

Studies on spray pyrolyzed molybdenum trioxide thin films

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Abstract. Semiconducting molybdenum trioxide thin films have been prepared by employing simple and inexpensive spray pyrolysis technique. Films are found to be polycrystalline in nature with hexagonal phase. Optical band gap energy (direct) and room temperature electrical resistivity are of the order of 2.9 eV and 10^8 ohm-cm, respectively. These films exhibit cathodic electrochromism.

Keywords. Molybdenum trioxide; spray pyrolysis; electrochromism.

1. Introduction

Electrochromic (EC) devices are of interest for smart windows in energy efficient architecture, non-emissive display devices, variable reflectance mirrors and surfaces with tunable thermal emittance (Granqvist 1992, 1993). Electrochromism was given wide spread attention through Deb's (1969) work on tungsten trioxide films. Consequently several other oxide materials based on molybdenum, nickel, cobalt, iridium, vanadium, titanium, niobium, several mixed oxides and many organic materials have been investigated for electrochromic properties.

Molybdenum trioxide (MoO_3) is a transparent, partially ionic 4d transition metal oxide which has a number of interesting optical and electrical properties. Various techniques such as vacuum evaporation (Deb 1968), anodic oxidation (Arora and Kelly 1977), physical vapour deposition (Krishnakumar and Menon 1993) and spin coating (Hinokuma *et al* 1994) have been employed to prepare MoO_3 thin films and their electrochromic and photochromic properties are reported. However no reports can be found on the preparation of MoO_3 thin films by spray pyrolysis technique (SPT). SPT is a simple and inexpensive method and hence requires less capital to deposit thin films over large areas than other conventional techniques. The relative packing density of the films depends strongly on the deposition conditions. SPT also offers an advantage in controlling the structure (crystalline or amorphous) of the films.

In this paper, preparation of MoO_3 thin films by spray pyrolysis technique and their structural, optical and electrical properties are reported. An attempt has been made to test the applicability of SPT to produce electrochromic MoO_3 films.

2. Experimental

MoO_3 powder (GR grade, Loba Chemie) was dissolved in ammonia solution at room temperature and doubly distilled water was added to obtain an appropriate quantity of the spraying solution. The solution was sprayed on to amorphous glass substrates maintained at 350°C temperature. The quantity of the solution, concentration of the solution, spray rate and time for the deposition were 50 c.c., 0.05 M, 2.5 c.c./min and 20 min respectively.

The film thickness was calculated by weight difference method and using the density of MoO_3 based on a 100% dense film. Since the film was certainly not 100% dense, the actual thickness would therefore be somewhat higher than the given thickness. The structural identification was carried out using Philips X-ray diffractometer (PW-1710). Optical absorption measurement in the range 350 to 850 nm was carried out by using Hitachi 330 spectrophotometer. The two-probe method was used for d.c. electrical resistivity measurement in the temperature range 400 to 560 K. The area of the films was defined and silver paste was applied to ensure good ohmic contacts to the film. A battery charger (30 V, 6A) was used to pass current through the film and high impedance voltmeter was used for the voltage measurement across the film sample. The size of the film was $1 \times 1 \text{ cm}^2$. To study temperature dependent resistivity measurement, strip type heaters (65 W) were used to heat the samples and Chromel-Alumel thermocouple was used to measure the temperature. Temperature was controlled with $\pm 2^\circ\text{C}$ accuracy using APLAB temperature controller.

The electrochromic cell has been prepared for the study of the electrochromic characteristics. It consists of two F.T.O. coated glass plates ($10 \text{ ohm}/\square$). One plate has been deposited with the MoO_3 film, which acts as a working electrode and other plate as a counter electrode. Saturated calomel electrode was the reference electrode. The cell was filled with an electrolyte of $1 \text{ N H}_2\text{SO}_4$. The electrochromic characteristics were

