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Preparation and characterization of electron beam evaporated WO_3 thin films

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Abstract

Thin film of tungsten oxide (WO_3) has been extensively studied as an electrochromic material and has numerous applications in electrochromic devices, smart windows, gas sensors and optical windows. In order to explore the possibility of using this in electrochromic devices, a preliminary and thorough study of the optical properties of the host material is an important step. Based on the above criterion, the effect of annealing temperature on the structural, surface morphological and optical properties of WO_3 films has been studied in the present work. The host material, WO_3 films, has been prepared by the physical vapor deposition method of electron beam evaporation (PVD:EBE) technique under a pressure of 1×10^{-5} mbar. The single phase nature, monoclinic structure and textured nature of the films have been confirmed by the X-ray diffraction analysis. The needle-like crystallites have been observed from surface morphological studies. The evaluated crystallite size is in the nanometer range. The shift in absorption edge towards the higher wavelength region observed from optical studies may be due to the coloration effect on the films.

PACS: 6855; 8115.G; 6170.A; 6110; 4280.E

Keywords: WO_3 films; Electron beam evaporation; Structural properties; Optical properties; Smart windows; Textured nature; Energy band gap

1. Introduction

There is a considerable interest in the research and development of materials and devices that can be used for optical switching of large-scale glazings. Several potential switching technologies are available for glazings, including those based on the electrochromism, thermochromism and photochromism phenomena. Tungsten oxide (WO_3) has been extensively studied and is reported to have interesting physical properties, which makes it suitable for electrochromic and a variety of potential applications [1]. These properties were first reported by Deb [2] and since then many theories have been proposed for the observed electrochromic mechanism [3] in WO_3. The physical properties of a material are greatly affected by its structural order and morphology. Different preparation methods have their specific advantages in viewpoint of film quality and production cost of materials for different applications. Thin films of tungsten oxide have two extreme structural orders like amorphous (a-WO_3) and polycrystalline (c-WO_3). The structural configuration of the WO_3 crystal lattice is the distorted rhenium trioxide (ReO_3) structure [4,5]. Though the tungsten oxide was known as a promising candidate for electrochromic devices [6], it was not popular because of the fast developments in the liquid-crystal displays (LCDs). Tungsten oxide films are presently used in sunglasses and automotive rear-view mirrors, sun roofs, variable-tinted windows for automotive

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glass and building windows. Many researchers have built and tested whole electrochromic devices with promising results [7,8]. The WO_3 film is quite porous and smaller alkali ions can be easily intercalated and deintercalated into it. The density of the films starts to increase significantly upto a deposition temperature of 200 °C, and upto a post annealing of 300 °C [3].

Moreover, the electrochromic device performance of WO_3 films basically depends on their structural, surface morphological, compositional and optical properties. It is important that the improvement of materials properties requires a closer inspection of preparation conditions and also the above said properties of the films. In this regard, a large number of techniques for preparing WO_3 films were employed [9,10]. Out of which the electron beam evaporation technique, one of the physical vapor deposition methods, has been considered largely for the growth of device quality thin films [11]. Indeed, a systematic characterization of the above mentioned properties is of great interest and is necessary to understand the electrochromic properties of the WO_3 films. Hence, in the present study we have investigated the structural, morphological and optical properties of electron beam evaporated WO_3 films and the effect of substrates and annealing temperature on these properties in a detailed manner and the results are presented.

2. Experimental

Thin films of tungsten oxides (WO_3) were prepared by electron beam evaporation technique using a HINDHIVAC vacuum coating unit (model: 12A4D) fitted with electron beam power supply (model: EBG-PS-3K). Well

