EFFECT OF ANNEALING ON STRUCTURAL, SURFACE AND OPTICAL PROPERTIES OF PVD-EBE α-MoO_3 THIN FILMS FOR ELECTROCHROMIC DEVICES

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Thin films of molybdenum oxide (MoO_3) were deposited by a physical vapour deposition method, i.e. the electron beam evaporation technique, using Corning 7059 microscopic glass and SnO_2:F as substrates. The effects of annealing temperature on the structural, surface morphological and optical properties of the films were studied and the results are discussed in detail. SE/S284

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INTRODUCTION

In recent years, a considerable amount of research has been focused on electrochromic oxide thin films owing to their potential application in 'smart windows' (regulation of radiated energy through glass by altering its transmission and reflection properties),[1] low refractive materials in filters and low cost electrochromic devices.[2] Recently,[3] the semiconducting and layered structure of orthorhombic phase molybdenum oxide (α-MoO_3) film has been used as a new gas sensing element in gas sensors owing to their excellent sensitivity to various gases, e.g. H_2, NO_2 and NH_3.

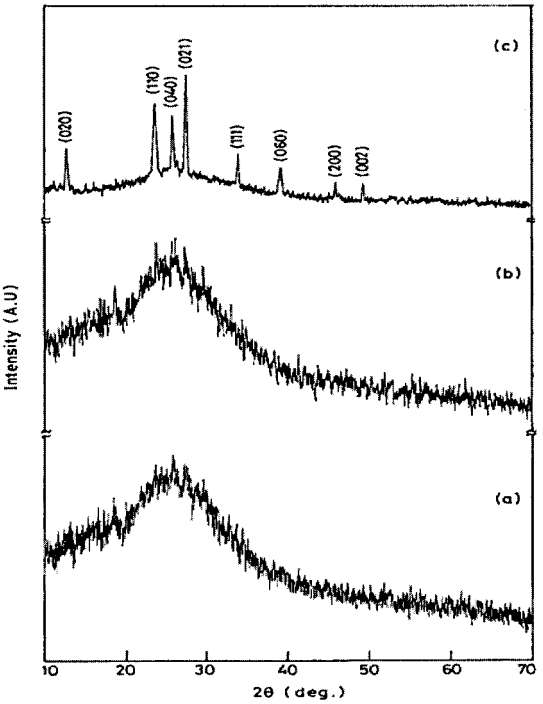
Electrochromism can be described by a reversible change in transmittance and/or reflectance, caused by an applied external voltage. To observe this change, it is necessary to incorporate the electrochromic layer in an electrochromic device. Molybdenum oxide is the widely used electrochromic material and is considered to be one of the best candidates for electrochromic devices. The device consists of electrochromic and ion storage layers separated by an ion conducting layer.

At present, different preparation techniques are available for MoO_3 films with an amorphous and polycrystalline nature. They include chemical methods such as electrodeposition,[4] spray pyrolysis[5] and the sol–gel process.[6] However, the device performance of the prepared films depends on their structural, surface morphological and physical properties and also on the method of preparing the films, in respect of which physical vapour deposition (PVD) methods have had some advantages over chemical methods. Molybdenum oxide films were prepared by different PVD methods, such as electron beam evaporation (EBE)[7] and flash evaporation.[8] Among the physical methods, the EBE technique is quite promising for fulfilling the above requirements.

