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Study on structural and optical properties of thermally evaporated MoO_3 thin films

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Abstract. Molybdenum trioxide (MoO_3) thin films are grown on ITO-coated glass substrates by thermal deposition technique under the presence of oxygen partial pressure (PO_2) about 2×10^{-3} mbar at various substrate temperatures to enhance electrochromic efficiency. Even at room temperature, the experimental films were crystalline, and crystallinity increased as the substrate temperature (T_s) was raised to 150°C. It is noted that the uniform spherical structure was transformed to a needle-like structure at T_s = 150°C. The transmittance of the films improved with substrate temperature, and corresponding bandgap values were measured. The films grown at T_s = 150°C reported the highest colouration efficiency.

Keywords. Molybdenum trioxide thin films; substrate temperature; structure and morphology; optical properties; electrochromic properties.

1. Introduction

In the modern era, transition metal oxides are attracting the attention of researchers towards variable transmittance electrochromic devices [1] based on the reversible intercalation of Li^+ [2], H^+ [3,4] and K^+ [5] ions. One of the important layers in this device is the electrochromic layer, where the variation of optical property takes place due to an applied external voltage [6]. The direction, magnitude of charge transferred, type of electrolyte, sweep rate and charge density affect the performance of the device. Optical modulation in the electrochromic layer depends on the growth and physical properties of the layer. The basic redox reaction in the electrochromic layer is as follows:

$$MoO_3 + xe^- + xM^+ \leftrightarrow M_xMoO_3$$
$$(M = Li, H, K, \text{etc.})$$

Among various electrochromic materials (MoO_3, V_2O_5, WO_3, various composites), molybdenum trioxide has a unique layered/open structure to intercalate the ionic species intensely, uniformly and shows interesting optical, catalytic and electrochromic properties [7–9]. In general, MoO_3 displays polymorphic structures based on the bonding of basic octahedral units, such as orthorhombic (α), monoclinic (β) and hexagonal (h) [10,11]. Furthermore, MoO_3 shows various oxidation states ranging from +2 to +7, is highly stable, catalytic, electrochemical active and produces stable colouration efficiency. Besides, MoO_3 exhibits a two-dimensional Vander Waal's layered structure with an orthorhombic phase, ReO_3-like structure for the metastable monoclinic phase and a one-dimensional tunnel-like structure for h-MoO_3 phase [12–14]. The flexibility in optical properties of MoO_3 makes it useful for chromogenic windows, reflection mirrors, electrochromic display devices, anti-dazzling coatings, automotive sunroof glazing, low-cost materials in filters, optical switching, chemical and biological sensors, supercapacitors and memory devices [15–20]. The pronounced electrochromism in MoO_3 is related to the polyvalent oxidation states, perovskite structure and oxygen deficiency that channels the ion intercalation/deintercalation.

Technological progress in society demands new electrochromic materials with enhanced electrochromic efficiency. Hence, our investigations are aimed at efficiently synthesizing MoO_3 thin films. As structure and growth play a key role in utilizing the developed films in electrochromic device applications, the structured tailoring of deposited films at various substrate temperatures is a prime significance of the present research.

Numerous synthesis processes were used to deposit MoO_3 thin films, which includes thermal evaporation [21,22], electron beam evaporation [23,24], pulsed laser deposition [25], electrodeposition [4], sputtering [2,26–28], chemical vapour deposition [29], spray pyrolysis [30] and sol–gel process [31]. Out of the above synthesis processes, thermal evaporation is the simple, low-cost technique for

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making high quality and uniform films for large-area applications. Hence, this work is focused on thermally grown molybdenum trioxide thin films to achieve stable and high colouration efficiency.