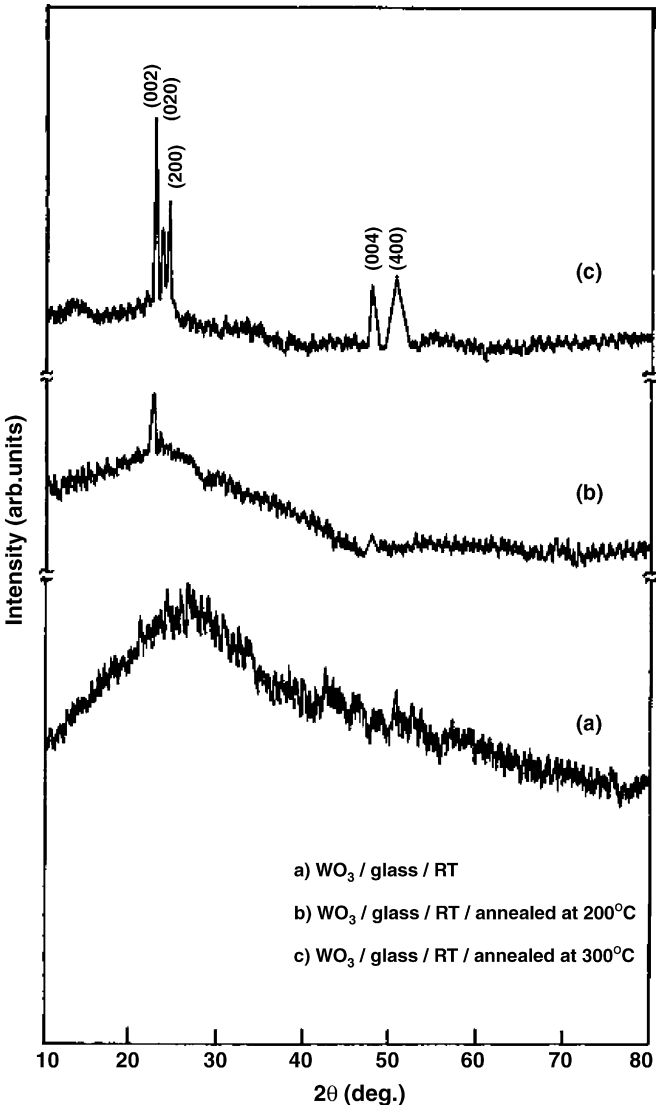

Fig. 1. X-ray diffractogram of WO_3 films prepared on glass substrates at room temperature and further annealed at different temperatures: (a) T_{sub} = RT, (b) T_{anne} = 200 °C and (c) T_{anne} = 300 °C.

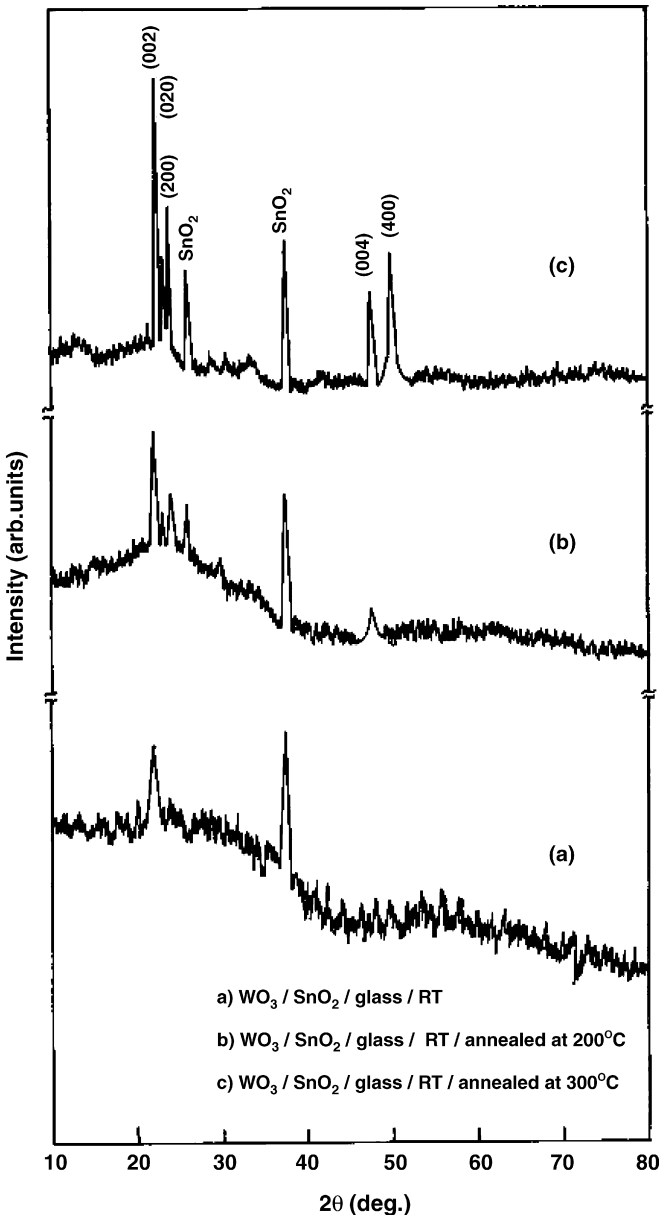

Fig. 2. X-ray diffractogram of WO_3 films prepared on SnO_2:F coated glass substrates at room temperature and further annealed at different temperatures: (a) T_{sub} = RT, (b) T_{anne} = 200 °C and (c) T_{anne} = 300 °C.

Table 1
Comparison between observed structural data and JCPDS (83-0950) data for monoclinic WO_3 films

Sample	Observed '*d*' values (Å)	JCPDS '*d*' values (Å)	Miller indices (*hkl*)	Crystallite size (nm)
WO_3/glass/RT	–[a]	–	–	–
WO_3/SnO_2:F/glass/RT	3.995	3.844	(002)	42
WO_3/glass/RT/annealed at 200 °C	3.995	3.844	(002)	65
	3.866	3.769	(020)	141
	1.923	1.922	(004)	36
WO_3/SnO_2:F/glass/RT/annealed at 200 °C	3.995	3.844	(002)	65
	3.866	3.769	(020)	141
	3.723	3.649	(200)	77
	1.923	1.922	(004)	45
WO_3/glass/RT/annealed at 300 °C	3.951	3.844	(002)	94
	3.825	3.769	(020)	121
	3.707	3.649	(200)	121
	1.923	1.922	(004)	75
	1.824	1.824	(400)	36
WO_3/SnO_2:F/glass/RT/annealed at 300 °C	3.995	3.844	(002)	84
	3.866	3.769	(020)	169
	3.785	3.649	(200)	141
	1.923	1.922	(004)	69
	1.841	1.824	(400)	60

