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Optical and structural characteristics of SnO_2 nanocrystalline thin film

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Abstract

Nanocrystalline tin dioxide (SnO_2) thin film was prepared on glass substrate by chemical vapour deposition (CVD), taking starting material tin chloride solution ($SnCl_2.2H_2O$). The thin film were characterized for the composition by x-ray diffraction, the XRD result shows a regular, smooth morphology. The deposited film was found to be polycrystalline and consisted only of the tetragonal phase SnO_2 with no structural change, and they were well crystallized during deposition. The average grain size was found to be 33.35 nm as calculated by XRD using Debye Scherror Formula. After annealing the films in air at 400, 500, and 600 ^oC the grain size was 27.905 nm, 27.263 nm, and 32.172 nm respectively. The optical properties (absorbance and transmittance) have been measured.

Key words: SnO_2 Nanocrystalline, Surface morphology, structural properties, optical properties.

1. Introduction

Transparent conducting films are commonly used in many applications such as autistatic coating, flat panel displays [1], electroluminescent devices [2], sensors [3], and solar cells [4] due to their outstanding properties. This oxide has been extensively described in the literature because of its importance as a gas and humidity sensor [5]. General requirements for transparent conducting film are low electrical resistivity and high transparency in visible spectral region. The film is highly transparent, chemically inert, and mechanically hard. Application of the tin oxide films are not limited to the research laboratory but are used commercially in environmental monitoring, industrial electronic sensor, liquid crystal displays etc [6]. SnO_2 can be prepared on a glass substrate by chemical vapour deposition [7], sputtering [8], spray pyrolysis [9], electron beam evaporation [10], and oxygen ion beam assisted deposition [11]. SnO_2 has a tetragonal structure, similar to the rutile structure, and behaves as n type semiconductor [12]. In solar cells, SnO_2 is used as a front contact, because of it allows most of the solar spectrum through because of its high band gap (E_g = 3.6 eV). The deposition conditions must be adjusted to optimize the properties of SnO_2 films for each type of application. To obtain smoother SnO_2 films, growth temperature must be reduced, which in turn, affects other properties of the films. Among all technique chemical vapour deposition (CVD) has been extensively beeing less expensive, large area deposition and chemically viable technique. That the grain size can be easily controlled at the atomic level.

2. Experimental details

2.1 Deposition Method of SnO_2 film

SnO_2 film has been successfully deposited by (CVD). First the glass to be made conductive must be cleaned with toothpaste because it is a mild abrasive, then washed in warm soapy water, then isopropyl – alcohol and then distilled water, finally dried with warm air. The film is then deposited using stannous chloride, the substrate and stannous chloride temperature was maintained at 500±10 ^{o}C.

2.2 Characterization of SnO_2 film

The deposited SnO_2 film is characterized by XRD measurement using a Philips X'pert Pro MPD diffractometer (PANalytical company). The optical transmittance spectra of the deposited films were recorded in the wavelength range of 200 nm to 1100 nm using UV – VIS spectrophotometer model thermo spectronic.

3. Result and discussion

3.1 Structural analysis

X-ray diffraction (XRD) patterns were recorded in the 2θ ranges from 20^{o} to 70^{o} with CuKα radiation (1.5406 Å). Figures.1(a), 1(b), 1(c), and 1(d) shows the XRD patterns of CVD tin oxide film which is crystalline in nature with well defined peaks that match standard interplanar spacing JCPDS card and (hkl) values are shown in Tables (1, 2, 3, and 4).

Table 1. (hkl) value of XRD unannealing film.

2θ	Grain size (nm)	hkl
26.5110	41.493	110
33.7868	40.393	101
37.8141	35.569	200
42.4329	18.0525	210
51.6009	24.924	211
54.5809	34.157	220
61.6317	23.513	310

Table 2. (hkl) value of XRD annealing at 400 ^{o}C.

