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Studies on the effect of substrate temperature on (VI–VI) textured tungsten oxide (WO_3) thin films on glass, SnO_2:F substrates by PVD:EBE technique for electrochromic devices

R. Sivakumar[a], M. Jayachandran[b], C. Sanjeeviraja[a,*]

[a] *Department of Physics, Alagappa University, Karaikudi 630003, Tamil Nadu, India*
[b] *ECMS Division, Central Electrochemical Research Institute, Karaikudi 630006, Tamil Nadu, India*

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Abstract

Electrochromic VI–VI compound semiconductor tungsten oxide (WO_3) thin films have pronounced feature in electrochromic devices. These films have been prepared by employing one of the physical vapour deposition methods (PVD), i.e., electron beam evaporation technique (EBE) at different substrate temperatures. The effects of substrate temperature on structural, surface morphological and optical properties of the films are studied.

Keywords: Thin films; Evaporation; Electron microscopy (SEM); Optical properties

1. Introduction

At present, coatings of transition metal oxides have an excellent technical interest due to their electrochromic, photochromic and gasochromic effect [1]. Semiconductor based metal oxides having pronounced feature in gas sensors [2]. Recently, the electrochromic devices made by using the electrochromic oxides like transition metal oxides have been extensively studied to regulate the radiated energy through glass with modifying their optical properties for the application in "smart windows" [3]. A material modify its optical properties, i.e., transmittance/reflectance in a reversible manner under the application of an external voltage pulse, that kind of material is referred as electrochromic material and it has been used in electrochromic devices. Among the semiconducting transition metal oxides, the tungsten oxide (WO_3) and molybdenum oxide (MoO_3) hold an important place in electrochromic display devices (ECD), because of their marvel performance in elctrochromic behaviour. In the present case, we discussed about the tungsten oxide thin films. The stoichiometric material is yellowish to greenish in bulk form. Tungsten oxide crystals have perovskite-like atomic configurations based on corner-sharing WO_6 octahedra. Deviations from ideal cubic perovskite-like structure correspond to antiferroelectric displacements of W atoms and to mutual rotations of oxygen octahedra. The perfect crystal of WO_3 is ReO_3 type with the corner-sharing packing of $[WO_6]^{6-}$ octahedra, which is distorted when the fabrication temperature is low [4].

Now varieties of preparation techniques are available for the preparation of electrochromic tungsten oxide thin films including electrodeposition [5], spray pyrolysis [6] and vacuum thermal evaporation [7]. However, there are few reports available for the preparation of WO_3 films by electron beam evaporation technique. In the present investigation we have adopted one of the physical vapour deposition methods, i.e., Electron Beam Evaporation (PVD:EBE) technique for the preparation of WO_3 thin films. In this technique, the

* Corresponding author. Tel.: +91-4565-225205; fax: +91-4565-225202.
E-mail addresses: krsivakumar1979@yahoo.com (R. Sivakumar), sanjeeviraja@rediffmail.com (C. Sanjeeviraja).

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impingement of WO_3 species on the substrates is in regular order and each grain is evaporated independently of the other grains, hence the grown films exhibit well reproducible quality of nature than those obtained by other techniques and it is a quite promising method for the preparation of device performance thin films. Therefore it (PVD:EBE) is a potentially useful technique for large area applications and it has been shown to be superior to other techniques, for growing highly pure and crystalline transition metal oxide thin films for electrochromic and photo-voltaic device applications.

In the present research work, we have analysed the effect of substrate temperatures on the structural, surface morphological and optical properties of the electrochromic, semiconducting transition metal oxide of WO_3 thin films prepared by electron beam evaporation technique.