[a] Amorphous nature.

degreased microscopic glass plates and FTO coated glass plates have been employed as the substrates in the present work. Dry WO_3 powder (Aldrich, 99.99%) was made into pellets, taken in a graphite crucible and kept in water-cooled copper hearth of the electron gun. The pelletized WO_3 targets were heated by means of an electron beam collimated from the d.c heated tungsten filament cathode. The surface of the WO_3 pellet was bombarded by 180° deflected electron beam with an accelerating voltage of 5 kV and a power density of about 1.5 kW/cm^2. The evaporated species from WO_3 pellet were deposited as thin films on the substrates in a pressure of about 1×10^{-5} mbar. Each substrate was placed normal to the line of sight from the evaporation source at a different polar angle to avoid shadow effects and also to obtain uniform deposition. WO_3 films were deposited on glass and fluorine doped tin oxide (FTO or SnO_2:F) coated glass substrates at a substrate temperature (T_{sub}) of 30 °C (room temperature, RT). The different preparation parameters such as, source to substrate distance (15 cm) and partial pressure (10^{-5} mbar) have been varied and optimized for depositing uniform, well adherent and transparent films. Normally the crystalline quality of WO_3 films was poor when prepared at room temperature. Hence, in order to enhance the crystalline quality of RT deposited films, they were further post heat treated (i.e., annealing) at different temperatures (T_{anne}) like 200 and 300 °C for one hour in vacuum. Annealing at low temperature releases internal stresses while high temperature annealing leads to the growth of crystallites at the grain boundaries [12].

The structural properties of the films were studied by the JEOL JDX X-ray diffractometer (XRD) with CuK_α radiation ($\lambda = 1.5418$ Å). Surface morphology of the films was studied by JEOL JSM-5610 LV (Japan) scanning electron microscope (SEM). The optical properties of the films were analyzed by using HITACHI-3400 UV–Vis–NIR spectrophotometer in the wavelength range 300–1100 nm.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction patterns of electron beam evaporated WO_3 films on glass and SnO_2:F substrates at $T_{sub} = RT$, further annealed at 200 and 300 °C are shown in Figs. 1(a–c) and 2(a–c), respectively. The amorphous nature of WO_3 films has been observed in the pattern (Fig. 1(a)) for films prepared on glass substrates at room temperature ($T_{sub} = RT$). This may be attributed to the fact that crystallization of WO_3 thin films and their crystal lattice orientation are not initiated on the amorphous glass substrates at room temperature. The XRD pattern of WO_3 films prepared on glass substrates at room temperature and further annealed at 200 °C in vacuum (Fig. 1(b)) indicates the transformation of amorphous films into crystalline ones. The pattern has a broad peak with preferred orientation along (002) direction accompanied by two small peaks indexed as (200) and (004) orientations (indexed with JCPDS No. 83-0950). This observation reveals the fact that the crystallization of WO_3 films starts only after a post annealing treatment at a temperature 200 °C. When the annealing temperature further raised to (T_{anne}) 300 °C, the broad and less intense peaks indicated in Fig. 1(b) have been enhanced with higher intensity and formed as the well textured and highly oriented triplet crystalline peaks along (002), (020) and (200) orientations (Fig. 1(c)).

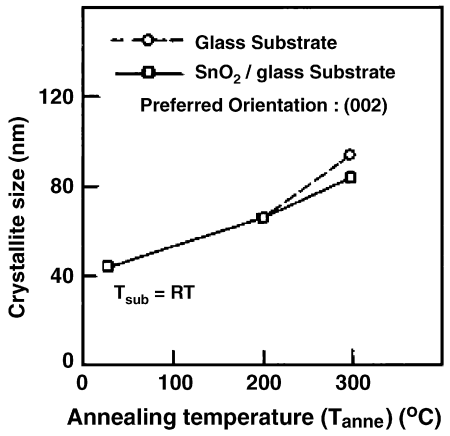

Fig. 3. Variation in crystallite size of the WO_3 films with respect to annealing temperatures.

The X-ray diffraction patterns of WO_3 films deposited on SnO_2:F substrates and further heat treated at the above mentioned conditions are shown in Fig. 2(a–c). It is observed from the XRD pattern that WO_3 films deposited even at room temperature (i.e., $T_{sub} = RT$) (Fig. 2(a)) are in crystalline nature. This can be attributed to the fact that the polycrystalline SnO_2:F substrate facilitates the growth of crystalline WO_3 films. When the as-deposited films on SnO_2:F substrates have been subjected to the annealing treatment at $T_{anne} = 200$ °C (Fig. 2(b)), the formation of triplet peaks has been observed. For the post heat treated films at 300 °C, the XRD pattern (Fig. 2c) shows high intensity and well oriented with the enhancement of crystalline quality. The observed structural parameters were compared with JCPDS (No. 83-0950) data and they are in good agreement as shown in Table 1. From this close agreement, it is confirmed that the electron beam evaporated WO_3 films belongs to the monoclinic crystal system. Also the formation of triplet peaks along (00*l*), (0*k*0) and (*h*00) growth orientations (where $h = k = l = 2$) shows that the films are grown along '*c*', '*b*' and '*a*' axes respectively confirming the columnar and textured growth nature of the films. The monoclinic crystal structure with a preferred orientation along (200) direction for thermally evaporated WO_3 films and annealed in air at 300 °C was reported by Lozzi et al. [13]. Nguyen Van Nha et al. [10] also reported that the evaporated WO_3 thin films belong to the monoclinic phase.