2. Experimental

Thermal evaporation technique was used to grow the thin films of molybdenum trioxide at various substrate temperatures onto ITO-coated glass substrates. Powder of pure (99.99%) molybdenum trioxide was obtained from the Sigma Aldrich Co., from which about 75 mg was taken in a molybdenum boat and electrically heated during the deposition. Initially, the vacuum of $\approx 5 \times 10^{-5}$ mbar was produced by a diffusion pump backed by a rotary pump in the deposition chamber. Digital Pirani and Penning gauge were being used to measure the pressure in the chamber. The system was connected to the chiller for the cooling system. The well-cleaned substrates were arranged on the substrate holder, which is in turn connected to the heater to vary the substrate temperature. The constant distance of 14 cm was maintained between the source and the substrate. The source material is evaporated by resistive heating in presence of a vacuum and allowed to condense on the clean substrates to get solid films. The experimental films were deposited under an oxygen partial pressure of 2×10^{-3} mbar at substrate temperatures, T_s = RT, 100 and 150°C. The deposited film has a thickness of about 200 nm, which was measured by the inbuilt quartz crystal thickness monitor. The deposited films were systematically characterized to study the structure (X-ray diffraction, (XRD) technique), morphology (scanning electron microscopy (SEM)), elemental composition (energy dispersive spectroscopy (EDS)), optical (Shimazdu U-V 1800 spectrophotometer) and electrochromic properties (electrochemical work station). The influence of substrate temperature on the growth and properties were analysed.

3. Results and discussion

3.1 *Structural study*

An X-ray diffractometer (SHIMAZDU XRD-7000) was used to study the systematic structural characterization. The XRD patterns of thermally grown molybdenum trioxide thin films on ITO-coated glass substrates under $PO_2 = 2 \times 10^{-3}$ mbar at various deposition temperatures are shown in figure 1. The influence of T_s on the structure of experimental MoO_3 thin films in the diffracting angle range of 10°–70° is observed in the figure. XRD pattern of MoO_3 films grown on ITO-coated glass substrates at room temperature shows small intensified resolved peaks, which propose the onset of crystallization of the films and that the films exhibit α-MoO_3 phase. The films exhibited (1 3 0), (0 4 1), (0 0 2), (2 6 0) Bragg reflections at 2θ = 30.71°, 35.42°, 50.78° and 60.42° for the films grown at room temperature. Whereas additional peak was observed for the films deposited at T_s = 100°C at 2θ = 45.79° for (200) Bragg reflection, which confirms that the films are strongly oriented in the orthorhombic phase. The films grown at T_s = 150°C showed additional Bragg reflections of (110), (221) at 2θ = 22.69° and 53.89°, respectively. The intensity of the existing peaks was found to be increased at T_s = 100 and 150°C due to high adatom mobility. The experimental films are highly oriented and the layered structure is packed in the direction of the *b*-axis. Also the films were observed to be thermodynamically stable at higher substrate temperatures. The observed data is compared with powder diffraction data (JCPDS), which confirms the orthorhombic α-MoO_3, with a two-dimensional layered structure formed by sharing of MoO_6 octahedral units.

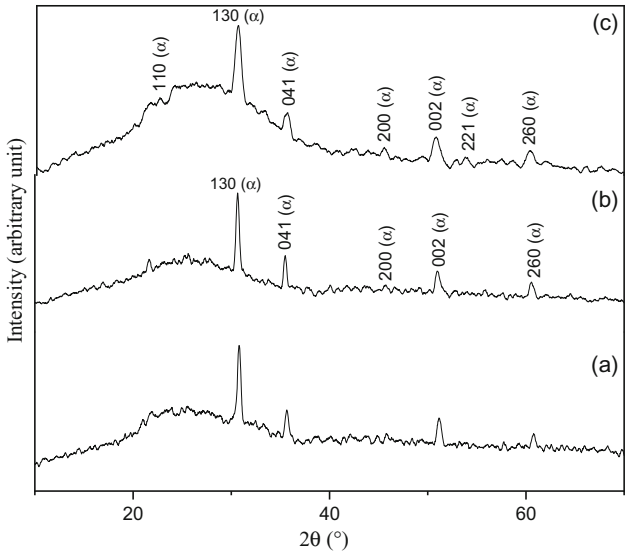

Figure 1. XRD spectra of MoO_3 films deposited at T_s: (**a**) RT, (**b**) 100°C and (**c**) 150°C.