2θ	Grain size (nm)	hkl
26.4977	34.571	110
33.7604	42.207	101
37.7750	35.566	200
42.4565	18.054	210
51.5849	28.033	211
54.5450	22.719	220
61.5859	20.196	310

Table 3. (hkl) value of XRD annealing at 500 ^{o}C.

2θ	Grain size (nm)	hkl
26.4963	34.574	110
33.8098	35.173	101
37.7748	42.686	200
42.4846	18.055	210
51.5849	25.245	211
54.5338	22.437	220
61.6004	23.510	310

Table 4. (hkl) value of XRD annealing at 600 ^{o}C.

2θ	Grain size (nm)	hkl
26.5119	41.493	110
33.8149	35.171	101
37.7956	35.567	200
42.4419	36.098	210
51.5852	28.033	211
54.5868	22.723	220
61.5690	26.120	310

These values were compared with the reported value [6]. SnO_2 with the rutile structure is tetragonal, and from figures (a = 4.7569 Å ; c = 3.1728 Å) with Sn atoms at (0,0,0) and (1/2a,1/2a,1/2c) and oxygen atoms at ± (ua,ua,0) and (1/2a,1/2a,1/2c)±(ua,ua,0), where u = 0.307. The substrate temperature plays an important role in the film formation. The optimum substrate temperature is in the range of 250 – 450 °C at this point the vapour very gently reaches the substrate and complete oxidation takes place. To obtain more quantitative information, the XRD pattern was analyzed with Gaussian Function where full width and half maxima [FWHM] was determined. The grain size of SnO_2 film D can be estimated by the Debye – Scherrer formula [13].

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

Where, D = crystalline grain size.
β = FWHM of the observed peak.
λ = wavelength of x-ray diffraction.
θ = Angle of diffraction.
The average grain size of SnO_2 film is calculated as (33.35 nm).Four-probe current-voltage(I-V) measurements were performed on SnO_2 films under synthetic air to estimated electrical resistance R ranged from 15Ω to 20 Ω depending on the compositional purity, surface chemistry, and annealing temperature. We can show the value of resistance R, and transparent of SnO_2 film in Figure 2.

Table 5. Values of grain size and lattice constant with annealing temperature.

Annealing temperature Ta (°C)	Crystallite size "D" (nm)	Lattice constant	
		a (Å)	c (Å)
Unannealed	33.35	4.7569	3.1728
400	27.905	4.7604	3.1957
500	27.263	4.7598	3.1931
600	32.172	4.7592	3.1929

The transmission spectra (normal incidence) of deposited film were recorded. It was found that the average transmittance of the film is ≈ 75 % Figure (3). From these spectral data optical absorption coefficient, α, was calculated using Lembert's law [13].

$$I = I_o e^{-\alpha t}$$

$$T = I/I_o = e^{-\alpha t}$$

$$\alpha = (1/t)\,\mathrm{Ln}\,(1/T) \qquad (2)$$

OR we can use another relation:

$$\mathrm{Ln}\,(I/I_o) = \alpha t = 2.303\,A$$

$$\alpha = \frac{2.303}{t}(A - A^{/}) \qquad (3)$$

Where, t = is a thickness of the film.
T = is a transmittance of the film.

I and I_o = are the intensity of incident and transmitted light, respectively.
A = is the optical absorbance.
$A^{/}$ = is the correct absorption limited.
Figures (4a, 4b, 4c, and 4d) shows the variation of $(\alpha h\nu)^2$ and (hν) for the determining the band gap E_g by extrapolation of curve. As SnO_2 is a direct band-gap, therefore the incident photon energy is related to the E_g by equation:

$$(\alpha h\nu) = [k\,(h\nu - E_g)^{1/2}] \qquad (4)$$

Here k is a constant, hν is the photon energy, and E_g is the band gap energy.

Optical analysis of the samples was carried out to calculate the band gap. The results are shown in Figure (4), the band gap for the unannealed sample deposited at growth temperature 500 °C is (3.62 eV), where the band gaps for annealed samples range are (3.75 eV,3.5eV and 3.7 eV)respectively.