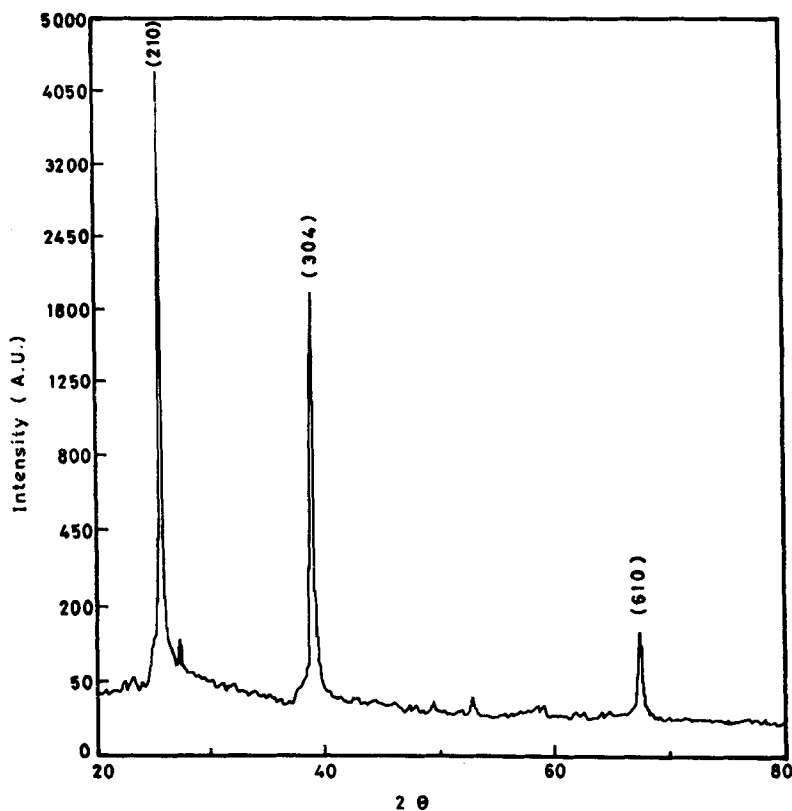


Figure 1. XRD pattern of MoO_3 thin films.

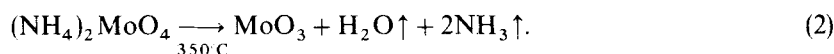
determined by using cyclic-voltammogram taken with EG and G model 362 potentiostat and X-Y recorder.

3. Results and discussion

MoO₃ powder was dissolved in ammonia solution thereby forming ammonium molybdate. The chemical reaction may be given as follows



This solution was then sprayed on to glass substrates kept at 350°C. The following reaction took place



MoO₃ films with 1.1 μ thickness were obtained.

Structural identification of MoO₃ film was carried out using X-ray diffraction pattern of MoO₃ and is shown in figure 1. It was found that films were polycrystalline in nature with hexagonal phase. Hexagonal phase is of particular relevance for electrochromism (Granqvist 1993). The spaces between the MoO₆ octahedra are large enough to accommodate ions, i.e. the Mo oxide framework serves as an excellent intercalation/deintercalation host.

The observed 'd' values are in good agreement with the standard 'd' values confirming the material deposited was MoO₃.

The optical density (αt) of the film was recorded in the wavelength range of 350 to 850 nm at 300 K. The values of α were not corrected for the transmittance and the reflectance of the film surface. The optical data were analysed from the following classical relation for near edge optical absorption in a semiconductor,

$$\alpha = \frac{K(h\nu - E_g)^{n/2}}{h\nu} \quad (3)$$

where K is constant, E_g is a semiconductor band gap and n a constant equal to 1 for direct gap and 4 for indirect gap compound (Moss 1961).

In order to confirm the nature of optical transition in MoO₃ film the plots of (αhν)² vs (hν) and (αhν)^{1/2} vs (hν) were studied and shown in figure 2. Linear portion of the curve was observed for the plot of (αhν)² vs (hν) and extrapolation of this portion to zero absorption coefficient gives optical band gap energy equal to 2.9 eV. However, estimation of band gap energy from the plot of (αhν)^{1/2} vs (hν) was outrageous. This observation therefore leads to the conclusion that optical absorption in MoO₃ film takes place through direct interband transitions.

In MoO₃, valence band consists of fully occupied σ and π bands and the oxygen pπ⁺ levels, while π* and σ* bands are empty and constitute conduction band. The absorption edge in the spectrum of MoO₃ is thus associated with the onset of promotion of electrons from pπ⁺ levels in to π* band and the energy gap between valence and conduction bands is assigned a value of 2.96 eV (Deb 1968; Dickens and Neild 1968). The value of band gap energy in the present study is in good agreement with the above value.

