Effect of annealing on the physical properties of WO₃ thin films

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Abstract: Tungsten trioxide (WO₃) thin films were deposited by electron beam evaporation technique at an oxygen partial pressure of 2 × 10⁻⁴ mbar and at different substrate temperatures ranging from room temperature (RT) to 450°C. The films were annealed at 400°C about 2 hours and the properties were studied systematically. The x-ray diffraction studies show the diffraction peak of (320) at 2θ = 44.07° which indicate the orthorhombic phase of WO₃ and also the other peaks represent the hexagonal phase of WO₃. Due to annealing of the films, the monoclinic phase is also observed. The surface morphology of WO₃ thin films was investigated by using atomic force microscopy and scanning electron microscopy, which supports the above data. The energy-dispersive x-ray (EDX) compositional analysis confirmed the presence of W and O. The optical properties were studied by UV-VIS spectrophotometer and hence the bandgap values are calculated.

Keywords: tungsten trioxide thin films; annealing; structural; morphological; optical and compositional.


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1 Introduction

Tungsten trioxide (WO₃) is one of the most significant transition metal oxide with motivating physical and chemical properties for diverse industrial and scientific applications. Because of moderately low cost, high stability and high coloration efficiency, WO₃ is further suitable for electrochromic applications and display devices. Compared with liquid crystal display (LCD), electrochromic display (ECD) has extensive advantages as no limitation to a view angle, open circuit memory and high contrast. So, ECD systems have potential applications for energy efficient smart windows, mirrors and other non emissive displays (Oi, 1986). Moreover, WO₃ is an optoelectronic material which finds application in optoelectronic devices, switching diodes and smart windows (Su et al., 2011; Chen and Ye, 2008; Sun et al., 2000, 2013; Zeng et al., 2012; Balaji et al., 2009; Lee et al., 2003). It has been confirmed that WO₃ films exhibit chemical sensing properties, hence this will have numerous valuable applications in environmental pollution monitoring and gas sensors (Santato et al., 2001; Djerad et al., 2004; Li et al, 2004; Ma and Frederick, 2003). The optical and electrochromic properties of WO₃ thin films are extremely sensitive to the structure of the films. The growth and properties of the deposited films depends mainly on two components, one is deposition parameters such as oxygen partial pressure, substratae temperature, deposition rate use and the other is chosen deposition method such as thermal evaporation, sputtering, electron beam evaporation (EBE) techniques. The films prepared at different deposition methods or films prepared at different deposition parameters by a particular method have different microstructures and show variation in optical and electrochemical responses (Bachelor et al., 1996; Maruyama et al., 1994a, 1994b; Babinec, 1992; Delichere et al., 1988; Mulenkamp, 1997). Thin films of WO₃ can be prepared by a variety of physical and chemical deposition techniques such as thermal evaporation (Patel et al., 2009), EBE (Sivakumar et al., 2007; Joraid and Alamri, 2007), sputtering (Stankova et al., 2005; Celine Lemire et al., 2002), chemical vapour deposition (Tagtstrom and Jansson, 2009), laser ablation technique (Lethy et al., 2008), sol-gel (Sharbatdaran et al., 2003) and electrodeposition (Leitheriotis and Yianoulis, 2008). However, there are few reports available for the preparation of WO₃ films by EBE technique. Consequently, the present investigations are aimed at EBE technique for the preparation of WO₃ thin films. In this technique, the impingement of WO₃ species on the substrates is in regular order and each
grain is evaporated independently of the other grains, hence the developed films show well reproducible quality of nature than those obtained by other techniques and it is a quite potential technique for the deposition 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 electrochemical device application (Sivakumar et al., 2004). The deposition of tungsten trioxide thin films onto the substrates and their use as active layers in advanced smart windows to enhance their indoor and outdoor compliance with persistent electrochromic properties is the current challenging and dynamic objective for the researchers. Hence, the present study is motivated towards the deposition of WO₃ thin films by EBE technique and to analyse the effect of annealing on the physical properties of deposit films.