The evaluated lattice parameter values of WO_3 films, deposited on SnO_2:F substrates at room temperature and further annealed at 300 °C, are $a = 7.364$ Å, $b = 7.732$ Å and $c = 7.692$ Å, which are in agreement with the reported values [10]. The crystallite size of the annealed WO_3 films was calculated by using the Scherrer's formula [14] and is about 94 and 84 nm for the preferred oriented peak (002) in the XRD spectra of Figs. 1(c) and 2(c) respectively which confirmed the nanocrystalline nature of the films. The variation of the crystallite size of the preferred oriented peaks with respect to annealing temperatures is shown in Fig. 3. It shows that crystallite size of the films is increased with increasing annealing temperature. The intense and sharp peaks in X-ray diffraction pattern reveal the good crystallinity of the films and also confirm the stoichiometric nature of WO_3 films. The single phase nature of the films was also confirmed from the presence of XRD peaks pertaining only to the WO_3 phase. With the increasing annealing temperatures the intensity of the diffracted peaks becomes more intense and sharp. The enhanced preferential orientation after annealing at high temperatures in vacuum may be due to the movement of depositing atoms

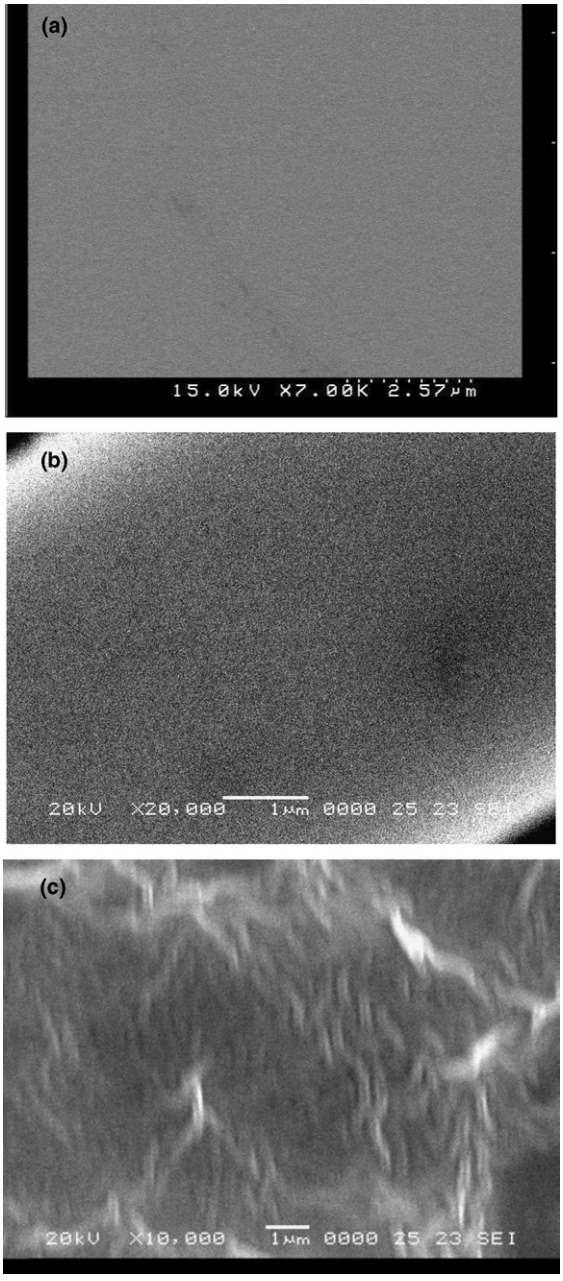

Fig. 4. SEM architecture of WO_3 films on glass substrates at different annealing temperatures: (a) $T_{sub} = RT$, (b) $T_{anne} = 200$ °C and (c) $T_{anne} = 300$ °C.

along the surface of the substrate to reach the low energy nucleation sites and growing preferentially there itself.