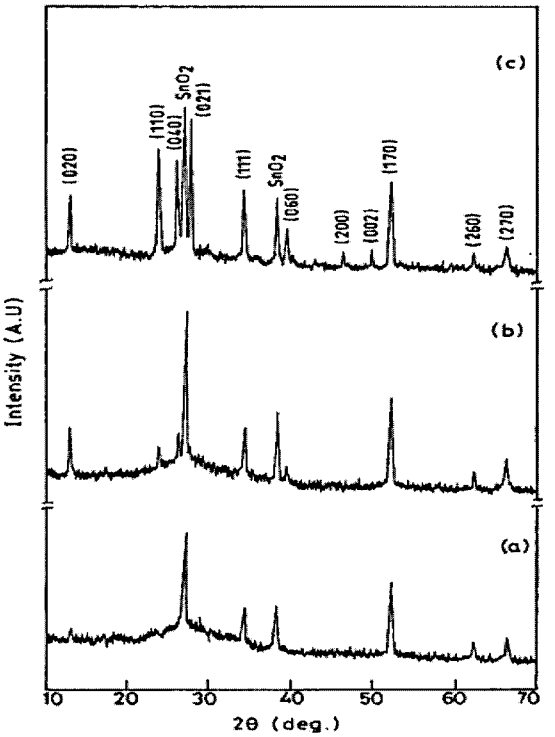
In the present investigation, molybdenum oxide films were prepared employing the EBE technique at room temperature, and the prepared films were further annealed at 200 and 300°C in a vacuum. The effects of the annealing temperature on the structural, surface morphological and optical properties of the films are reported.

EXPERIMENTAL

Molybdenum oxide films were prepared by the EBE technique using a HINDHIVAC vacuum coating unit (model 12A4D) with an electron beam power supply (model EBG-PS-3K). The films were prepared on Corning 7059 microscopic glass substrates and fluorine doped tin oxide coated (SnO_2:F) glass (R_{sh}=15 Ω sq^{-1}) substrates. The glass substrates were degreased in hot chromic acid, rinsed in deionised water and dried with acetone. MoO_3 powder (99·99%) was made into pellets $\sim$20 mm in diameter and 4 mm thick. These palletised MoO_3 targets were placed in graphite crucibles on the water cooled copper hearth of the electron gun inside the vacuum chamber. In the electron gun, the electrons were extracted from a dc heated tungsten filament cathode, through the electric field, past the anode and deflected through an angle of $\sim$180° by the magnetic field to reach the target material. The surface of the MoO_3 pellets (targets) on the graphite crucible was scanned by the resultant and deflected electron beam with an accelerating voltage of 5 kV and a power density $\sim$1·5 kW cm^{-2}. The ablated material (MoO_3 pellets) was evaporated, and the evaporated vapour phase condensed and deposited as thin films on the substrates. During the deposition process, the chamber was evacuated in a high vacuum of order 1×10^{-5} mbar using rotary and diffusion pumps. The homogeneous distribution of evaporated MoO_3 particles on the substrate surface was achieved by the continuous rotation of the substrate, positioned 20 cm above the target material. The depositions



1 *XRD pattern for MoO_3 film on glass substrates*



2 *XRD pattern for MoO_3 film on SnO_2 substrates*

were carried out at room temperature, and these films were further annealed at different temperatures in a vacuum.

X-ray diffraction (XRD) analysis of the films was done using a Philips X-ray diffractometer with CuK_α radiation (λ=1·5418 Å). Surface morphological studies were performed by SEM using a JEOL JDX microscope. The optical absorption and transmittance spectrum were recorded employing a Hitachi-3400 UV-Vis-NIR spectrophotometer in the wavelength range 300–1100 nm.

RESULTS AND DISCUSSION

Structural characterisation

EBE MoO_3 films were found to be uniform, transparent, pinhole free and very adherent to the substrates. The structural properties of the optimised films were confirmed by XRD analysis. Figures 1 and 2 show the XRD patterns of the as deposited and annealed MoO_3 films deposited on glass and SnO_2:F coated substrates, respectively. It was found that the as deposited films on the glass substrate (Fig. 1*a*) at room temperature have an amorphous nature. This may be due to the incomplete formation of the MoO_3 particles on the glass substrates. These films were subjected to heat treatment (annealing). The crystallinity increases with increase in annealing temperature, and the typical crystalline peaks of MoO_3 appear in the spectrum. The XRD pattern of the films on glass annealed at 200°C in vacuum (Fig. 1*b*) also have an amorphous nature.