2. Experimental

2.1. Preparation

Tungsten oxide films were prepared by electron beam evaporation technique using a HINDHIVAC vacuum coating unit (model: 12A4D) with electron beam power supply (model: EBG-PS-3K). The films were deposited onto corning 7059 microscopic glass substrates and fluorine doped tin oxide coated (SnO_2:F) ($R_{sh} < 15\ \Omega$/sq) substrates. The glass substrates were degreased in hot chromic acid and rinsed in de-ionised water and dried with acetone. Tungsten oxide powder (purity > 99.99%) was made into pellets (by compressing in a die) of about 20 mm diameter with 4 mm thickness. These palletised WO_3 targets were taken in graphite crucibles and kept on water-cooled copper hearth of the electron gun, inside the vacuum chamber. In the electron gun, the electrons extracted from a dc heated cathode of tungsten filament, by the application of electric field, pass through an anode, and deflected through an angle of about 180° by the magnetic field and reach the target material. The surface of WO_3 pellet (target) on the graphite crucible was scanned by the resultant and deflected electron beam with an accelerating voltage of 5 kV and a power density of about 1.5 kW cm^{-2}. The chamber was evacuated to a high vacuum of the order of 1×10^{-5} mbar using rotary and diffusion pumps. The ablated material (WO_3 pellet) was evaporated and the vapour phase condensed and deposited as thin film on the substrate. The homogeneous distribution of evaporated WO_3 particles on the substrate was attained by continuously rotating the substrate during deposition. The distance of the substrate from the target material is about 20 cm. The depositions were carried out at different substrate temperatures (T_{sub}) viz. T_{sub} = 30 (room temperature, RT), 100 and 200 °C.

2.2. Characterization

The X-ray diffraction (XRD) analysis of the films was made using JEOL JDX X-ray diffractometer with Cu Kα (Ni-filtered) radiation (λ = 1.5418 Å). Surface morphological studies were performed by using JEOL JSM-5610 LV (Japan) scanning electron microscope. The optical absorption and transmittance spectra were recorded by using the HITACHI, 3400 UV–vis–NIR spectrophotometer in the wavelength range 300–1100 nm.

3. Results and discussion

3.1. X-ray diffraction analysis

The PVD:EBE deposited WO_3 films (on glass and SnO_2:F substrates) under optimised conditions have been subjected to X-ray diffraction to analyse their structural behaviour. The films are observed to be uniform and more adhesive with the substrates. Fig. 1a–c shows the X-ray diffraction pattern of WO_3 films on 7059 corning microscopic glass plates at different substrate temperatures. It is observed that the films deposited at lower substrate temperature (i.e., T_{sub} = RT) (Fig. 1a) is amorphous in nature. It is because of incomplete formation of WO_3 species on the substrates at lower

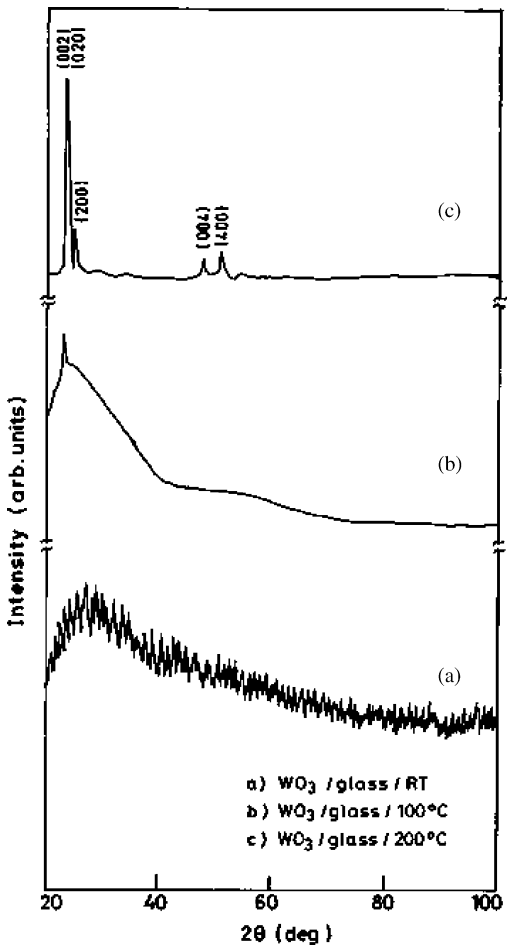

Fig. 1. X-ray diffraction pattern of WO_3 films on glass substrates at different substrate temperatures: (a) T_{sub} = RT, (b) T_{sub} = 100 °C and (c) T_{sub} = 200 °C.

substrate temperature (T_{sub}). When it is deposited at higher substrate temperatures say T_{sub} = 100 and 200 °C, the crystalline WO_3 film is obtained, due the complete coalescence formation followed by perfect growth alignment of WO_3 particles on the substrates. Fig. 1b and c show the X-ray diffractograms of WO_3 films on glass substrates for T_{sub} = 100 and 200 °C, respectively, which reveal the crystalline and single phase nature of the films. The XRD pattern of the film deposited at T_{sub} = 100 °C, gave broad crystalline peaks and it is transformed to well and highly oriented like peaks when the substrate temperature was increased, the grain growth is promoted pronouncedly.