2 Experimental details

WO₃ thin films were prepared onto clean glass and indium tin oxide (ITO) coated glass substrates by EBE technique (3 KW Electron beam gun power supply, V.R. Technology). The substrates were cleaned thoroughly by ultrasonic agitator in methanol, acetone and after that washed with deionised water and drying to 20 minutes. Pure WO₃ (99.99%) powder was obtained from Sigma Aldrich and Co. was taken in the required proportion and grinded into fine powder. The powder was pressed under pressure of 5 tons and formed into pellet by using pellet maker. These pellets are having diameter of 1 cm and thickness was around 0.15 cm. The pellets were sintered at 1,073 K for 7 hours. The pellet was taken in a graphite crucible and kept in water cooled copper hearth of electron beam gun. The source to substrate distance was fixed at about 14 cm. The films were coated under the oxygen partial pressure of $2 \times 10^{-4}$ mbar and at substrate temperatures 250 and 350°C with pure WO₃ pellet as the source material. The pelletised WO₃ targets were heated by means of an electron beam collimated from the dc heated tungsten filament cathode. The electron beam bent into 270° and the bent beam is incident on the pelletised WO₃ target. The target surface was bombarded with electron beam to deposit the film on the well cleaned substrates. The process of evaporation is taken place in a high vacuum area to enter the molecules to move freely in the chamber and then condense on whole surface of the substrates. The thickness of the films was found to be 200 nm which was measured approximately by using in built quartz crystal thickness monitor. The above deposited thickness was controlled by the deposition rate 0.2 nm/sec and deposition time 16–18 minutes. The prepared films were further annealed at 400°C in air about 2 hours. The deposited and annealed films were characterised for structural, morphological, compositional and optical properties.

2.1 Characterisation techniques

The structure, phase and orientation of the deposited films were analysed by x-ray diffraction (XRD) technique with Philips x-ray diffractometer with Cu Kα ($\lambda = 1.5418$ Å) target in the scanning angle range 10–80° in continuous scan mode. The system is operating at the voltage of 40 KV and current of 30 mA. The surface morphology and topography of the experimental films was observed by NT-MDT solver next atomic force microscope (AFM) and scanning electron microscopy (SEM). The elemental composition
was carried out by energy dispersive spectroscopy (Model: Oxford instruments IncaPenta FET X3) attached with SEM (Model: EVO ma 15 manufactured by Carl Zeiss). UV-VIS Shimadzu spectrophotometer was used for the optical transmission spectra in the wavelength range of 300–1,100 nm with respect to air in the reference beam in.

3 Results and discussion

3.1 X-ray diffraction

The x-ray diffractograms of WO\(_3\) thin films were deposited by electron beam deposition technique in an oxygen partial pressure of \(2 \times 10^{-4}\) mbar and at substrate temperatures 250°C, 350°C and annealed the same at 400°C in the air about 2 hrs are shown in Figure 1. It was observed that the films exhibit amorphous nature at lower temperatures than 250°C. The XRD patterns deposited at higher substrate temperatures, i.e., 250°C and 350°C show the observable diffraction peaks at (210), (402) and (320) with corresponding values of \(\theta\) as 37.84°, 77.54° (hexagonal phase) and 44.08° (orthorhombic phase) respectively (JCPDS: 33-1387 and 20-1324). This observation reveals that the films show the orthorhombic structure predominantly due to the high intense peak of (320) at 44.07° (Bujji Babu and Madhuri, 2017). The observed peak at 64.44° corresponds to the mixed phase of orthorhombic and hexagonal which is observed to be shifted towards higher \(\theta\) values with an increase of substrate temperature. The XRD pattern of annealed films at 400°C about 2 hours showed the peak at (002) corresponds to \(\theta = 37.77°\) (JCPDS – 820728) which lead to orthorhombic phase of WO\(_3\) thin films. The hexagonal phase [in Figure 1(a) and 1(b)] is changing completely to orthorhombic phase [in Figure1(c) and 1(d)] at \(\theta = 37.77°\) (JCPDS – 820728) which is attributed to annealing of the films. It is also observed that the mixed phase is shifted to higher 20 (observed at 64.5°) values which emphasises that the hexagonal phase is slowly transforming into orthorhombic phase due to annealing (JCPDS-201324). In addition to this change in the phase of the films is clearly appreciable with additional peak (2 0 16) at 20 = 30.30°, showed monoclinic structure (JCPDS-301387). From Figure 1, it is clearly observed that the intensity of the orthorhombic phase is slowly decreasing and the intensity of peaks related to monoclinic structure is increasing. Hence, as the annealing temperature is raised up to higher temperatures about 600°C, the films have completely turned to monoclinic structure from orthorhombic structure (Ahn et al., 2007).

