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Structural and optical characterisation of thermally evaporated tungsten trioxide (WO_3) thin films

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ABSTRACT. Thin films of amorphous tungsten trioxide (WO_3) have been thermally evaporated onto quartz substrates held at 350K. Annealing at 725K caused the formation of crystalline WO_3. XRD analysis revealed monoclinic structure with lattice parameters of a=7.311±0.05 Å, b=7.603±0.05 Å, c=7.713±0.05 Å and β=91.137°. Optical properties were investigated for both the amorphous and annealed films by using spectrophotometric measurement of transmittance and reflectance at normal incidence in the wavelength range of 200-2500 nm. The obtained spectra showed that all the films are transparent above λ=500 nm and the measured optical constants are independent of the film thickness. Both the refractive index, *n*, and absorption index, *k*, were determined for the amorphous and crystalline films. The optical dispersion parameters have been analysed by single oscillator model. The values of E_o and E_d were found to be 5.86, 14.43 eV for the amorphous films and 2.96, 11.30 eV for the crystalline films. Indirect optical transitions with corresponding energy gaps = 3.28 and 3.03 eV for amorphous and crystalline films, respectively, were obtained. The obtained results are compared and discussed.

Keyword: Thin films, Tungsten trioxide, Optical constants

1. Introduction

Transition metal oxides constitute a very interesting class of materials because of the various properties that they exhibit. Among the thin films of transition metal oxides, tungsten trioxide (WO_3) has received increasing attention because of their electrochromic properties in the visible and infrared. Their optical properties can be switched reversibly under certain electrochemical conditions (Smith, 1982). During the last several decades, many materials have been examined with respect to their use in switchable windows (Lampert *et al.* 1989, Agrawal *et al.* 1993, Akl *et al.* 2003). WO_3 still seems to be among

the best inorganic electrochromie material due to its high coloration efficiency and relatively low price. Thc eleetrochromic materials ean bc switched from transparent to coloured state by using an external voltage and a proton source. In this way, the change of state can be described by a simultaneous injeetion and extraction of the eleetrons and protons (Lampert *et al.* 1989, Agrawal *et al.* 1993). This phenomenon is applied in electrochromie, optiochromic and thermo-chromic dcviees, sueh as energy saving windows (smart windows), solar roofing, anti glare rear-view mirrors and gases sensors (Hoei *et al.* 2000).

In polycrystalline films, the injected cleetrons behave as free-carriers leading to an increase in near infrared (NIR) reflectivity (Goldner *et al.* 1986, Kamal *et al.* 2004). Nevertheless, scattering of the excess free electrons by extended defects, leads to lower reflectivity in this region (Goldner *et al.,* 1984) The characteristics of WO_3 films depend strongly on the eondition of film preparation. Different techniques used for WO_3 films preparation such as, thermal and electron beam evaporation (Agrawal *et al.,* 1993), RF sputtering, chemical vapour deposition (CVD), anodic oxidation, sol-gel (Ozkan *et al.,* 2001), spray pyrolysis (Regragui *et al.,* 2003) and magnetron sputtering (Akl *et al.* 2003, Kamal *et al.* 2004) are used..

In this work, amorphous tungsten oxidc films have been prepared by thermal evaporation. The changes in the structural and optical properties of the as deposited and annealed films as a function of film thickness in thc amorphous and polycrystalline were investigated. The structural and morphological changes duc to annealing are pitied. Thc optical properties for both types of films have been invcstigatcd

2. Experimeutal procedure

Tungsten trioxide (WO_3) powder used in this study was obtaincd from BDH chemical Ltd Co., with purity of 99.986%. Thin films of different thicknesses werc deposited by vacuum thcrmal evaporation method, using a high vacuum coating unit (Edwards, E306A). The films were deposited onto prc-eleaned glass (for structural investigation) and optically flat quartz substrates (for optical investigation) maintained at 350 K. Thin films wcrc deposited from a molybdenum evaporator charged by WO_3 in a vacuum of 10^{-5} Pa. Thc deposition rate was controlled at $1 nms^{-1}$ using a quartz crystal thickness monitor (FTM6, Edwards). The film thickness ranged bctween 100 nm and 300 nm. Thickness of thc film is determined by Tolansky's technique (Tolansky, 1988). The films were thcn annealcd at 723 K for 2 hour in air.