Fig. 2a–c shows the XRD pattern of WO_3 on SnO_2:F substrates at T_{sub} = RT, 100 and 200 °C. It is observed from Fig. 2a that the films prepared at room temperature on SnO_2:F substrates are having some crystalline peaks of WO_3. It is concluded that the WO_3 films on SnO_2:F substrates at lower substrate temperature (i.e., T_{sub} = RT) are of crystalline nature. The X-ray diffractograms of WO_3 films on SnO_2:F substrates at higher substrate temperatures (i.e., T_{sub} = 100 and 200 °C) are shown in Fig. 2b and c. They are having diffraction peaks for WO_3 films and the intensity of these peaks is higher than that of the peaks obtained on glass substrates. The crystalline SnO_2:F substrates enhance the crystallinity of the WO_3 films. The interplanar distances (d_{hkl}) of the observed data were indexed with the standard JCPDF (No. 83-0950) data; they are in good agreement with JCPDF and is shown in Table 1. From the JCPDF data the crystalline peak is identified at 2θ = 23.2° as ⟨0 0 2⟩ and ⟨0 2 0⟩ directions, i.e., the film grew along the "*c*" and "*b*" axes. The peak at 2θ = 47.2° is due to the reflections along the ⟨0 0 4⟩ orientation. It is concluded that these well marked texture columnar growth peaks correspond to monoclinic crystal system of the films. Antonaia et al. [7] reported the monoclinic crystalline structure for WO_3 films prepared at the substrate temperature of 300 °C and further annealed at 465 °C with the preferred columnar growth peak along the ⟨0 2 0⟩ and ⟨2 0 0⟩ directions. The monoclinic phase of the WO_3 films (prepared at 300 °C) with preferred orientation along ⟨2 0 0⟩ and a broad peak along ⟨$\bar{2}$ 0 2⟩ and ⟨2 0 $\bar{2}$⟩ directions, was reported by Regragui et al. [8]. Cantalini et al. [9] also reported the vacuum thermal evaporated WO_3 films at room temperature and post heat treated at 600 °C for 24 h, are having monoclinic crystal phase.

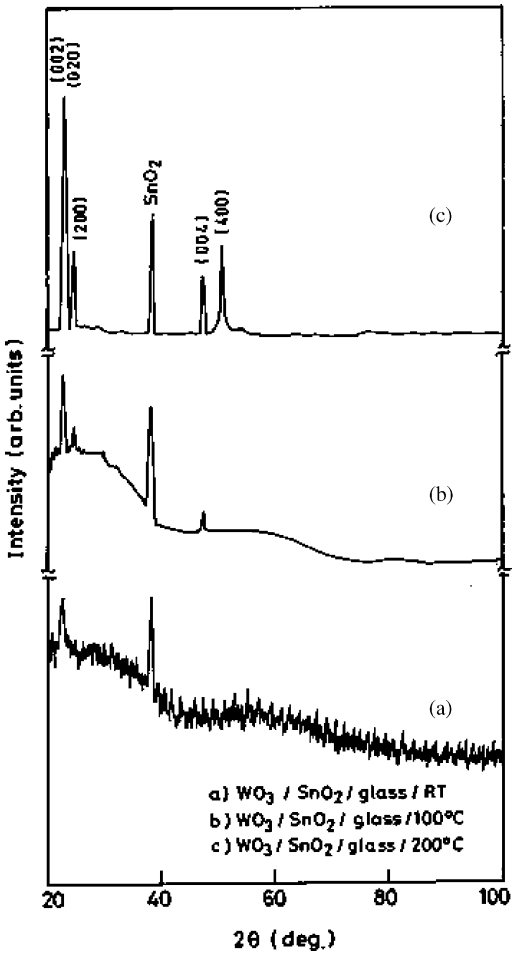

Fig. 2. X-ray diffraction pattern of WO_3 films on SnO_2:F substrates at different substrate temperatures: (a) T_{sub} = RT, (b) T_{sub} = 100 °C and (c) T_{sub} = 200 °C.