3.2 Atomic force microscopy

The surface morphology of WO\(_3\) thin films deposited at 250°C and 350°C in an oxygen partial pressure of \(2 \times 10^{-4}\) mbar and annealed in air about 2 hours at 400°C was visualised by AFM in contact mode and the 3D AFM images are shown in Figure 2. The films prepared at room temperature are smooth and homogeneous surface. As the substrate temperature increases the root mean square roughness increases and hence the grain size increases from 42.5 to 86.52 nm due to the agglomeration of the atoms (Patel et al., 2009). After annealing of the deposited samples at 400°C in air about 2 hours, the small grains merged together to form larger ones. The annealed films are much smoother than the as deposited films with lower surface roughness values. After the films are
annealed there was not much variation in the morphology of the films except the slight increase of grain size and slight lowering of surface roughness.

**Figure 1** The XRD pattern of the WO₃ films grown at substrate temperatures (Tₛ) at (a) 250°C (b) 350°C (c) 250°C annealed at 400°C and (d) 350°C and annealed at 400°C in air about 2 hrs (see online version for colours)

3.3 Scanning electron microscopy

SEM is one of the versatile technique for the examination and analysis of microstructural species and topography of the films deposited on the substrate. The SEM images of WO₃ thin films at various deposition parameters is shown in Figure 3. There is an observable difference between the samples deposited and annealed at 400°C. The SEM images of the WO₃ thin films shows well adherent and uniform surface morphology without any visible cracks and pinholes as shown in Figure 3. The as-deposited films have minute granular structure which is covered by smooth thin layer. On the other hand, samples annealed at 400°C has appeared to have special topography which inturn consists of agglomerated grains, hence the surface appears to be non uniform but continuous. This may be due to
the thermal properties of WO₃. Furthermore, from Figures 3(c) and 3(d) showed that the annealed films have surface looks like fine resolved and crystallised with uniform needle like textured grain morphology. This indicates the crystalline nature of the films subjected to annealing effect at 400°C. This needle like crystallites confirms the highly textured nature of the analysed films (Kim et al., 2000).

Figure 2  AFM images of the WO₃ films grown at substrate temperatures (Tₛ) at (a) 250°C (b) 350°C (c) 250°C annealed at 400°C and (d) 350°C and annealed at 400°C in air about 2 hrs (see online version for colours)
3.4 Energy dispersive spectroscopy

The composition and elemental analysis of WO$_3$ films were analysed by taking EDX spectra in the energy range between 0 and 10 KeV. The EDX spectra for the films is shown in Figure 4. The presence of characteristic peaks of tungsten and oxygen atoms are
Effect of annealing on the physical properties of WO$_3$ thin films clearly observed in the given spectra, which confirms the stoichiometry of WO$_3$ thin films (Ramana et al., 2006) and also the quality of the films deposited by EBE technique.