Debye-Scherrer's equation was used to evaluate the average crystallite size, which is given below.

$$D = \frac{K\lambda}{\beta\cos(\theta)}, \tag{1}$$

where K is Debye-Scherrer constant (0.90), λ denotes the wavelength of CuK_α radiation (1.54 Å), β is FWHM (full-width at half-maximum) and Bragg angle is θ.

The average crystallite size for the above films was in the range from 9.2 to 17.7 nm and the crystallite size increased with an increase in substrate temperature.

3.2 *Morphological study*

3.2a SEM study: The topographical studies as a function of substrate temperature were performed by SEM. The films prepared below T_s = 150°C were found to be uniform and

crack-free surfaces. Figure 2 shows the SEM images of the films prepared at various substrate temperatures. With the rise of substrate temperature to 150°C, the surface of the films turns to a needle-like structure due to high thermal energy, adatom mobility and agglomeration of the grains on the surface [32,33]. The crystallinity of the films was observed to be increased at higher substrate temperatures, and the films were grown continuously on the substrate without any cracks.

3.2b EDS study: The purity of the experimental films was identified by the energy dispersive spectra, as given in figure 3. The presence of only Mo and O elements shows that the films are very pure and follow the target material composition without any contaminants. The presence of Sn peak is due to the nature of the substrate (ITO) used in the experiment. It was found that the substrate temperature did not influence the purity of the films.

3.3 *Optical study*

The wavelength dependence of transmittance spectra for grown MoO_3 thin films is shown in figure 4. It discloses that transmittance increases in the ambience of an oxygen atmosphere, $PO_2 = 2 \times 10^{-3}$ mbar with an increase of substrate temperature from RT to 150°C. The less optical transmittance, about 40.37%, was given by the grown thin films at room temperature, which might be due to sub-stoichiometry and the films look like a pale blue. The colour of the films slowly changes with the raise in substrate temperature due to the filling of oxygen ion vacancies and the orientation of the atomic arrangement. At higher substrate temperatures, the transmittance was raised to 92.52% [34]. Also, it was found that the optical absorption edge was shifted towards the lower wavelength side with raise in substrate temperature. If 'T' represents the optical transmittance and 't' denotes the thickness of the film, α the optical absorption coefficient is given as follows:

$$\alpha = \frac{-[\ln(T)]}{t}. \tag{2}$$

Power law [35] was used to measure the bandgap (E_g) and type of transition (n) from the above optical data and the relation is given as equation (3).

$$(\alpha h\nu) = B(h\nu - E_g)^n, \tag{3}$$

where B is a constant.

Figure 5 shows $(\alpha h\nu)^2$ *vs.* photon energy ($h\nu$) curves for grown molybdenum trioxide films. The current investigated data is fit for $n = ½$, which signifies direct allowed