Table 1
Structural parameters of WO_3 film with the standard JCPDF (number 83-0950) file

Sample	Observed data		JCPDF data		Miller indices ⟨*h k l*⟩
	'2θ' (°)	'd_{hkl}' (Å)	'2θ' (°)	'd_{hkl}' (Å)	
WO_3/glass at 200 °C and WO_3/SnO_2:F/glass at 200 °C	23.200	3.864	23.117	3.8443	⟨0 0 2⟩
			23.583	3.7694	⟨0 2 0⟩
	24.200	3.675	24.366	3.6499	⟨2 0 0⟩
	47.200	1.924	47.248	1.9221	⟨0 0 4⟩
	50.400	1.809	49.931	1.8249	⟨4 0 0⟩

Since, without annealing of the films (i.e., post-heat treatment) and also at lower substrate temperatures, we have achieved the well textured WO_3 films on the amorphous and crystalline media.

The lattice parameters and crystallite size were calculated by the following relations [10]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2/a^2 + l^2/c^2 - (2hl/ac)\cos\beta}{\sin^2\beta} + \frac{k^2}{b^2} \quad (1)$$

where (*hkl*) are Miller indices of diffracted planes.and

$$r = \frac{k\lambda}{\beta_{2\theta}\cos\theta} \quad (2)$$

where $\beta_{2\theta}$ is the full width at half maximum (FWHM) of the preferred growth peak, λ is the wavelength of Cu Kα line, θ is the Bragg's angle and *k* is the shape factor and it is taken as 0.94.

The evaluated lattice parameter values are *a* = 7.350 Å, *b* = 7.728 Å and *c* = 7.696 Å, which are in good agreement with literature (JCPDF No. 83-0950). The calculated crystallite

size is of the order of 94 nm for WO_3 preferred columnar growth peaks in the spectra 1c and 2c, respectively.

3.2. Surface morphological study

Surface morphological study of the deposited films was analysed by the scanning electron microscope (SEM). The surface morphological images of WO_3 films on glass substrates at T_{sub} = RT, 100 and 200 °C are shown in Fig. 3a–c. The surface images of the films prepared at lower substrate temperature (T_{sub} = RT) (Fig. 3a) are having uniform surface, indicate their amorphous behaviour. Fig. 3b and c show the SEM images of WO_3 films prepared at higher substrate temperatures, T_{sub} = 100 and 200 °C, respectively. They are having smooth and netted surface. Galatsis et al. [11] reported identical morphology for WO_3 films on Si substrates and further annealed at 500 °C. The surface morphological architectures of WO_3 films prepared at T_{sub} = RT, 100 and 200 °C on SnO_2:F substrate are shown in Fig. 4a–c, respectively. From the micrograph (Fig. 4a) it is observed that the crystalline nature of the films in the lower substrate temperature