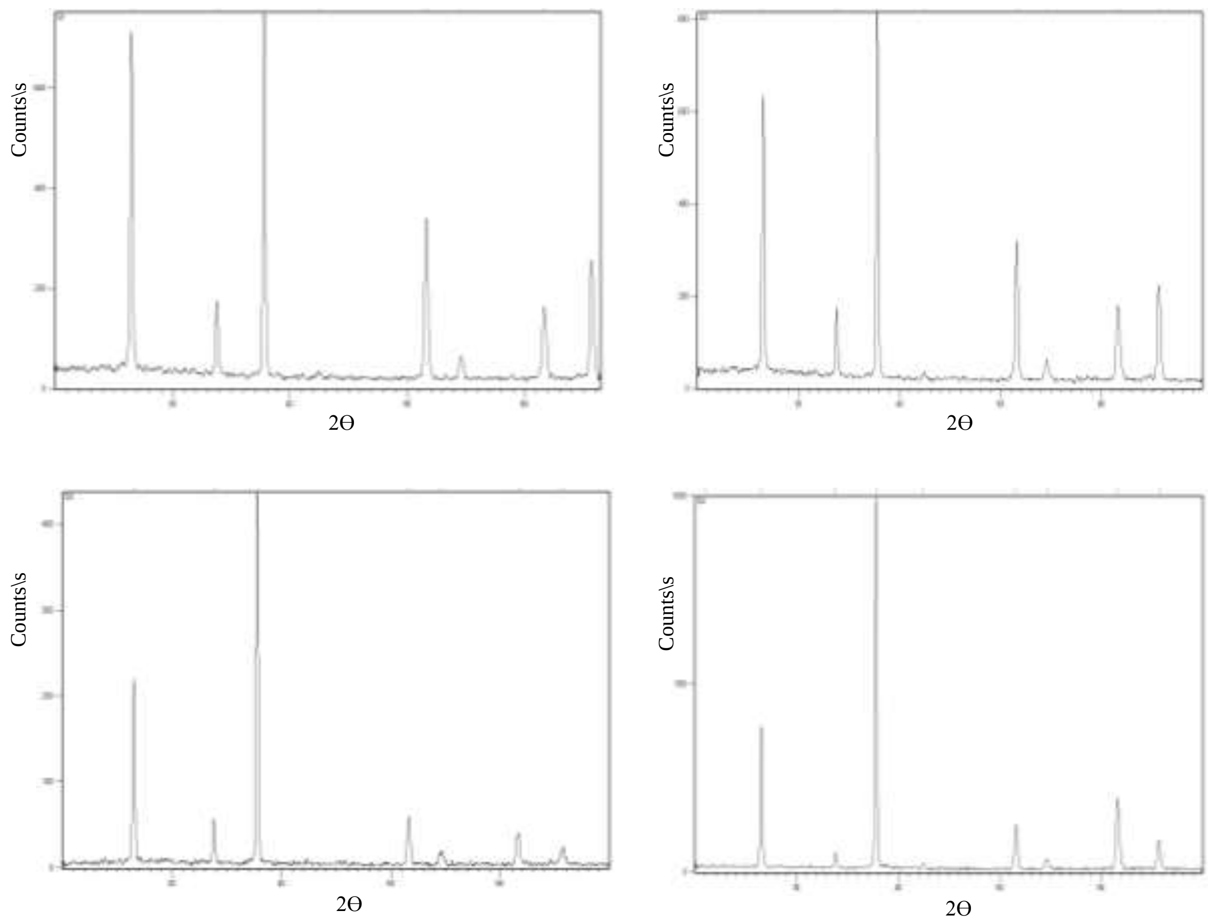

Fig. 1. XRD patterns of CVD tin oxide film (a)-unannealed (b)-annealed at 400 ^{o}C (c)-annealed at 500 ^{o}C (d)-annealed at 600 ^{o}C.

Fig. 2. Show low electrical resistance and high transparency in visible spectral region for CVD SnO_2 film.