3.2. Scanning electron microscopic analysis

JEOL JSM-5610 LV scanning electron microscope has been used for the surface morphological analysis of WO_3 films prepared at room temperature (as-deposited) and further annealed at 200 and 300 °C. The SEM pictures of as-deposited (T_{sub} = RT) and annealed (T_{anne} = 200 °C and 300 °C) WO_3 films on glass substrates are shown in Fig. 4(a–c). The image of the as-deposited film (Fig. 4(a)) reveals the uniform amorphous surface nature. When the films were annealed at 200 °C (Fig. 4(b)), the morphology becomes a netted surface. As the annealing temperature increases beyond 200 °C i.e., T_{anne} = 300 °C, an entirely different surface morphology (Fig. 4(c)) is obtained. The

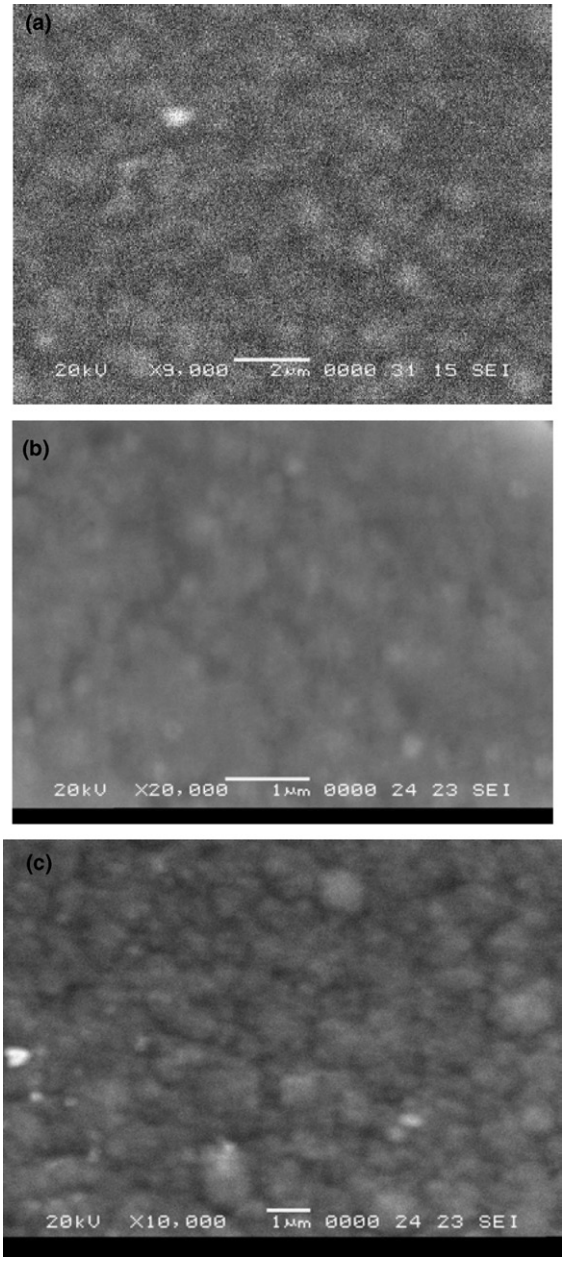

Fig. 5. SEM architecture of WO_3 films on SnO_2:F substrates at different annealing temperatures: (a) T_{sub} = RT, (b) T_{anne} = 200 °C and (c) T_{anne} = 300 °C.

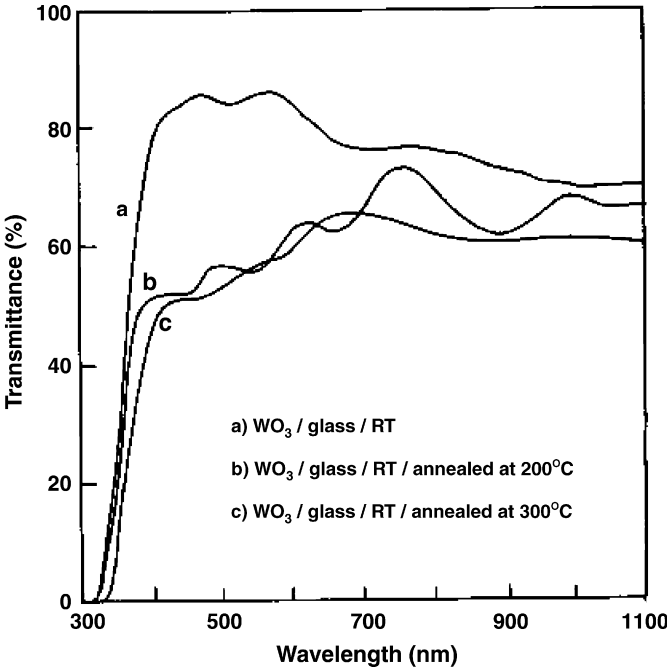

Fig. 6. Optical transmittance spectrum of WO_3 films on glass substrates at different annealing temperatures: (a) T_{sub} = RT, (b) T_{anne} = 200 °C and (c) T_{anne} = 300 °C.