Thc structural properties of powder and thin films wcrc studied using X-ray diffraction technique. A Philips X-ray diffractometer (model X' pert) was used for thc measurements, which utilized monochromatic Cuk_α radiation operatcd at 40kV and 25mA. Thc diffraction patterns were recorded automatically with a scanning speed of 0.05 degrees per minute.

Optical propcrties werc investigatcd for both the as depositcd and annealed films by spectrophotometric measurement of transmittance, T, and reflectancc, R, at normal incidence in the wavelength range of 200-2500 nm using a double beam spectrophotometer (JASCO modcl V570-UV-VIS-NIR).

Thc $T(\lambda)$ and $R(\lambda)$ werc calculated according to the relations (Agiev *et al.* 1978, Shklyarevskii *et al.* 1969).

$$T(\lambda) = (I_{fr}/I_q)(1-R_q) \quad (1)$$

and

$$R(\lambda) = (I_{fr}/I_{Al})R_{Al}[1+(1-R_q)^2]-TR_q \quad (2)$$

where I_{fr} and I_q are the intensities of light passing through film-quartz system and referenee quartz substrate respectively. I_{fr} and I_{Al} are the intensities of light reflected from the sample and that from the referenee mirror, respectively, and R_q is the reflectance of quartz. The refractive index, n, and the absorption indcx, k, were computed by a modified version (El-Nshass *et al.,* 1988) of Abélés technique (Abeles & Theye, 1966) based on solving the two non-liner equation:

$$f_t(n,k) = T_{n,k} - T_{exp} = 0 \quad (3)$$

$$f_r(n,k) = R_{n,k} - R_{exp} = 0 \quad (4)$$

wherc $T_{n,k}$ and $R_{n,k}$ refer to Murmann's exact equations (Heavens, 1965). The experimental errors were taken into account as ±5% for the film thickness measurements and ±1% for T and R. Calculations revcaled error of ±5% for the refractive and 3 % for the absorption index.

3. Results and discussion

3.1. *Structural properties*

X-ray diffraction (XRD) patterns obtained from powder and thin film forms of tungsten trioxide (WO_3) are shown in Fig 1. It shows that the X-ray diffraction pattern of the as-deposited films is amorphous in naturc and it exhibits a broad peak around $2\theta = 23°$. The effect of anncaling on thc structure of the WO_3 film is, also, shown in Fig. 1. When the amorphous film was annealcd at 723 K 2h, the X-ray diffraction pattern exhibited a new diffraction pattern with four peaks, which was identified primarily as polycrystalline monoclinic WO_3 phase with reference to thc powder diffraction pattern. It can be noted that the pattern for both powdcr and thin film show polycrystalline form. Indexing was carried out for the patterns and thcir peaks were identified as monoclinic crystal system with lattice constants of $a = 7.311 \pm 0.05$ Å, $b = 7.603 \pm 0.05$ Å, $c = 7.713 \pm 0.05$ Å and $\beta = 91.137°$ (ICDD Card No.83-0951 for WO_3).