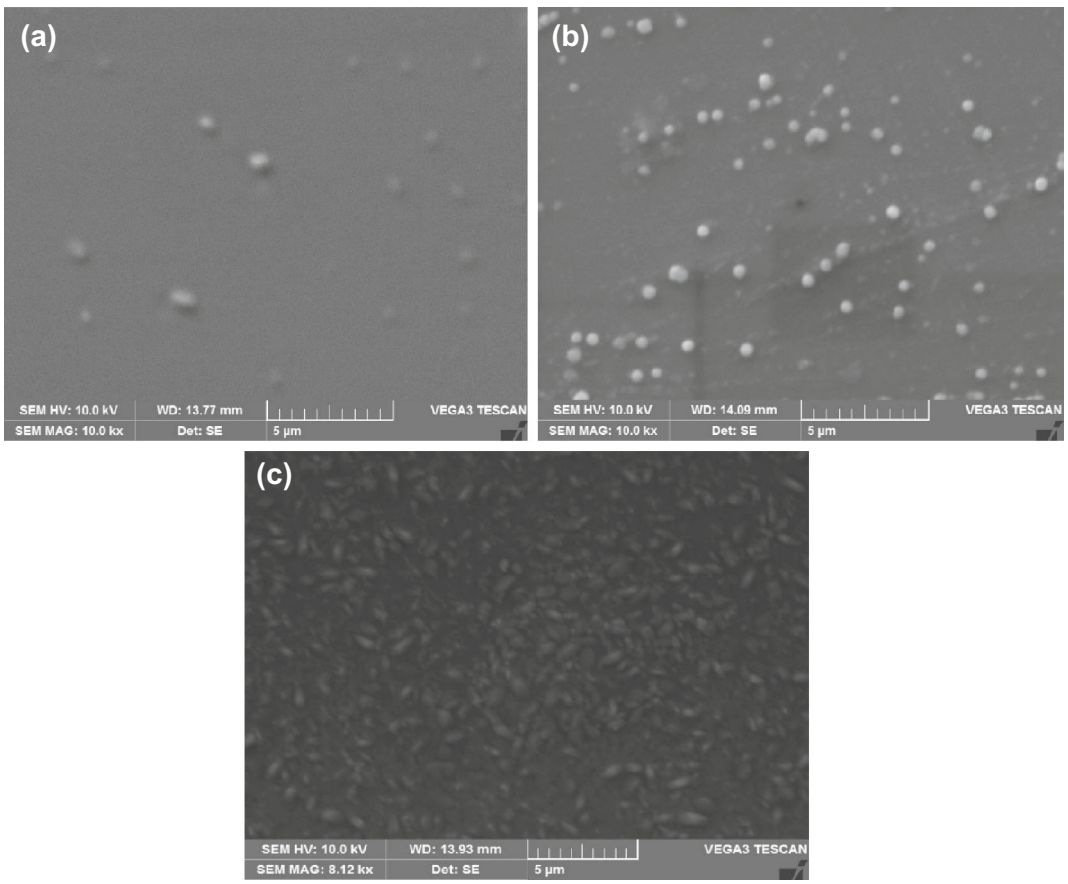

Figure 2. SEM images of MoO_3 films grown at T_s: (**a**) RT, (**b**) 100°C and (**c**) 150°C.

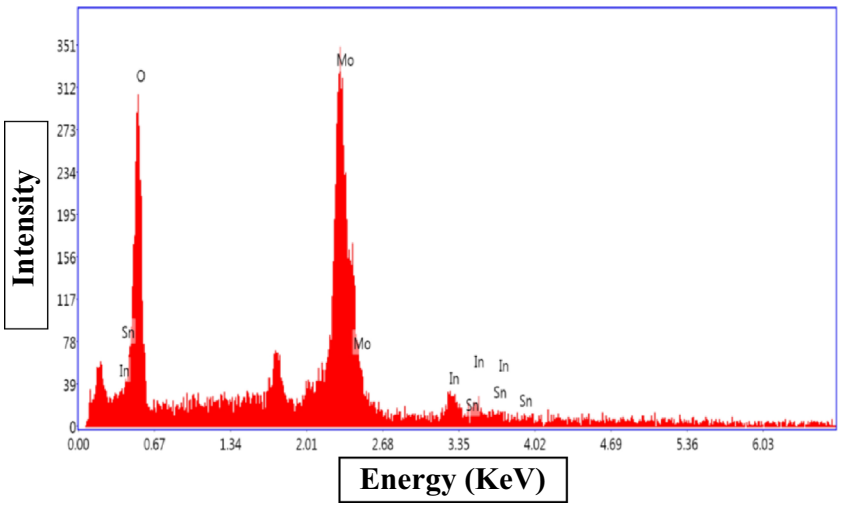

Figure 3. EDS of experimental MoO_3 thin films.