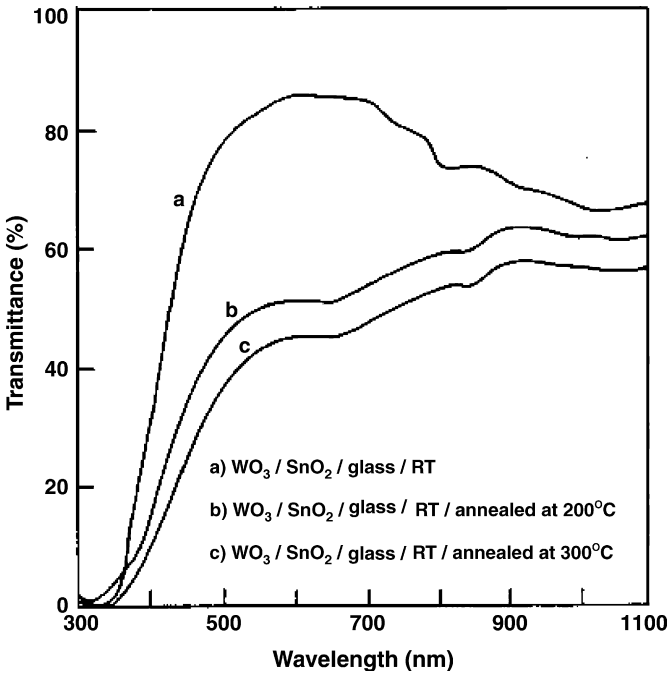

Fig. 7. Optical transmittance spectrum of WO_3 films on FTO substrates at different annealing temperatures: (a) T_{sub} = RT, (b) T_{anne} = 200 °C and (c) T_{anne} = 300 °C.

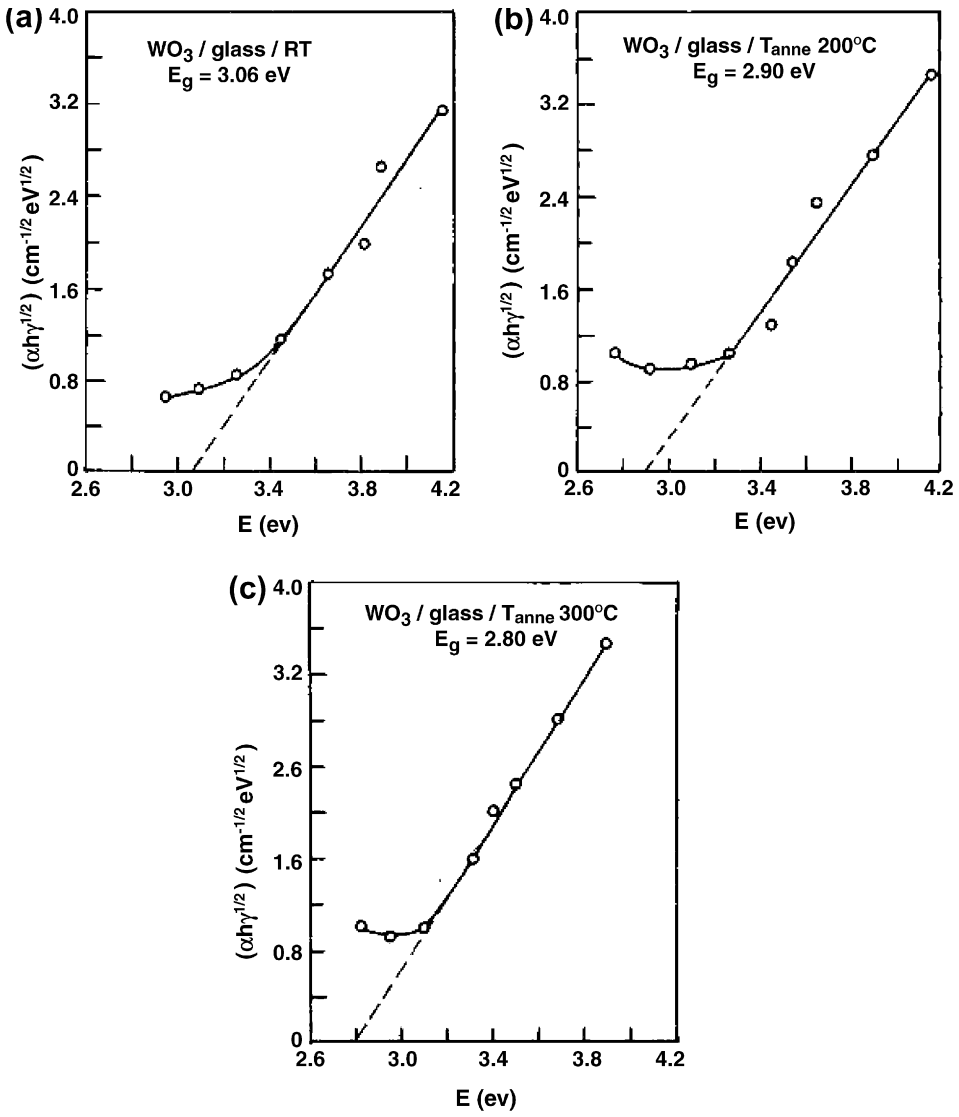

Fig. 8. $(\alpha h\nu)^{1/2}$ against E graph of WO_3 films on glass substrates at different annealing temperatures.

surface looks like well resolved and crystallized with uniform needle-like textured grain morphology. This indicates the crystalline nature of the films subjected to a post heat treatment at 300 °C. These needle-like crystallites confirm the highly textured nature of the annealed films. Also, the XRD pattern supports the formation of these WO_3 films with textured nature as evident from the prominently observed triplet peaks along (002), (020) and (200) orientations (Fig. 1(c)).