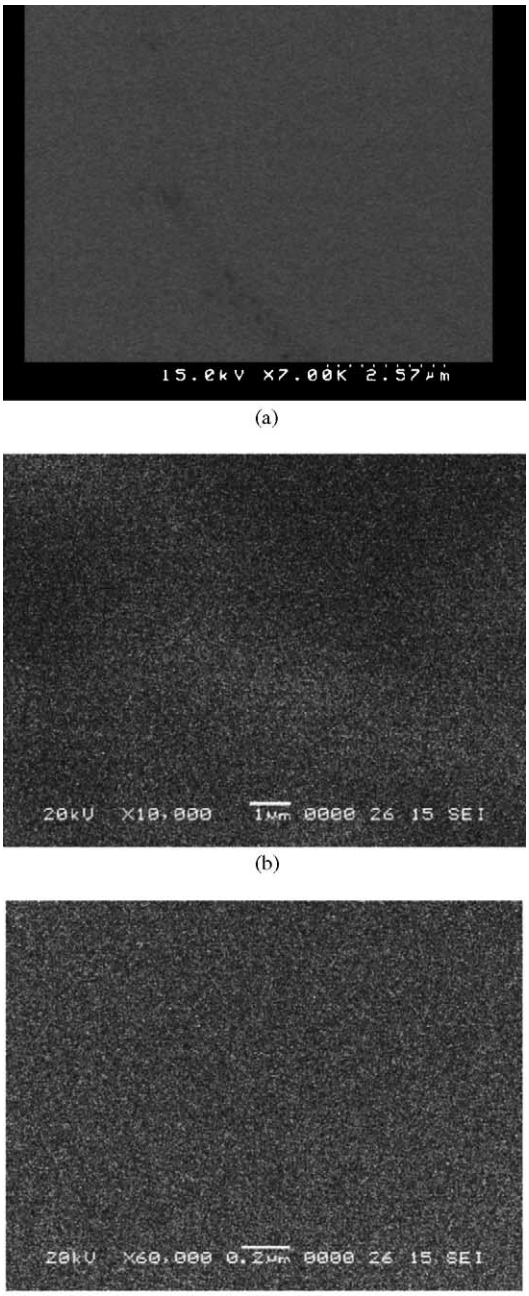

Fig. 3. Surface morphology of WO_3 films on glass substrates at different substrate temperatures: (a) T_{sub} = RT, (b) T_{sub} = 100 °C and (c) T_{sub} = 200 °C.

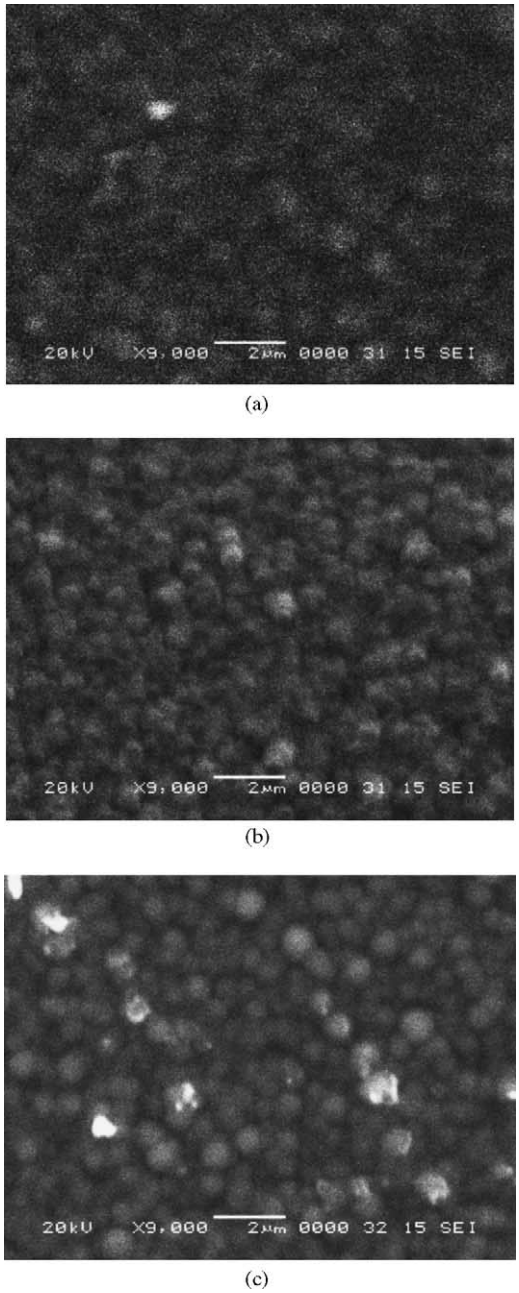

Fig. 4. Surface morphology of WO_3 films on SnO_2:F substrates at different substrate temperatures: (a) T_{sub} = RT, (b) T_{sub} = 100 °C and (c) T_{sub} = 200 °C.

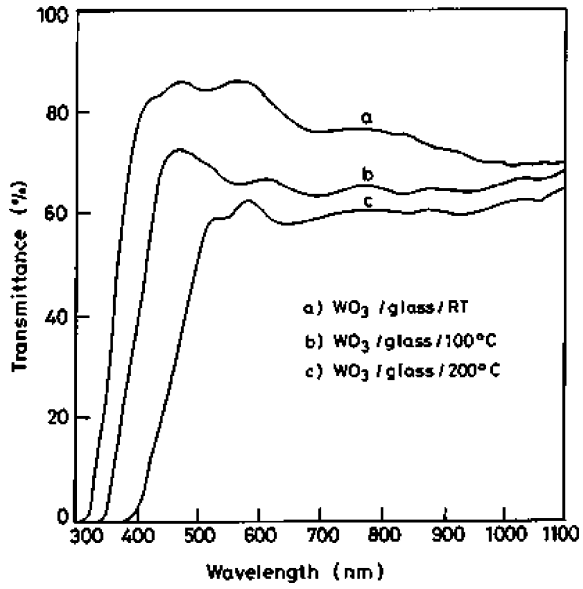

Fig. 5. Optical transmittance spectrum of WO_3 films on glass substrates at different substrate temperatures: (a) T_{sub} = RT, (b) T_{sub} = 100 °C and (c) T_{sub} = 200 °C.