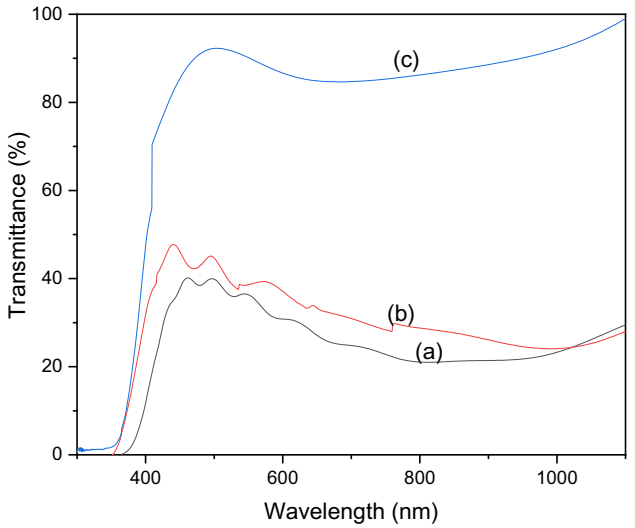

Figure 4. Transmittance spectra of MoO_3 films grown at T_s: (**a**) RT, (**b**) 100°C and (**c**) 150°C.

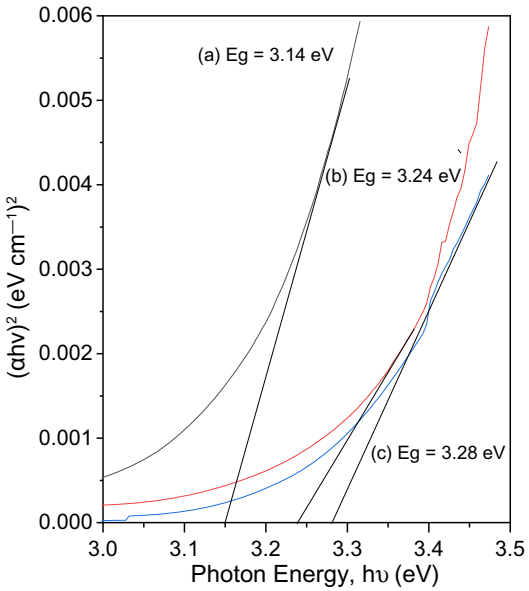

Figure 5. $(\alpha h\nu)^2$ *vs.* photon energy ($h\nu$) curves for MoO_3 films deposited at T_s: (**a**) RT, (**b**) 100°C and (**c**) 150°C.

transition. The optical bandgap of MoO_3 thin films increased with respect to substrate temperature and was found to be in the range of 3.14 to 3.28 eV [25,36,37]. The increase in the bandgap might be attributed to the decrement in the oxygen deficiencies, and the films are nearly stoichiometric at T_s = 150°C.

3.4 *Electrochromic study*

Grown thin films are verified for their electrochromic properties and it is observed that the film deposited in the presence of oxygen partial pressure 2×10^{-3} mbar at 150°C shows good electrochromic performance.

The electrochromic property of molybdenum trioxide thin film was studied by cyclic voltammetry, which consists of three electrodes. In the set up, molybdenum trioxide thin film deposited at T_s = 150°C is used as a working electrode, platinum as a counter electrode and SCE (saturated calomel) as a reference electrode. The electrochromic properties are studied in 0.1 M KCl electrolyte solution, where the insertion/extraction of K^+ ions is possible and the mechanism of electrochromism in the experimental films is given below [7].

$$MoO_3 + xK^+ + xe^- \leftrightarrow K_xMoO_3 \quad (4)$$

An intercalation/deintercalation of the ion process was recorded during the cycling of the scan rate at 10 mV s^{-1}. The potential applied in this process is in the range from –1 to +1 V. The grown film, which appeared blue during the cathodic scan (at negative potential scan), transformed into a dark blue film. At the positive potential of the scan

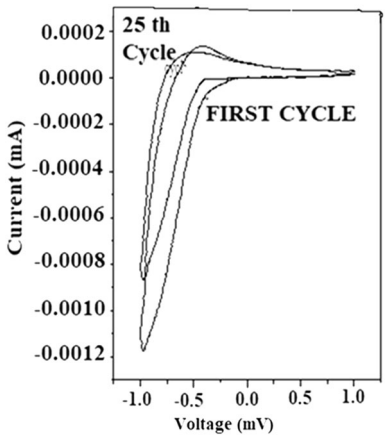

Figure 6. *C–V* curves of experimental MoO_3 thin films deposited at T_s = 150°C.