The surface architecture of WO_3 films coated on SnO_2:F substrates are shown in Fig. 5(a–c). The crystallinity of the film prepared at room temperature is evident from the spherical grains observed in Fig. 5(a). This may be attributed to the polycrystalline nature of SnO_2:F substrate which provides nucleation sites and enhances the crystalline quality of films. Homogeneous, well ordered and uniform sized grain morphology was obtained when the as-deposited WO_3 film on SnO_2:F substrate was subjected to annealing at higher temperatures such as 200 °C and 300 °C (Fig. 5(b) and (c)). The grain size of these homogenous crystallites is of the order of about 92 nm. This reveals the nanocrystalline nature of the films prepared by the electron beam evaporation technique in the present study.

It is clearly observed from the surface morphological studies by scanning electron microscope that all the films have surfaces with uniform, homogenous and spherical grain morphology. No crack was observed even on the surface of the films treated at higher annealing temperatures. The sharp cleavage edge indicates the well adhesive nature of the films onto the substrates. It is noted from the morphological study that the surface uniformity, crystallinity and homogeneity were improved with increasing annealing temperature. While increasing the annealing temperature, the film looses its roughness and gains continuous and smooth morphology. At higher temperatures, the optimal thermal gradient, low stress and mild shocks influence the quality of the films, favouring the formation of ordered

crystallites in their preferred sites and forming a continuous structure in the film.

3.3. Optical spectral studies by UV–Vis–NIR spectrophotometer

The optical absorption and transmittance spectra of WO_3 films have been recorded in the wavelength range 300–1100 nm. The effect of annealing temperature on the optical properties including percentage of transmittance (% of T) and energy band gap (E_g) are studied in detail. Figs. 6 and 7 show the transmission spectra of WO_3 films prepared at room temperature, further heat treated (annealed) (T_{anne}) at 200 and 300 °C on glass and SnO_2:F coated glass substrates respectively. The observed transmittance of the films is in the range between 80% and 60%. The decrease in transparency of the films with increased annealing temperature in vacuum environment may be due to the formation of more oxygen-ion vacancies in the films. This causes the slight decrease in optical energy band gap. It confirms that the improvement in crystallinity of the films increases with increasing annealing temperature. It is observed from the transmittance spectra that the absorption edge is also slightly shifted towards the longer wavelength region for the films annealed at higher temperatures, owing to preferred colouration effect on the films. The colour of the films also changes with the annealing temperatures, due to the excellent electrochromic nature.

The intrinsic absorption edge of the films can be evaluated and discussed in terms of the indirect interband transition. Thus, the plot $(\alpha h\nu)^{1/2}$ vs. E, called 'Tauc plot', is expected to show a linear behaviour in the higher energy region which corresponds to a strong absorption near the

