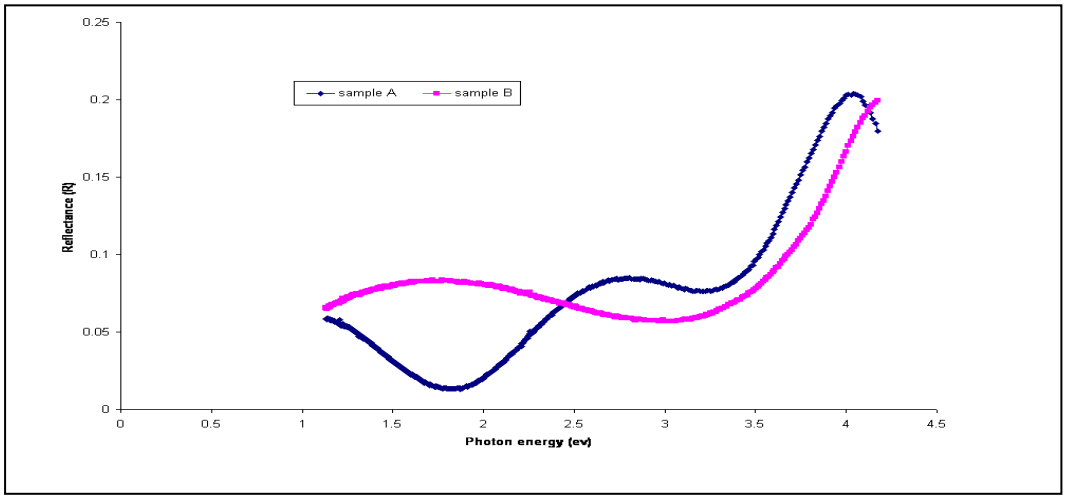

Fig. (6) Reflectance vs. photon energy of SnO_2 thin film.

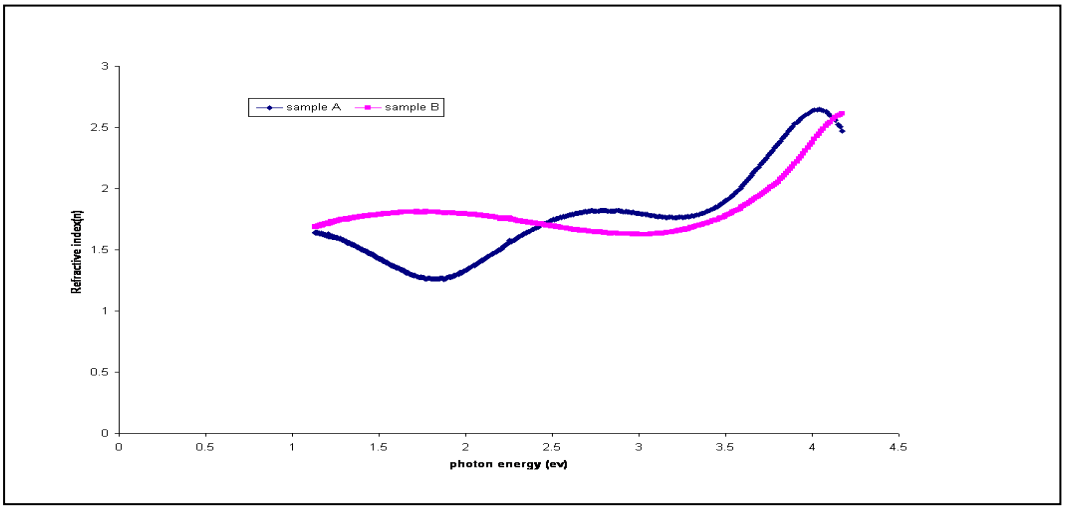

Fig. (7) Refractive index vs. photon energy of SnO_2 thin films.

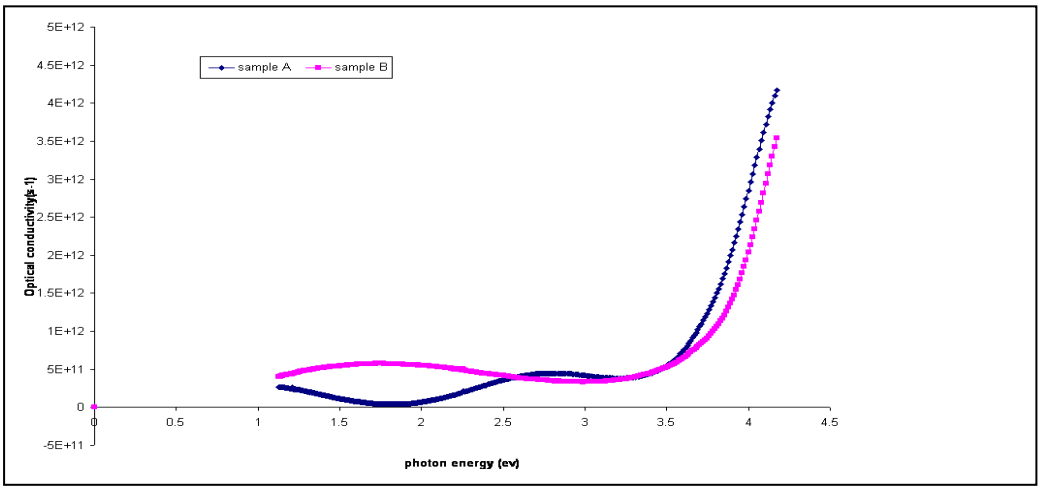

Fig. (8) Optical conductivity vs. photon energy for SnO_2 thin films.