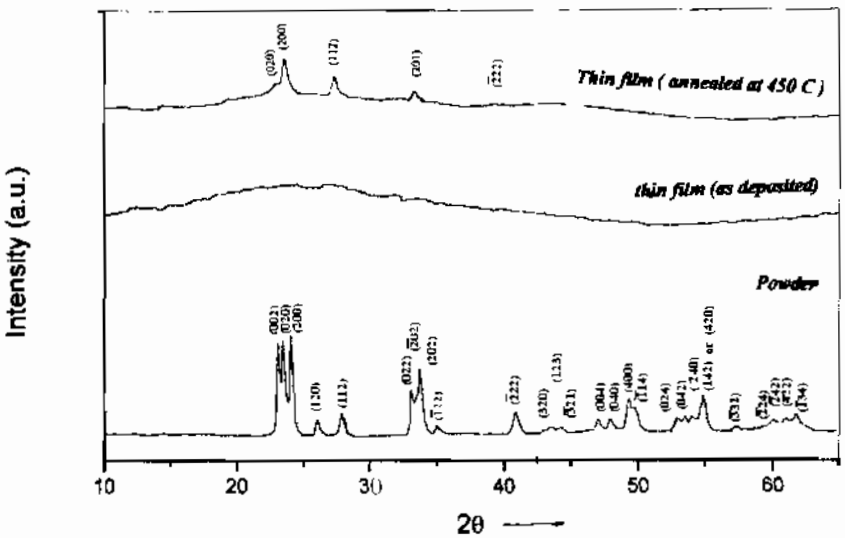


Fig. 1. X-ray diffraction pattern of WO_3 in powder and thin film forms.

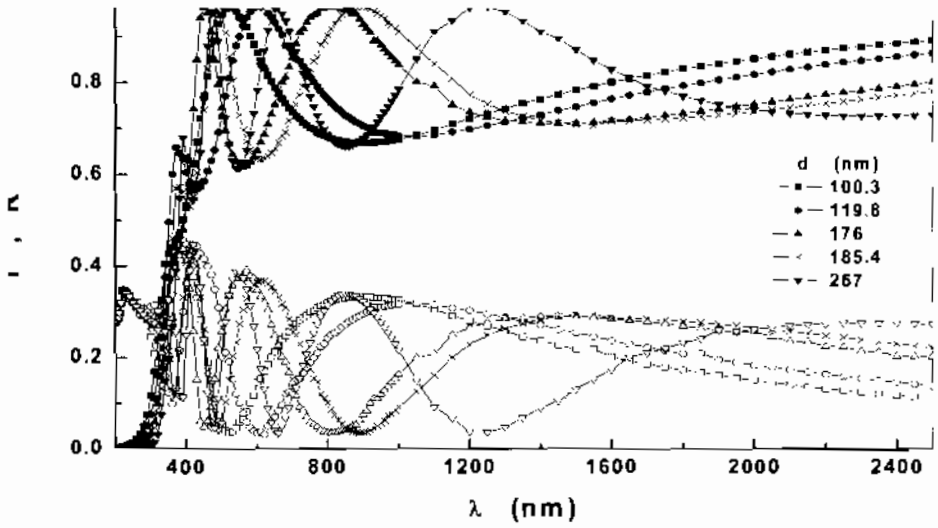


Fig. 2. Spectral distribution of normal incidence transmittance, T, and reflectance, R, for amorphous WO_3 films with different thicknesses.

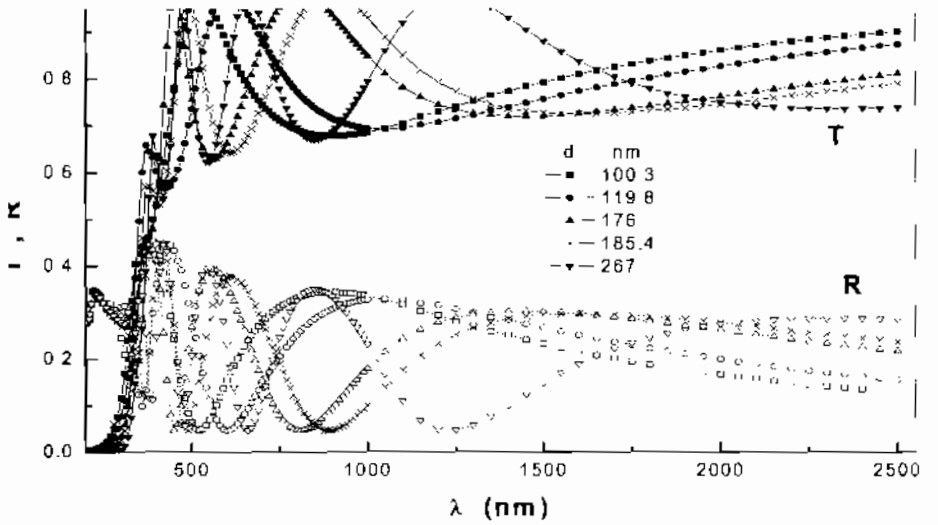


Fig. 3. Spectral distribution of normal incidence transmittance, T, and reflectance, R, for Crystalline WO_3 films with different thicknesses