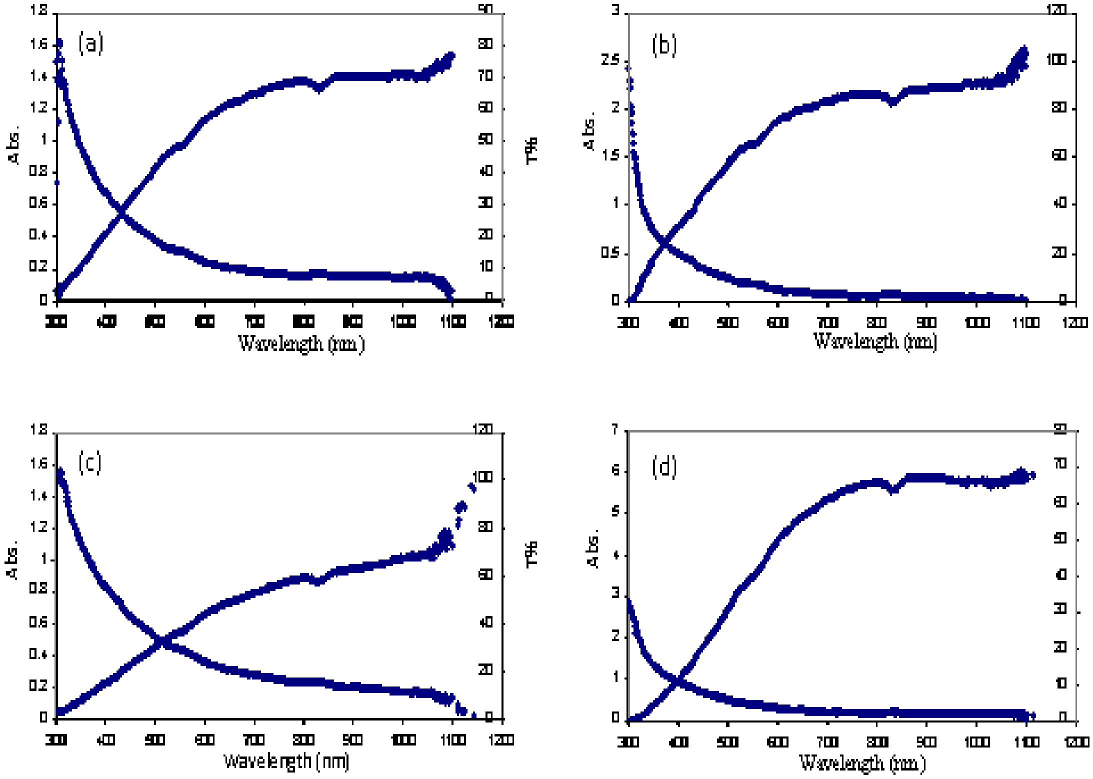

Fig.3. Absorption and Transmission Spectrum of SnO_2 film (a)-unannealed (b)-annealed at 400 ^oC (c)-annealed at 500 ^oC (d)-annealed at 600 ^oC.