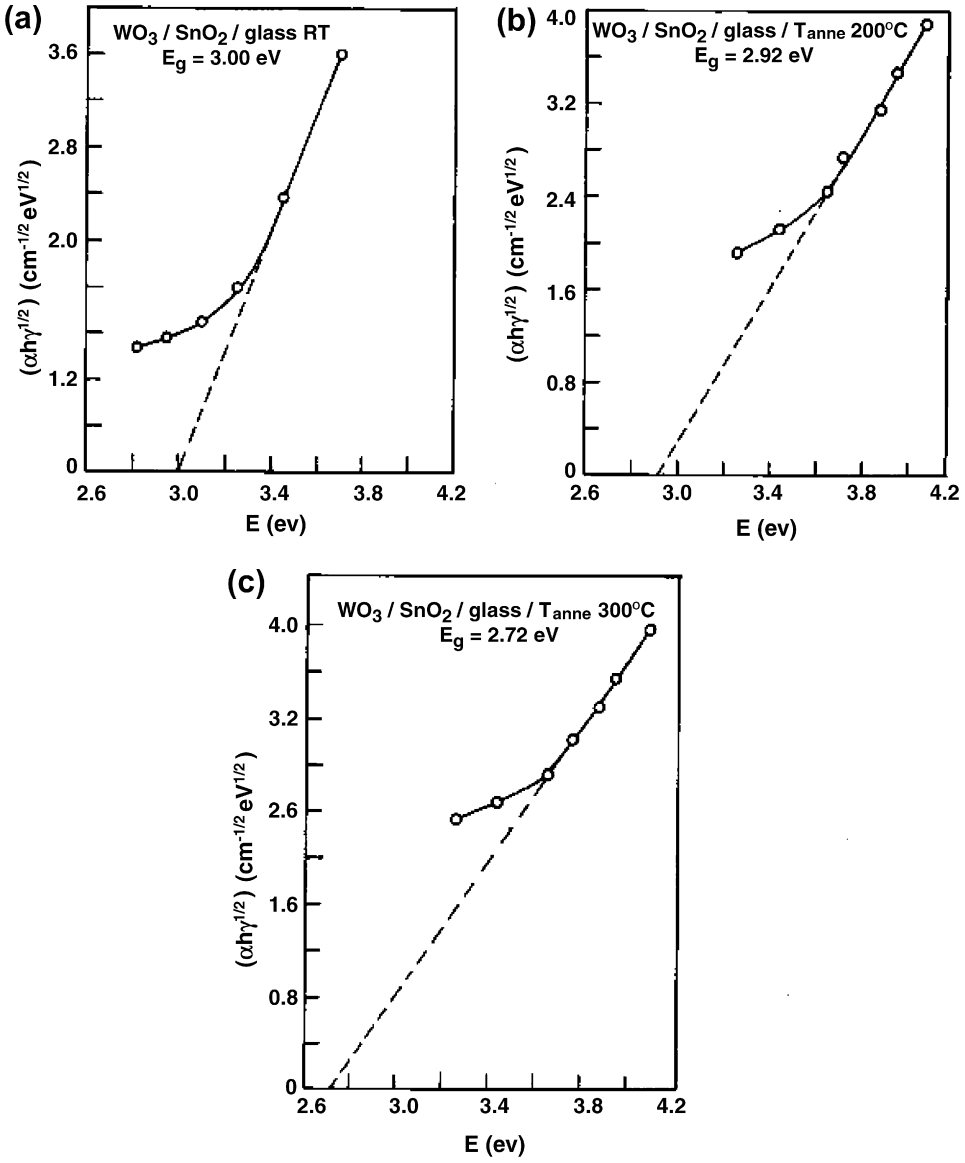

Fig. 9. $(\alpha h\nu)^{1/2}$ against E graph of WO_3 films on FTO substrates at different annealing temperatures.

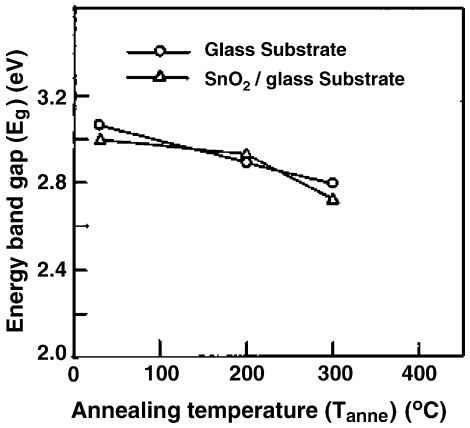

Fig. 10. Variation of energy band gap, E_g of WO_3 films with respect to annealing temperatures.

absorption edge. Extrapolating the linear portion of this straight line to zero absorption edge gives the optical energy band gap, E_g of the films. Figs. 8(a–c) and 9(a–c) show the optical energy band gap spectrum of as-deposited WO_3 films prepared at room temperature and further annealed at 200 and 300 °C on glass and SnO_2:F substrates respectively. The linear region in each graph also confirms the indirect band gap nature of the films. The observed E_g values for the as-deposited WO_3 films deposited at room temperature on glass and SnO_2:F substrates are 3.06 and 3.00 eV respectively. The energy band gap of the films annealed at 200 °C is found as 2.90 eV (Fig. 8(b)) and 2.92 eV (Fig. 9(b)) for glass and SnO_2:F substrates respectively. But the E_g value further decreases to 2.80 and 2.72 eV when increasing the annealing temperature to 300 °C (Figs. 8(c) and 9(c)). The variation in energy band gap values with respect to substrates (glass and SnO_2:F) and annealing temperatures is graphically shown in Fig. 10.

The slight variation in the values of energy band gap from room temperature to higher annealing temperatures may be due to the formation of more oxygen-ion vacancies in the films during the post heat treatment in vacuum. The decrease in concentration of oxygen in WO_3 films with increasing substrate and annealing temperatures was identified from the particle induced X-ray emission spectroscopic (PIXE) analysis [15], which confirms the formation of oxygen ion vacancies in the annealed films. The variation in energy band gap values between 3.36 and 2.95 eV have been reported for the WO_3 films prepared by sputtering technique with different pressures and O_2 concentrations [1]. For the vacuum evaporated WO_3 films, Miyake et al. [11] have found that the E_g values decrease from 3.25 and 2.70 eV when the substrate temperature was increased from 50 to 500 °C.

4. Conclusions

In this paper, we have described in detail the effect of annealing temperature on structural, surface morphological and optical properties of electron beam evaporated WO_3 films. X-ray diffraction analysis clearly shows the formation of predominant triplet peaks along (002), (020) and (200) growth orientations, which exhibits the monoclinic, single phase and textured growth nature of the films. The transformation of amorphous to polycrystalline nature of the films deposited on glass substrates was observed when we increase the annealing temperature. The better aligned and highly oriented growth peaks enumerate the stoichiometric nature of the films. The nanostructural nature of WO_3 films prepared at various substrates and different annealing temperatures are evident from the surface morphological results reported here. Higher annealing temperature enhances the growth of oriented nanocrystalline thin films. The highly transparent nature of the films has been observed from the optical transmittance spectra. The decrease in transmittance with increasing annealing temperatures reveals the formation of oxygen vacancies in the films. The shift in absorption edge towards longer wavelength region has been assigned to the coloration effect of the films. The slight shrinkage in the evaluated optical energy band gap values towards the increasing annealing temperature may be due to the optical band filling effect that reveals the crystallization of the films. We believe that these preliminary characteristic observations on the electron beam evaporated WO_3 films will be helpful to explore the device performance of the films for electrochromic and smart window applications.

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