3.2. *Optical properties*

Figs. 2 and 3 show the spectral transmittance and reflectance for as-deposited films at different thieknesses and for the same films annealed at 723 K for 2h, in the wavelength range 200-2500 nm, respectively. As a general observation, it can be noted that beyond the absorption edge, λ>500 nm, T + R = 1 which implies that all films become transparent and no light is scattered or absorbed. The optical constants (real and imaginary parts of the complex refractive index) were determined from the absolute values of transmittance and reflectance of films by exact formulas (Heavens, 1965).

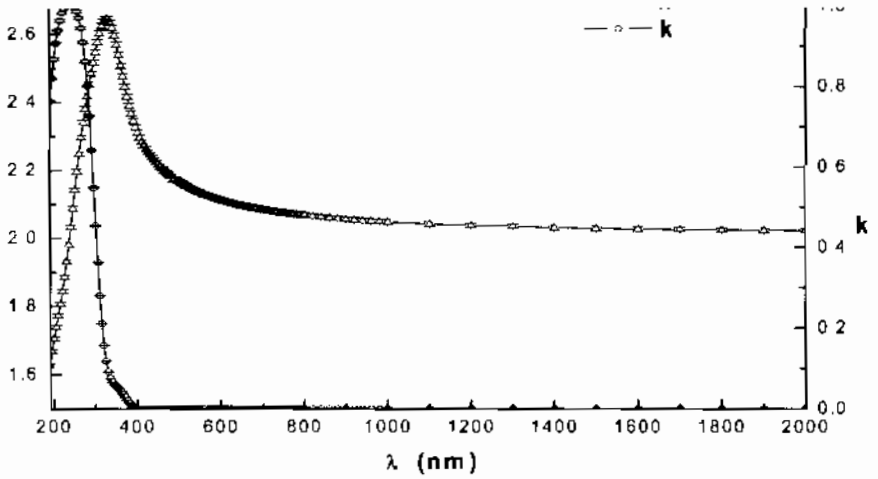


Fig. 4. Spectral behaviour of both n and k for amorphous WO_3 films

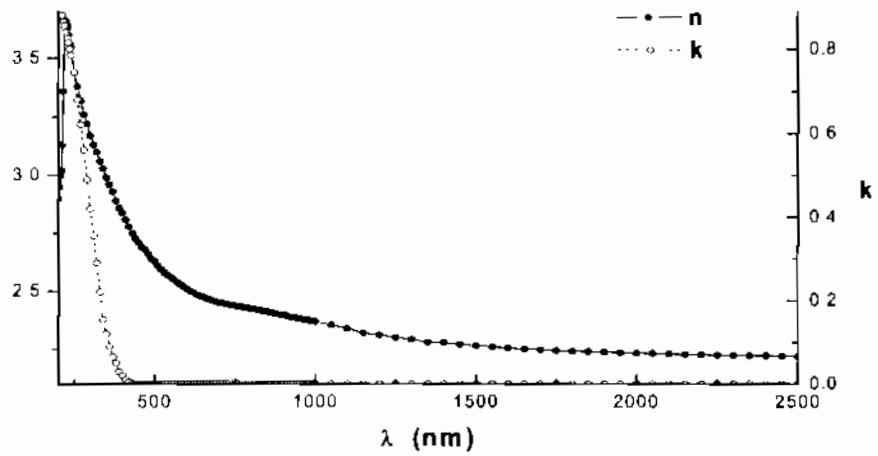


Fig. 5. Spectral behaviour of both n and k for crystalline WO_3 films

Fig. 4 and Fig. 5 show the spectral behaviour of both the refractive index, *n,* and the absorption index, *k,* in the wavelength range 200–2500 nm for the amorphous and crystalline films, respectively, they represent the average values of both *n* and *k* for the investigated thickness range 100-267 nm as a function of wavelength. The calculated standard deviation was found to be within the calculated experimental error