At higher annealing temperatures, the pattern exhibits many peaks in different orientations, indicating the polycrystalline nature of the MoO_3 films. The patterns obtained for MoO_3 films annealed at 300°C in vacuum (Fig. 1*c*) show several peaks in different directions with higher intensity, which indicate an improvement in crystallinity and transformation from amorphous to polycrystalline. These XRD patterns clearly show that crystallisation of MoO_3 films (on glass substrates, i.e. an amorphous medium) occurs in the temperature range 200–300°C.

The XRD pattern for MoO_3 films on SnO_2:F substrate at room temperature (Fig. 2*a*) has some peaks, which shows its polycrystalline nature. Several peaks with higher intensity were obtained when the films were annealed at 200 and 300°C respectively, as shown in Fig. 2*b* and *c*; this indicates the improvement in the MoO_3 crystal lattice.

The d_{hkl} observed values are indexed with standard JCPDF (No. 05-0508) d_{hkl} values, which are in good agreement as shown in Table 1.

The predominant peaks along (0*k*0), (110) and (021) orientations (where k=2, 4 and 6) represent the orthorhombic phase (α-MoO_3) of MoO_3. The intensity of the XRD pattern for MoO_3 peaks is relatively

Table 1 Comparison between observed and JCPDF (No. 05-0508) d_{hkl} values

Observed *d* values, Å			
MoO_3/glass annealed at 300°C	MoO_3/SnO_2/ glass annealed at 300°C	JCPDF *d* values, Å	Miller indices, *hkl*
6·915	6·915	6·930	020
3·788	3·788	3·810	110
3·463	3·463	3·463	040
3·254	3·254	3·260	021
2·651	2·651	2·655	111
2·307	2·307	2·309	060
1·979	1·979	1·982	200
1·847	1·847	1·8490	002
…	1·768	1·771	170
…	1·502	1·504	260
…	1·419	1·400	270

higher in SnO_2:F coated substrates than in the glass substrates because, during the deposition process, the arrangement of MoO_3 particles is comparatively linear and in repetitive order in the SnO_2:F substrates, as they are already crystalline in nature. Bouzidi *et al.*[5] reported the orthorhombic phase with layered structure for the spray deposited MoO_3 films at substrate temperatures ranging from 250 to 300°C.

The lattice parameters were calculated by the following relation

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{-\frac{1}{2}} \quad \ldots\ldots\ldots (1)$$

where (*hkl*) are the Miller indices of the diffracted planes and $a \neq b \neq c$ for an orthorhombic phase.

The grain size of the film was estimated employing Scherrer's formula[9]

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

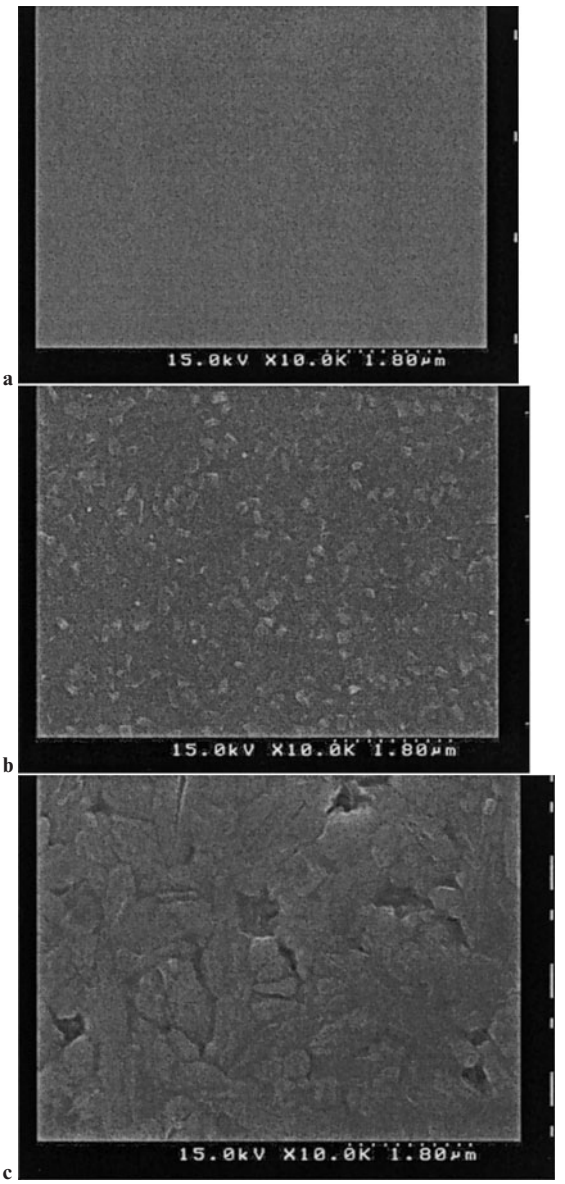
where $\beta_{2\theta}$ is the full width at half maximum (FWHM) of the preferred growth peak, λ is the wavelength of the CuK_α line, θ is the Bragg angle, and k is the shape factor, taken as 0·94.