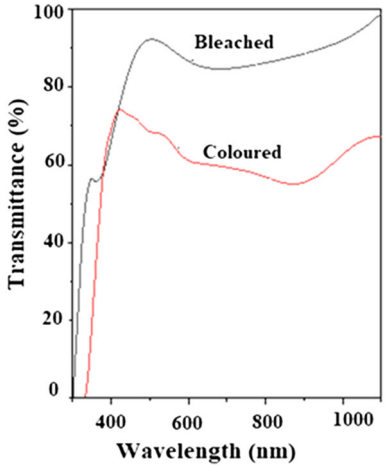

Figure 7. Transmittance spectra before and after colouration for molybdenum trioxide thin films deposited at T_s = 150°C.

(anodic scan), the films turned to light yellow [38]. This change in the colouration of films from blue to light yellow might be due to the formation of 'molybdenum bronze'. The grown films at deposition parameters $PO_2 = 2 \times 10^{-3}$ mbar, T_s = 150°C, seem to be stable throughout the scan rates and the cyclic voltammograms are shown in figure 6. The optical transmittance of the coloured and bleached state of MoO_3 film deposited at 150°C was examined by UV Spectrophotometer and are shown in figure 7. The transmittance of the films in bleached and coloured states is significantly different in the visible range.

The optical density and hence colouration efficiency (CE) were calculated from the above data at various electromagnetic radiation (i.e., visible, UV and IR regions) with the help of the following formula:

$$\mathrm{CE} = (\Delta \mathrm{OD})/Q \tag{5}$$

Here, ΔOD represents optical density, which is given as the logarithmic ratio of transmittance at bleached state (T_b) to coloured (T_c) state and 'Q' is the charge inserted. The corresponding equations are given below:

$$\Delta \mathrm{OD} = \log(T_b/T_c), \tag{6}$$

$$Q = I \times t/A, \tag{7}$$

where I is total current passed per unit area, t is the total time taken to pass the current and A the area of the electrode.

Molybdenum oxide is known to have optical absorption maximum closer to the human eye's sensitivity. Hence, this study focused on studying the spectral transmittance of MoO_3 films in the visible region (λ = 633 nm). Enhanced colouration efficiency of 36.17 $cm^2\ C^{-1}$ in the visible region (λ = 633 nm) was achieved in films grown at $PO_2 = 2 \times 10^{-3}$ mbar [5,39]. The electrochromic performance of various transition metal oxides like WO_3 is given for reference [5,40–48].

To recognize the performance of the films in the IR and UV range, the studies were extended to analyse the colouration efficiency at a wavelength of 1033 and 442 nm, and the colouration efficiencies were found to be 36.69 and 12.63 $cm^2\ C^{-1}$, respectively. The films show stable and repeatable electrochromic efficiency for 25 cycles. The films were found to be fairly adherent during the deposition at T_s = 150°C by thermal deposition technique, which was sustained up to 25 cycles and then the film layer slowly peeled off from the substrate. The growth and adherence of the film on the substrate play a vital role in this aspect. Experimental films with this efficiency can be used in electrochromic display devices and smart window applications.

4. Conclusion

This research work was focused on analysing the influence of substrate temperature on the growth and physical properties of MoO_3 thin films deposited under $PO_2 = 2 \times 10^{-3}$ mbar. Grown films on ITO-coated glass substrates showed onset crystallization at room temperature itself and the films exhibited the orthorhombic-layered structure of α-MoO_3 phase. The experimental films were pure and the morphology was observed to be drastically changed at higher substrate temperatures due to the agglomeration of the grains. Optical data suggested the direct allowed transitions, and the bandgap raised to 3.28 eV at 150°C. The stable, recyclable and high colouration efficiency of 36.17 $cm^2\ C^{-1}$ was found for the experimental films deposited at T_s = 150°C. These films are used as the electrochromic layer in electrochromic devices, optical switches and smart windows.

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