**Figure 3** SEM images of the WO$_3$ films grown at substrate temperatures ($T_s$) at (a) 250°C (b) 350°C (c) 250°C annealed at 400°C and (d) 350°C and annealed at 400°C in air about 2 hrs (see online version for colours)
Figure 3  SEM images of the WO₃ films grown at substrate temperatures (Tₛ) at (a) 250°C (b) 350°C (c) 250°C annealed at 400°C and (d) 350°C and annealed at 400°C in air about 2 hrs (continued) (see online version for colours)

3.5 Optical properties

The optical transmittance spectra of the WO₃ films were recorded within the 300 \( \leq \lambda \leq \) 1,100 nm wavelength range by UV-VIS double beam spectrophotometer are shown in
Figure 5. The optical transmittance of the films seems to be decreased with increasing substrate temperature. It is also observed that due to annealing of the films in air at 400°C about 2 hours, the films still show the decrement in the transmittance (Sivakumar et al., 2007). The optical absorption edge is slightly shifting towards the higher wavelength region due to the increase of substrate temperature and it is still shifted to the higher wavelength region due to annealing.

The optical absorption coefficient was calculated from the relation (Chopra, 1969)

$$\alpha = 1/t \ln \left( \frac{T}{(1-R)^2} \right)$$

where ‘\( \alpha \)’ is the absorption coefficient, ‘t’ is thickness ‘R’ is reflectance and ‘T’ is amount of transmission.
Figure 5  Optical transmittance spectra of the WO$_3$ films grown at substrate temperatures ($T_s$) at (a) 250°C (b) 350°C (c) 250°C annealed at 400°C and (d) 350°C and annealed at 400°C in air about 2 hrs (see online version for colours)

Figure 6  $(\alpha h \nu)^{1/2}$ versus $h \nu$ plots for WO$_3$ thin films grown at substrate temperatures ($T_s$) at (a) 250°C (b) 350°C (c) 250°C annealed at 400°C and (d) 350°C and annealed at 400°C in air about 2 hrs (see online version for colours)
The optical energy band gap of the films was determined from the transmission spectra by using Tauc’s relation (Sivakumar et al., 2007; Miyake et al., 1984), which is given as

\[(\alpha h \nu) = \beta (h \nu - E_g)^n\]

where \(h \nu\) is the incident photon energy, \(\beta\) is the edge width parameter and \(n\) is the exponent. The exponent determines the type of electronic transition which causes the absorption. It can take values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively (Davis and Mott, 1970). The optical data for the above deposited films gave a better fit for the value of exponent \(n = 2\) signifying the indirect allowed transitions (Patel et al., 2009; Miyake et al., 1984).

Figure 6 shows \((\alpha h \nu)^{1/2}\) versus \(h \nu\) plots for the above mentioned WO\(_3\) thin films. The estimated bandgaps from the plots \((\alpha h \nu)^{1/2}\) versus \(h \nu\) were 3.2 and 3.08 eV at the substrate temperature of 250 and 350°C (Patel et al., 2009). These optical energy band gap values of the films decrease to about 2.67 eV and 2.60 eV due to the annealing of the as deposited films at 400°C in air about 2 hrs. This is attributed to the crystallinity of the films with annealing.

4 Conclusions

Thin films of WO\(_3\) were prepared by EBE technique in an oxygen partial pressure of \(2 \times 10^{-4}\) mbar and at substrate temperatures 250 and 350°C. The deposited films are annealed at 400°C in air about 2 hours. The structural, morphological, topographical and optical properties were studied as a function of annealing. From the XRD pattern, it was observed that the phase is changing from orthorhombic to monoclinic at higher annealing temperatures. The peak (2 0 16) at \(2 \theta = 30.30°\) was observed in diffractograms which indicates the WO\(_3\) has monoclinic phase due to annealing. AFM images reveal that the grain size increased due to the merging and the surface roughness slightly decreased because of annealing of the samples. In addition to these images, the change of topography of the thin films was highlighted. The films deposited and annealed exhibit characteristic peaks of W and O present in the film which was seen in EDX spectrum. The change in the colour of the films was observed due to annealing. The optical transmittance is decreased with annealing and the optical absorption edge was shifted to higher wavelength regions. The optical energy band gap values were found to be decreased to 2.6 eV. This decrement is attributed to the increase in the crystallinity of the films due to annealing.

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