The evaluated lattice parameters a=3·938 Å, b=13·852 Å and c=3·686 Å are in good agreement with the literature[5] and also agree with the JCPDF (No. 05-0508). The calculated grain size is of the order of 0·341 and 0·170 μm for the MoO_3 preferred growth peak along (021) orientation in spectra 1c and 2c, respectively.

Surface morphological study

The surface morphology of the MoO_3 films was observed by SEM. Figures 3 and 4 show the SEM micrographs of the as deposited and annealed MoO_3 films on glass and SnO_2:F substrates, respectively.

The SEM micrograph (Fig. 3*a*) shows that the as deposited films on glass substrates have a uniform and soft surface; this is attributed to the amorphous nature of the as deposited MoO_3 films at room temperature on glass. Some crystal grains are observed, however, for the MoO_3 film on SnO_2:F substrates at room temperature (Fig. 4*a*); this demonstrates the crystalline nature of the films on SnO_2:F substrates at room temperature. MoO_3 films deposited on glass at room temperature and further annealed at 200°C (Fig. 3*b*) have a very compact structure, and some small crystal grains exist, homogeneously distributed on the surface. This demonstrates the transformation from the amorphous to the polycrystalline phase with treatment by the heating process. An SEM micrograph of MoO_3 films on a SnO_2:F substrate at room temperature which has been further annealed at 200°C is shown in Fig. 4*b*. Straight grain boundaries are shown consisting of several elongated crystal grains. Imawan *et al.*[3] reported the same feature for MoO_3 on a SiO_2/Si substrate. As the annealing temperature increases beyond 200°C, the crystallinity of MoO_3 increases, which is also shown by the XRD pattern (Figs. 1 and 2*c*). The morphology of the film annealed at 300°C is shown in Figs. 3 and 4*c*. Figure 3*c* reveals the SEM micrograph of MoO_3 films on glass substrates, and clearly shows the smooth surface with a dense and needle-like crystalline