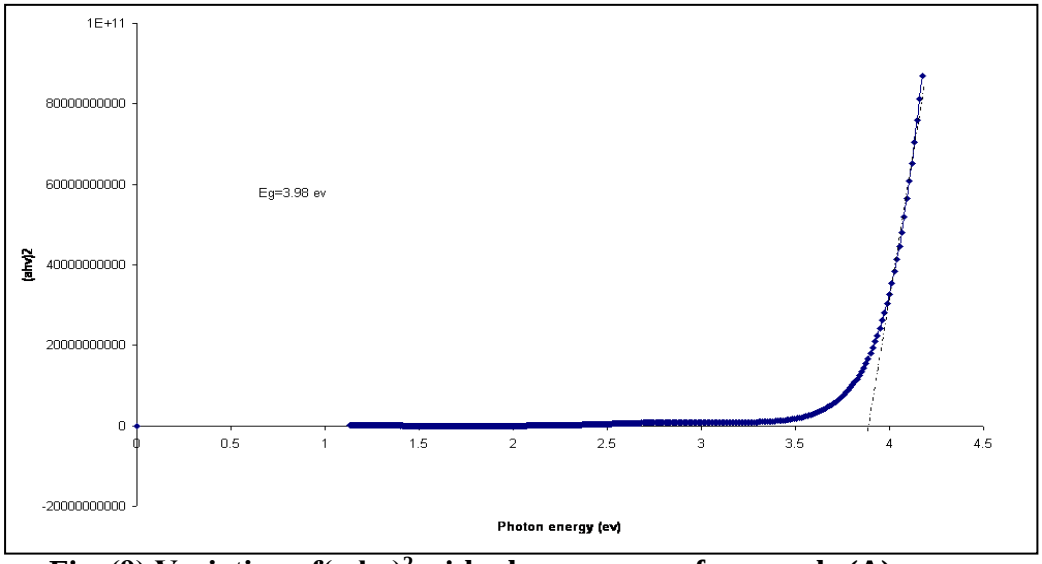

Fig. (9) Variation of$(\alpha.h\upsilon)^2$ with photon energy for sample (A).

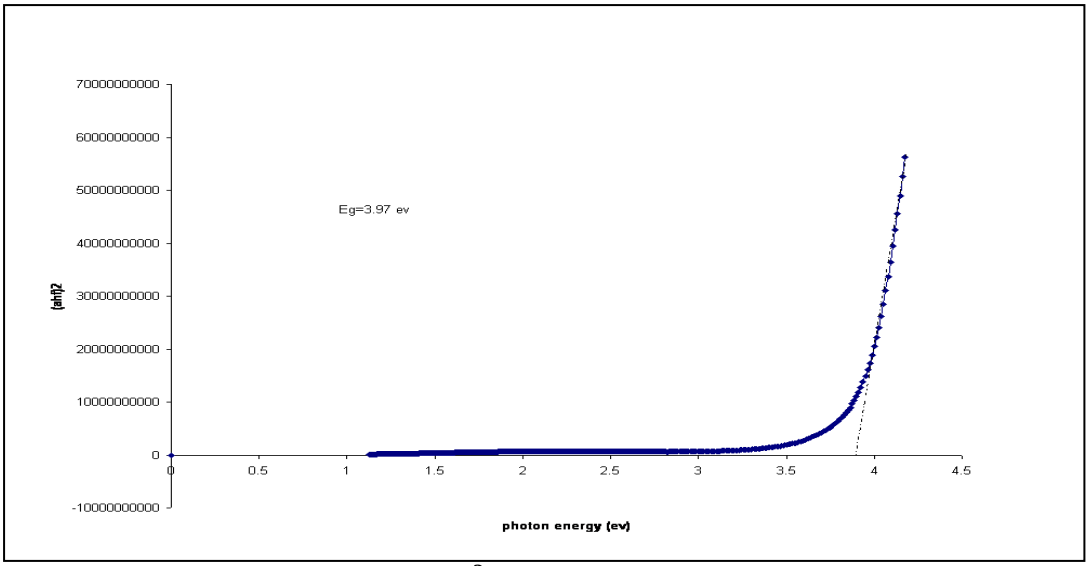

Fig. (10) Variation of $(\alpha.h\upsilon)^2$ with photon energy for sample (B).