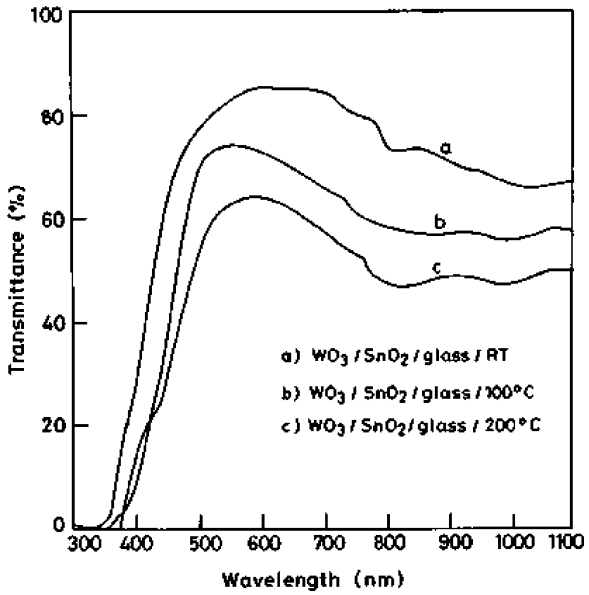

Fig. 6. Optical transmittance spectrum of WO_3 films on SnO_2:F substrates at different substrate temperatures: (a) T_{sub} = RT, (b) T_{sub} = 100 °C and (c) T_{sub} = 200 °C.

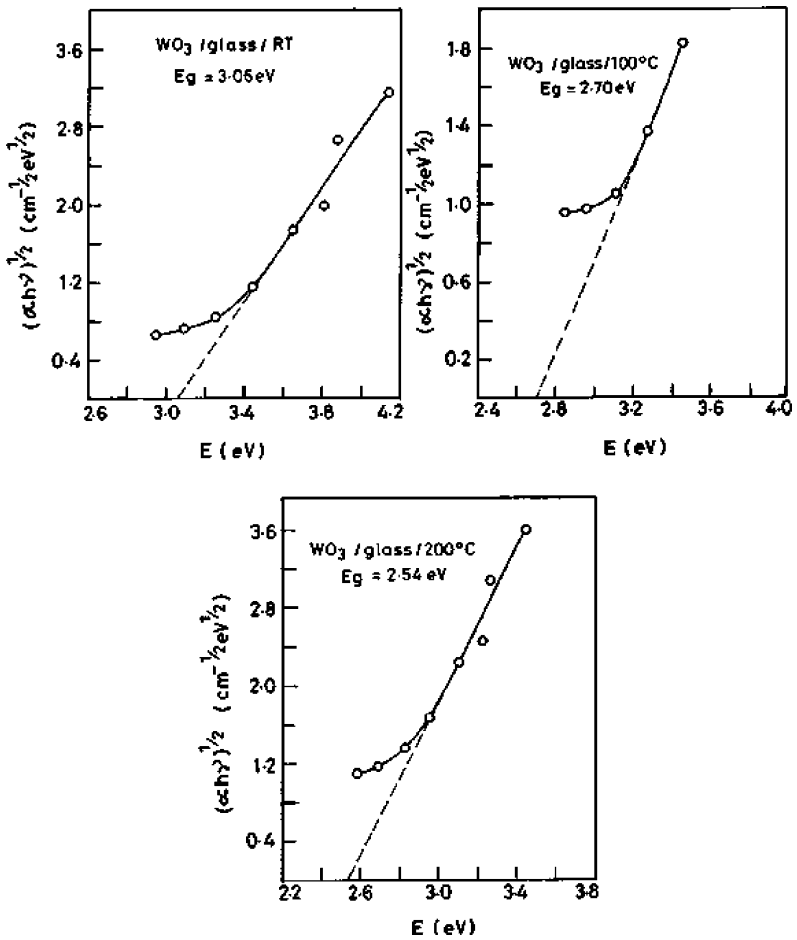

Fig. 7. Energy band gap graph of WO_3 films on glass substrates at different substrate temperatures.