indicating that the optical constants are indepeudent of the film thickness for the all studied films. It is clear that the peak value of n observed for amorphous films disappear upon annealing, which reflects structural changes as confirmed by X-ray study. Both curves show normal dispersion beyond $\lambda = 500$ nm.

The dispersion of refractive index, *n*, in WO_3 films was analysed using the concept of the single oscillator and can be expressed by the Wemple and DiDomenico relationship (Wemple & DiDomenco, 1971) as

$$n^2 - 1 = E_d E_0 / [E_0^2 - E^2] \qquad (5)$$

where E is the photon energy, E_o is the oseillator energy and E_d is the dispersion energy. The parameter E_d, which is a measure of the intensity of the inter-band optical transition, does not depend significantly on the band gap. A plot of $(n^2 - 1)^{-1}$ versus E^2 of amorphous and crystalline films is illustrated in Fig. 6 (a & b). The values of E_d and E_o were obtained

from the slope and the intercept resulting from the extrapolation of the lines as 14.43, 5.86 eV and 11.30, 2.96 eV, respectively, for the amorphous and crystalline films. As observed

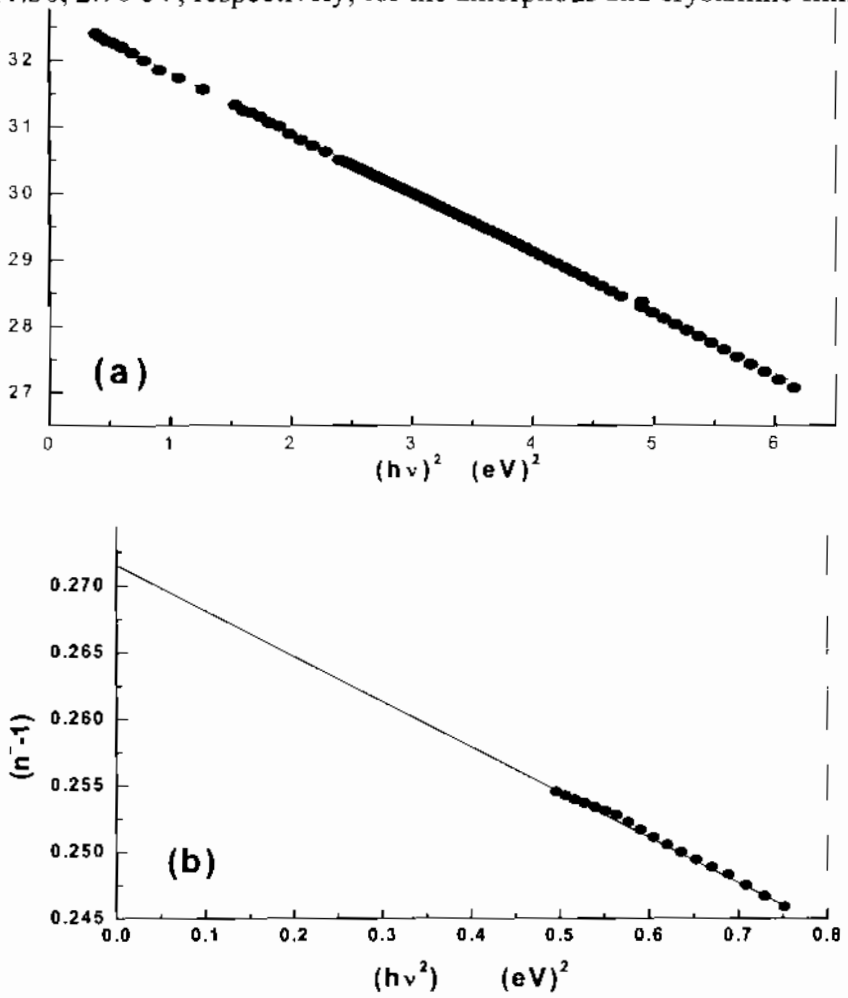


Fig. 6. A plot of $(n^2-1)^{-1}$ versus E^2 of (a) amorphous and (b) crystalline films