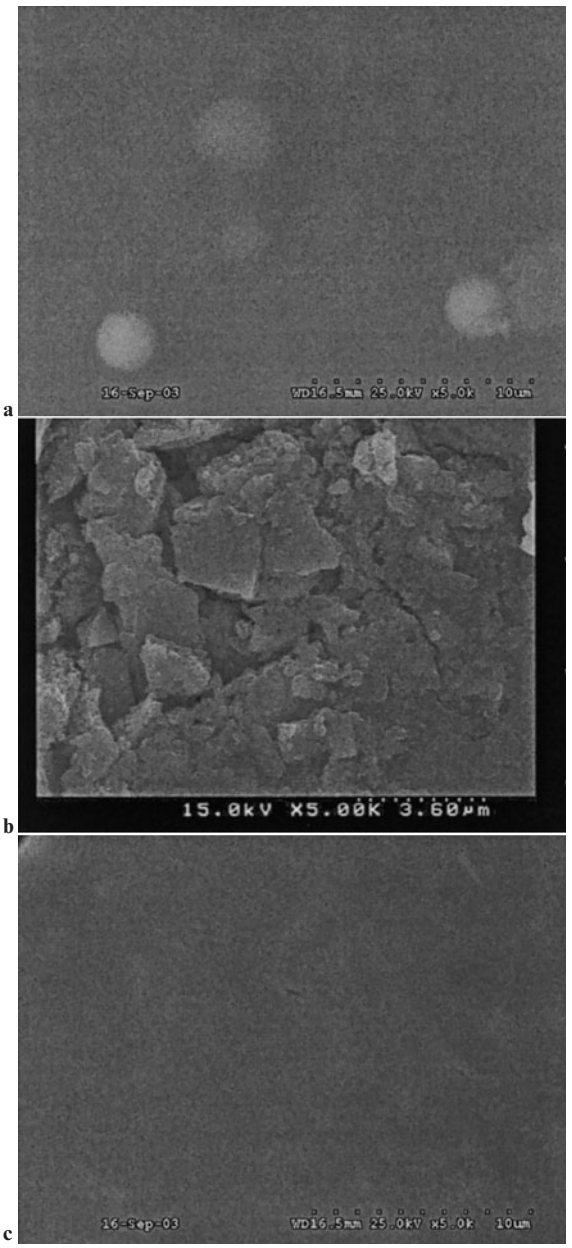


3 *SEM micrograph of MoO_3 film on glass substrates*

structure. The morphology is in accordance with the earlier report.[10] This reveals the polycrystalline nature of the films. While the same structure is slightly visible in the micrograph of the films on SnO_2:F substrates (Fig. 4*c*), this may be due to the SnO_2:F substrate. The morphology of the MoO_3 films on polycrystalline CdS substrate also shows slightly elongated grains, when studied by atomic force microscopy analysis.[11] Comini *et al.*[12] reported needle-like morphology for the post-annealed MoO_3 films at 800 K. In the present case, the needle-like crystallites are optimised even at lower annealing temperatures (i.e. 300°C). There is no crack, and holes were observed on the film surface as a result of heat treatment, which indicates the uniformity and pinhole free nature of the films.

Optical properties

The effect of annealing temperature on the optical properties of EBE MoO_3 films was studied by recording the optical absorption and transmission spectrum in the wavelength range 300–1100 nm.



4 *SEM micrograph of MoO_3 film on SnO_2 substrates*

The optical absorption coefficient α of MoO_3 film was calculated by the relation[13]

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

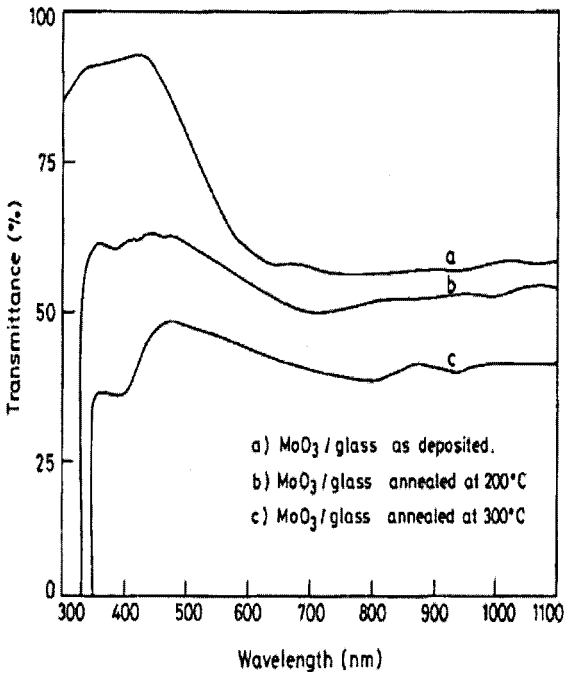
where δ is the thickness, T is the transmittance, and R is the reflectance of the film.