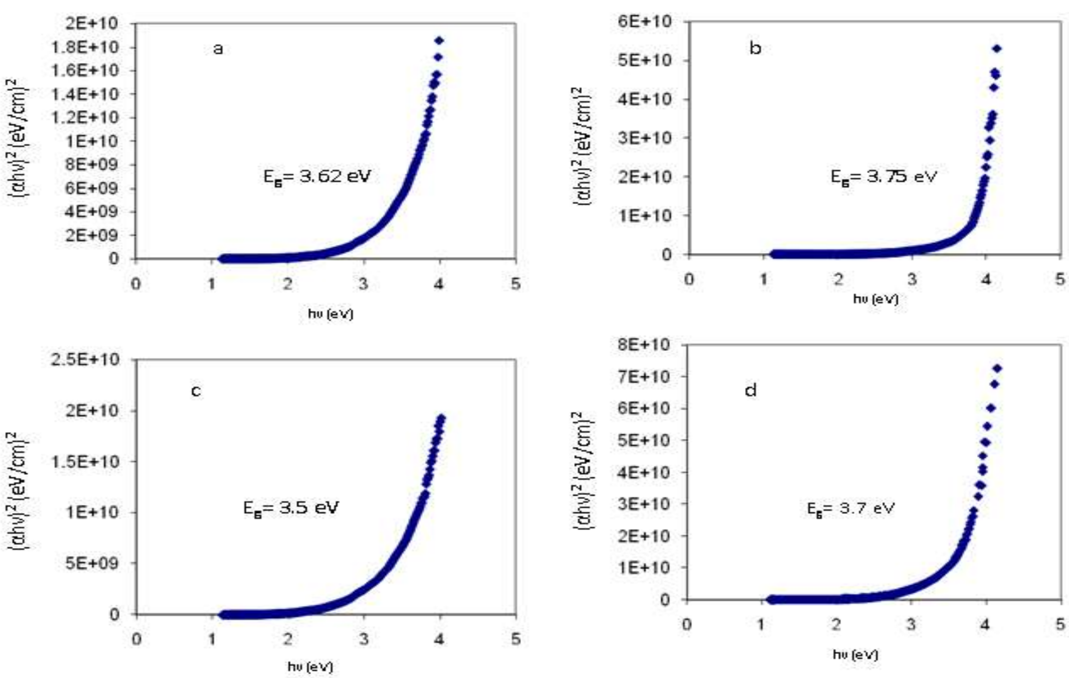

Fig. 4. Plot of $(\alpha h\nu)^2$ with photon energy in SnO_2 film (a)-unannealed (b)-annealed at 400 ^oC (c)-annealed at 500 ^oC (d)-annealed at 600 ^oC.

4. Conclusions

Transparent and conducting SnO_2 nanocrystalline film has been deposited by CVD. Structural and optical properties of the film studied as a function of annealing temperature. The average grains sizes of the films are 33.35 nm and 27.905 nm, 27.263 nm, and 32.172 nm annealed at 400 ^oC, 500 ^oC, and 600 ^oC respectively. The average transmittance is ≈ 75%, and electrical resistance R of the films ranged from 15-20 Ω. The observed direct band gaps E_g are 3.62 eV for unannealed and 3.75 eV, 3.5 eV, and 3.7 eV for annealed at 400 ^oC, 500 ^oC, and 600 ^oC respectively.

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المميزات الضوئية والتركيبية للأغشية الرقيقة دقيقة التبلور لمركب SnO_2

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الخلاصة

البلورات الدقيقة لأغشية (SnO_2) حُضرة بتقنية الترسيب الكيميائي (CVD) على قواعد من الزجاج, عن طريق أستخدام محلول ($SnCl_2.2H_2O$) حيث تم تشخيص تراكيب الأغشية بواسطة حيود الأشعة السينية (XRD), ونتيجة حيود الأشعة السينية تبين أن الأغشية متناسقة وناعمة ومتعددة التبلور وتمتلك طور واحد فقط وهو الرباعي Tetragonal phase بدون حدوث أي تغيير في التركيب البلوري (الطور) على طول فترة التحضيرات للأغشية والتي صاحبها تغير في درجة حرارة التلدين (المعاملة الحرارية). كان معدل الحجم الحبيبي للأغشية (33.35 nm) والمحسوب من حيود الأشعة السينية بأستخدام علاقة ديباي - شيرار (Debye Scherror). وبعد عملية التلدين للأغشية المحضرة بدرجات حرارة 400^oC و 500^oC و 600^oC فان معدل الحجم الحبيبي أصبح 27.905 nm و 27.263 nm و 32.172 nm على التوالي, لقد أمتلكت الأغشية المحضرة توصيلية كهربائية عالية حيث كانت مقاومتها تتراوح مابين 15 الى 20 أوم عن طريق القياس المباشر. الخواص الضوئية (الأمتصاصية والنفاذية) التي تم قياسها توضح نفاذية جيدة لضوء الشمس.