(T_{sub} = RT) and it is also seen from the X-ray diffractogram (Fig. 2a). We obtained several well textured patterns in the SEM micrographs, when the films prepared at higher substrate temperatures like 100 and 200 °C. Fig. 4b and c show the surface morphology of WO_3 films prepared at substrate temperatures of 100 and 200 °C, respectively. They show many, well shaped nano particle grains (about ∼100 nm) homogeneously distributed all over substrate surfaces. We noted from the SEM micrographs of WO_3 on SnO_2:F substrates, the crystalline nature improves with the substrate temperature. It is because the heat emerges immediately at higher temperature to the films from coalescence stage to the perfect growth nature and all the evaporated particles get well shape. This may also depend on the crystalline nature of the substrates. The results of surface morphological studies can be correlated qualitatively to X-ray diffraction patterns of almost well oriented films, though the SEM images at 100 and 200 °C on microscopic glass substrates show the poor quality of grains and they are having netted surface, which may be due to amorphous nature of the substrates.

3.3. Optical properties

The effect of substrate temperature on the optical properties of WO_3 film was studied by recording the optical absorption and transmission spectrum in the wavelength range 300–1100 nm using the HITACHI, 3400 UV–vis–NIR spectrophotometer. In the double beam UV–vis–NIR optical measurements, the optical contribution from the glass and SnO_2:F substrates were compensated by introducing them as a reference in the measurements. The contribution from the substrates was nullified and the final optical spectrum is only due to deposited WO_3 films. Therefore all the absorption and transmission spectra are normalised with respect to the substrates.

The optical absorption coefficient (α) of WO_3 film was calculated by the relation [12]:

$$\alpha = \frac{1}{\delta} \ln \left[\frac{T}{(1-R)^2} \right] \tag{3}$$

where δ is the thickness, T is the transmittance and R is the reflectance of the film.

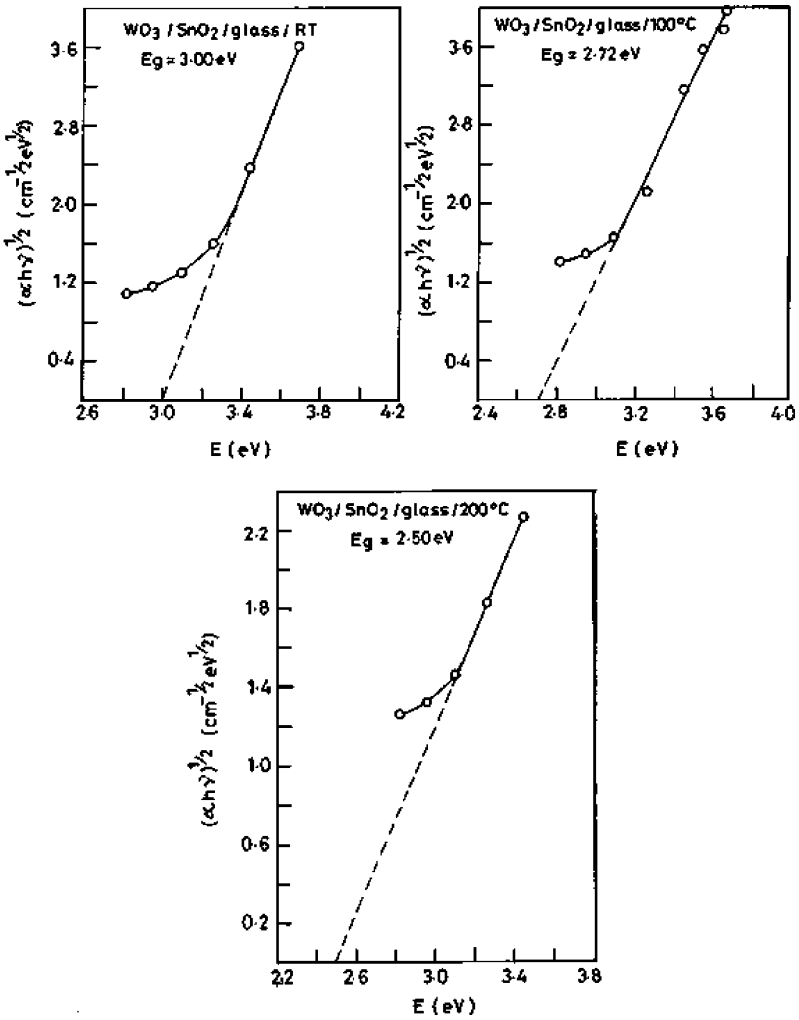

Fig. 8. Energy band gap graph of WO_3 films on SnO_2:F substrates at different substrate temperatures.