there is a little effeet of annealing on the oscillating and dispersion energies. The optical dielectrie constant ($\varepsilon_\infty = n_\infty^2$) was calculated as 4.72 and 3.52 for amorphous and crystalline films, respectively. A simple connection between the single oscillator parameters E_0 and E_d and the imaginary part of the dielectric constant $\varepsilon_2(v)$ spectrum can be expressed in terms of the r th moments of the $\varepsilon_2(v)$ as (Wemple & DiDomenco, 1971)

$$E_0^2 = M_{-1} / M_{3} \qquad (6)$$

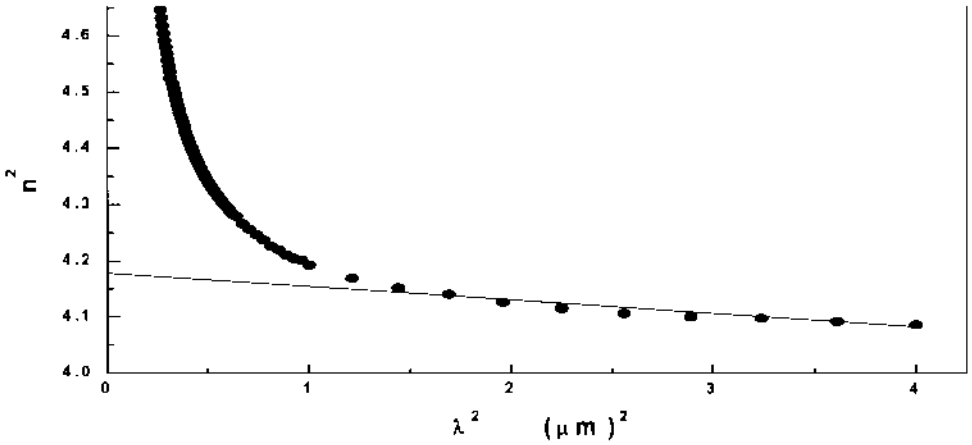
and

$$E_d^2 = M_{-1}^3 / M_{3} \qquad (7)$$

The oscillator energy E_0 is independent of the scale of ε_2. The values of M_{-1} and M_{-3} are 3.03 and 2.46 eV^{-2}, respectively, for the amorphous films and 0.09 and 0.07 eV^{-2}, respectively, for the crystalline films.

The relation between thc lattice dielectric constant, ε_L, wavelength, λ, and refractive index, n, is given by the relation (Robert *et al.* 1985)

$$n^2 = \varepsilon_L - e^2 / \pi c^2 (N / m^*) \lambda^2 \qquad (8)$$



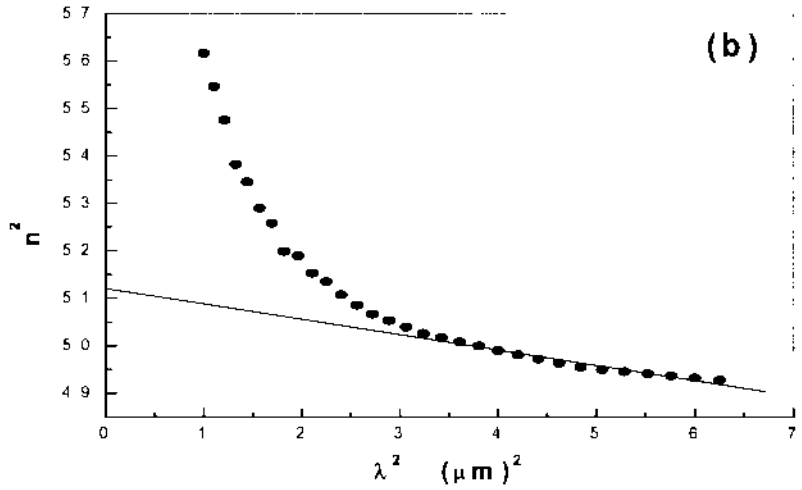


Fig. 7. Variation of n^2 versus λ^2 for (a) amorphous and (b) crystalline films.