The energy band gap of the film was evaluated using the relation[7]

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

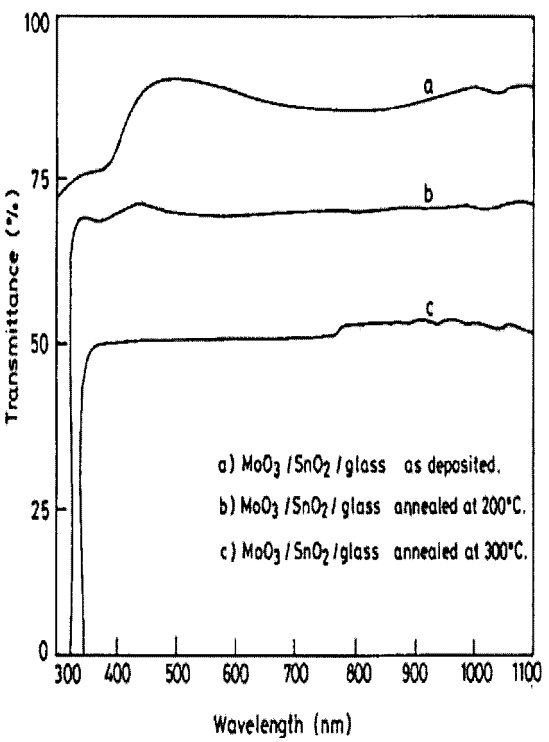
where E_g is the semiconductor energy band gap, and B is a constant. The exponent n has the value 1 for the direct transition band gap and 4 for the indirect transition band gap.

Figures 5 and 6 show the optical transmission spectra of the MoO_3 film prepared at room temperature and further annealed at 200 and 300°C on glass and SnO_2:F substrates, respectively. It is observed that the absorption edge starts from 300 nm and the

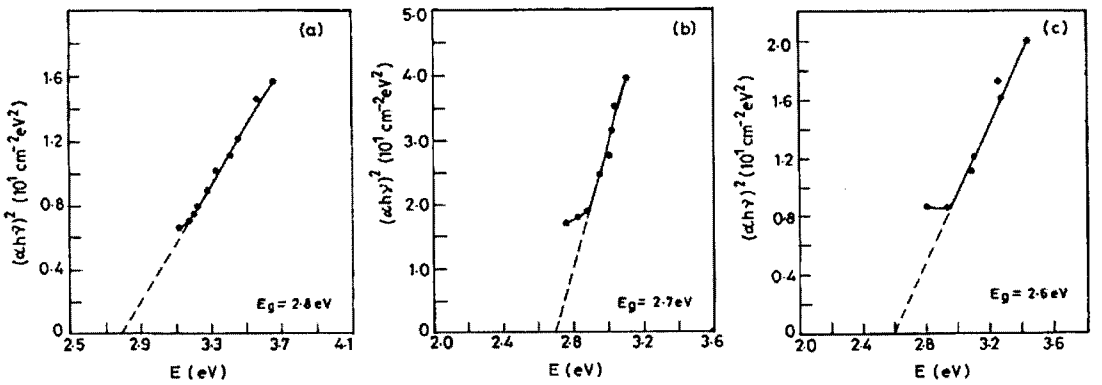


5 *Optical transmission spectrum for MoO_3 film on glass substrates*

maximum transmission of ~95% was observed in the visible region for the as prepared films, it indicates the transparent nature of the films. The optical transmission range of the films above the absorption edge decreases with increase in annealing temperature and also the absorption edge slightly shifts towards the higher wavelength region. This may be due to the coloration effect on the films during the heat treatment. The films prepared at room temperature are light grey in colour and, after the heat treatment,



6 *Optical transmission spectrum for MoO_3 film on SnO_2 substrates*



7 *$(\alpha hv)^2$–E graph for MoO_3 film on glass substrates*

the colour of the films changes, depending on the annealing temperature. The coloration effect of the films is connected with the absorption edge shift.[8]

From this, it can be concluded that the optimised MoO_3 films in the present work have a perfect coloration effect, and it may be one of the best candidates for low cost electrochromic devices.