The energy band gap of the film was evaluated by using the relation [13]:

$$\alpha = \frac{B(h\upsilon - E_g)^{n/2}}{h\upsilon} \quad (4)$$

Here E_g is the energy band gap, B is the constant. The exponent n has the value 1 for direct transition band gap and 4 for indirect transition band gap.

Figs. 5 and 6 show the optical transmittance spectra of the PVD:EBE grown WO_3 films at different growth conditions on glass and SnO_2:F substrates, respectively. The maximum transmittance range of about 85% was observed in the visible region of the spectrum and it decreases to about 65% with increasing the substrate temperature. This may be due to the increasing of crystallization from amorphous nature with increasing of substrate temperatures from room temperature to 200 °C. The absorption edge is also slightly shifted towards the higher wavelength region for the films deposited at higher T_{sub} values, owing to perfect colouration effect on the films. The colour of the films change with the substrate temperatures, due to excellent electrochromic nature. The thickness of the optimised films is of the order of about 0.59 μm. From this we concluded that the prepared WO_3 films in the present technique possess well colouration and electrochromic nature and it may be a good candidate for electrochromic devices and also for photo-voltaic applications.

The energy band gap graphs ($(\alpha h\upsilon)^{1/2}$ versus E) for WO_3 films on glass and SnO_2:F substrates are shown Figs. 7 and 8, respectively. By extrapolating the straight line portions of curve in the graph ($(\alpha h\upsilon)^{1/2}$ against E) along the energy (E) region, resulted the optical energy band gap, E_g of films. It is observed that, the optical absorption of WO_3 films occurs through the indirect interband transitions and also these films are having indirect band gap nature. The estimated energy band gap, E_g values of the films varied as 3.06, 2.70 and 2.54 eV (Fig. 7) for the films prepared on glass substrates with T_{sub} = RT, 100 and 200 °C, respectively. Whereas the E_g values of the films on SnO_2:F substrates were calculated as 3.00, 2.72 and 2.50 eV (Fig. 8). The slight variation in the values of energy band gap from room temperature to higher substrate temperatures may be due to the formation of more oxygen-ion vacancies in the films during deposition at higher substrate temperatures; hence the conductivity of the film gradually increases because of decreasing of resistivity (sheet resistance) in films. So, the energy gap between the conduction and valance bands is slightly reduced. The obtained band gap values are in accordance with the earlier report of Miyake et al. [14]. They reported the E_g values of WO_3 films prepared by the evaporation technique, are varied between 3.25 and 2.70 eV with the substrate temperatures from 50 to 500 °C. Manno et al. [2] reported the energy band gap of WO_3 films varied from 3.36 to 2.95 eV with various sputtering pressures and O_2 concentrations. The band gap widening (narrowing) through the substrate temperature enumerates the crystallization of the films.

4. Conclusions

We have optimised the preparative conditions for electron beam evaporation (PVD:EBE) technique for highly textured WO_3 films on glass and SnO_2:F substrates. The structural studies showed that the films are transformed from amorphous to crystalline nature by increasing the substrate temperatures. The well resolved peaks confirm the textured and stoichiometric nature of the films. The surface morphological study also revealed the crystalline nature of the films at higher substrate temperatures. The well shaped nano grains confirm the stoichiometric and nano crystalline quality of the films. The optical studies showed the films are having well colouration effect and stoichiometric nature. The estimated energy band gap values are in good agreement with the literatures and the variations in band gap while the deposition at higher substrate temperatures owing to the oxygen ion vacancies. The band gap narrowing also suggests the crystalline nature of the films.

From the above studies and results we would like to state that the optimised WO_3 thin films prepared by the physical vapour deposition of electron beam evaporation (PVD:EBE technique) is suitable to develop the economical electrochromic devices.

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