Where ε_L is the lattice dielectric constant and N/m^* is the ratio of carrier concentration to the effective mass. The n^2 versus λ^2 plot shown in Fig. 7 (a & b) is linear at higher wavelengths verifying equation (8). The values of ε_L and (N/m^*) were determined from the extrapolation of these plots to $\lambda^2 = 0$ and from the slopes of the graph. The obtained values are 4.18 and 1.40639×10^{46} $gm^{-1}cm^{-3}$ respectively for the amorphous films and 5.125 and 2.27444×10^{47} $gm^{-1}cm^{-3}$, respectively, for the crystalline films. The disagreement between the values of ε_∞ and ε_L may be due to free carrier contribution.

In order to study the type of optical transitions as well as the value of the energy gap, the Bardeen equation was used in the following form (Bardeen *et al.* 1965)

$$(\alpha h\nu)^r = A\,(h\nu - E_g) \qquad (9)$$

Where A is a parameter that depends on the transition probability, E_g is the energy band gap and r is a number which characterizes the transition process, where r=2 and r=2/3 for direct allowed and forbidden transitions, respectively and r= 1/2 and 1/3 for indirect allowed and forbidden transitions, respectively. The plot of $(\alpha h\nu)^{1/2}$ versus hv give a straight line over a range above the absorption edge as shown in Fig. 8a for the amorphous and Fig. 8b for polycrystalline films. The weak absorption is assumed to be due to indirect transition involving participation of phonons in the process. A phonon is either emitted or

absorbed, depending on whether the energy of the phonon is more than the indirect band gap or less. The phonon associated with the transition process might be attributed to the stretching band of WO_3 having energy of 3.27 and 3.45 eV respectively for the amorphous and crystalline WO_3 films.