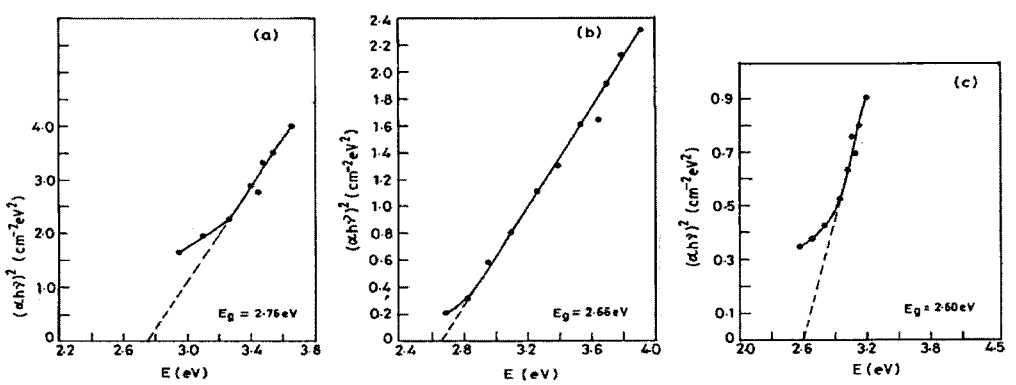
Figures 7 and 8 show the optical energy band graph $(\alpha hv)^2$–E of the MoO_3 films on glass and SnO_2:F substrates, respectively.

The optical energy band gaps E_g of the films were obtained by extrapolating the straight line portions of the $(\alpha hv)^2$–E curve. From this energy graph, it is observed that the optical absorption of MoO_3 films occurs through the direct interband transitions and also reveals that these films have a direct band gap nature. The estimated energy band gap for the films prepared at room temperature on glass substrates is 2·80 eV and reduced to 2·70 eV for the films annealed at 200°C. The E_g value of the MoO_3 films annealed at 300°C is 2·60 eV, whereas the E_g values vary from 2·76 to 2·60 eV for the films prepared on SnO_2:F coated substrates. The variation in energy band gap values from those at room temperature is due to the formation of more oxygen ion vacancies in the films during heat treatment, hence the conductivity of the film which lies close to the valance band is gradually increased. The value E_g=2·80 eV for the flash evaporated MoO_3 films at the substrate temperature of 300°C was reported by Julien *et al.*[8] Abdellaoui *et al.*[14] reported that the E_g value of MoO_3 varies from 2·79 to 3·10 eV for various annealing temperatures in different environments. It is therefore concluded that the estimated band gap values for the MoO_3 films in the present work are close to those in earlier reports.

CONCLUSIONS

Device quality orthorhombic α-MoO_3 molybdenum oxide thin films were prepared by the EBE method on glass and SnO_2:F substrates. The optimised films are transparent, uniform and adhere well to the substrates. XRD analysis showed that the prepared MoO_3 films belong to the orthorhombic phase. The well textured crystalline XRD peak reveals the stoichiometric nature of the films. It is observed from the XRD pattern that the MoO_3 is transformed from amorphous to polycrystalline α-MoO_3 when the films are annealed at higher temperatures. The pattern obtained at an annealing temperature of 300°C (Figs. 1 and 2*c*) yields MoO_3 films with good stoichiometric and well oriented peaks in XRD. The surface morphological study reveals that the crystallinity of the films improves with annealing temperature, and the films annealed at 300°C have a good crystal texture with a smooth surface. The elongated and needle-like crystallites confirm the crystalline nature of the films. The optical studies show that the films have a good coloration effect and stoichiometric nature. The estimated energy band gap values are in good agreement with the literature, and the variation in the band gap during heat treatment may be due to oxygen vacancies.

The above studies and results show that the optimised MoO_3 thin films prepared by the PVD-EBE technique are suitable for use in the development of electrochromic devices.



8 *$(\alpha hv)^2$–E graph for MoO_3 film on SnO_2 substrates*

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