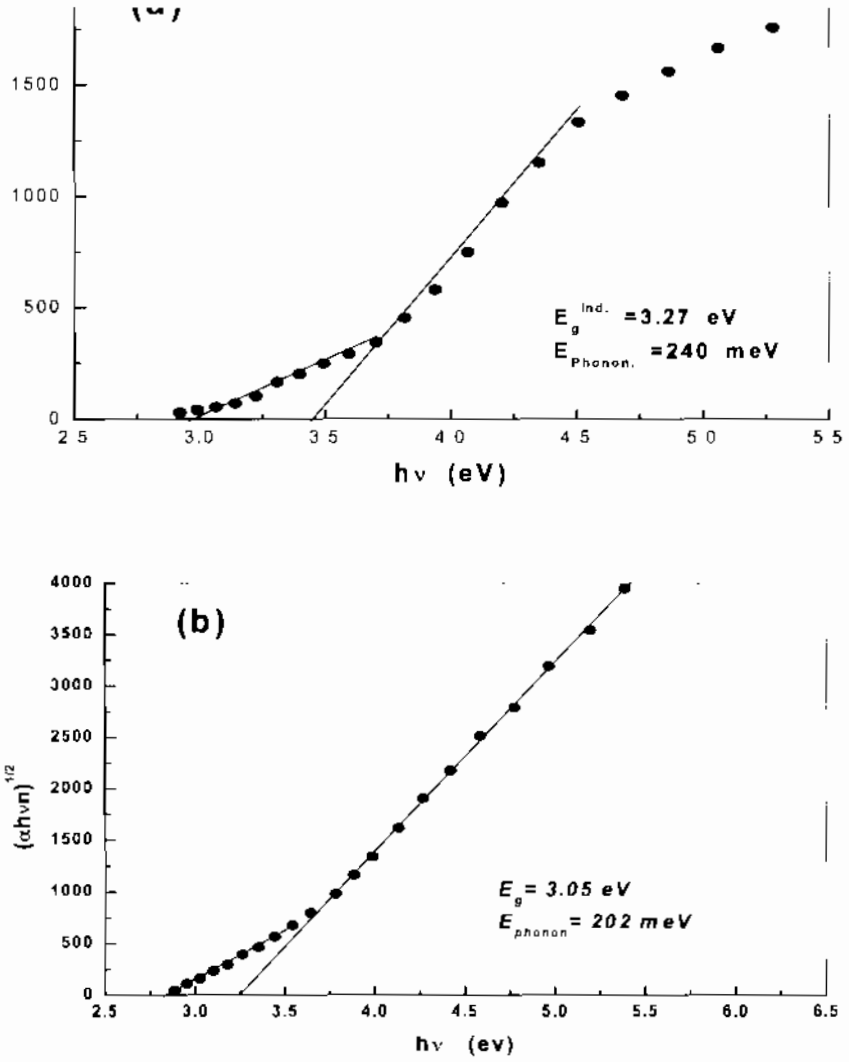


Fig. 8. Plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ for (a) amorphous aud (b) crystalline films

4. Conclusions

Amorphous tungsten oxide thin films have been thermally evaporated under vacuum of ~10^{-5} Pa. The X-ray study shows that transformation of the amorphous to crystalline occur at annealing temperature of 725 K. Formation of monoclinic phase of lattice constants of a=7.311±0.05 Å, b=7.603±0.05 Å, c=7.713±0.05 Å and β=91.137°. Calculation of the optical constants showed that both types of film pass normal desperation beyond λ=500 nm. Analyses of absorption part revealed an indirect gap for amorphous films.

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الخصائص التركيبية والضوئية لأفلام رقيقة من أكسيد التانجستين الثلاثي (WO_3) المحضرة بطريقة التبخير الحراري

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المستخلص. حضرت أفلام من أكسيد التنجستن الثلاثي بتقنية التبخير الحراري على شرائح من الزجاج المبلور (كوارتز) عند درجات حرارة ٨٠ الى ٢٥٠ درجة مئوية . وتم تلدين الأفلام عند درجة حرارة ٤٥٠ درجة مئوية مما أدى إلى تحولها من الحالة الأمورفية إلى المتبلورة وبتحليل نتائج الأفلام المتبلورة بتقنية حيود الأشعة السينية (XRD) اتضح تبلور المركب في نظام احادي الميل بثوابت شبكية

$$a = 7.311 \pm 0.05,\ b=7.603 \pm 0.05,\ c=7.713 \pm 0.05,\quad \beta=91.137^{\circ}$$

درست الخواص الضوئية للأفلام كما رسبت وبعد تلدينها باستخدام جهاز الطيف الضوئي (Spectrophotometer) من خلال قياس الانعكاسية والنفاذية للأطوال الموجية للمدى مابين ٢٠٠-٢٥٠٠ نانومتر وحدد معامل الامتصاص k ومعامل الانكسار n لحالتي الأفلام.

تم تحليل عوامل التشتت الضوئية باستخدام نموذج المتذبذب الأحادي وحددت طاقة التذبذب E_o وطاقة التشتت E_d المطورة بطريقة ويمبل وداي دومينكو وقيمتهما ٥,٨٦-١٤,٤٣ إلكترون فولت للأفلام الأمورفية و ٢,٩٦-١١,٩٨ إلكترون فولت للأفلام المتبلورة على التوالي. وحسبت فجوة الطاقة غير المباشرة E_g لكلى الحالتين وكانت ٣,٢٣ إلكترون فولت للأفلام الأمورفية و ٢,٢٨ إلكترون فولت للأفلام المتبلورة .

وتمت مقارنة النتائج مع النتائج المنشورة وشرحت .