The room temperature electrical resistivity was of the order of 10^8 ohm-cm. The variation of resistivity with temperature in the range 400 to 560 K was studied. Resistivity decreases with increasing temperature showing that MoO_3 film is a semiconductor. Arrhenius plot for MoO_3 film is shown in figure 3. The plot shows two distinct regions, one corresponding to the low temperature region and the other corresponding to the

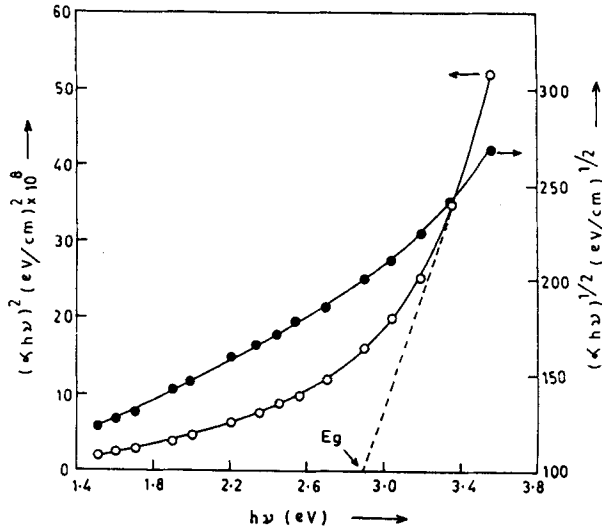


Figure 2. Plot of $(\alpha hv)^2$ vs hv and $(\alpha hv)^{1/2}$ vs hv for MoO_3 thin film.

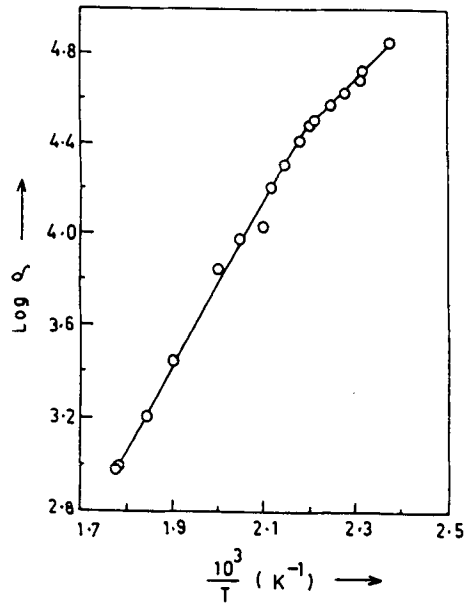


Figure 3. A plot of $\log \rho$ vs $1/T$ for MoO_3 thin film.

high temperature region. From these two regions, activation energies E_a , are calculated by using the relation,

$$\rho = \rho_0 \exp(-E_a/kT), \quad (4)$$

where ρ_0 is the pre-exponential factor, k the Boltzmann's constant and T the absolute temperature. In high temperature region, E_a is of the order of 0.29 eV and in low temperature region it is of the order of 0.19 eV and represents the average energy of the carriers with respect to the Fermi energy, if the carriers can only move at the bottom or top of the well defined band. Similar results have been reported by others for vacuum evaporated (Deb 1968) and physical vapour deposited (Krishnakumar and Menon 1993) thin films.

Figure 4 shows cyclic-voltammogram of the FTO/MoO₃/H₂SO₄/FTO Cell. In cyclic-voltammogram a voltage between the working electrode and counter electrode is swept back and forth between two setpoints with scan rate 200 mV/sec, and the electrical currents associated with ion intercalation/deintercalation are measured. When a voltage of about +0.25 V (SCE) is applied, cathodic current flows and the film rapidly switched from transparent to a deep blue, indicating that H⁺ ions are intercalating into MoO₃ as it is being reduced. Anodic (bleaching) current starts ~500 mV after reversal of the potential scan. The complete bleaching of the film occurs within 40 sec. The electrochromic electrode is reoxidized and deintercalates H⁺. The coloration-bleaching process may be expressed by

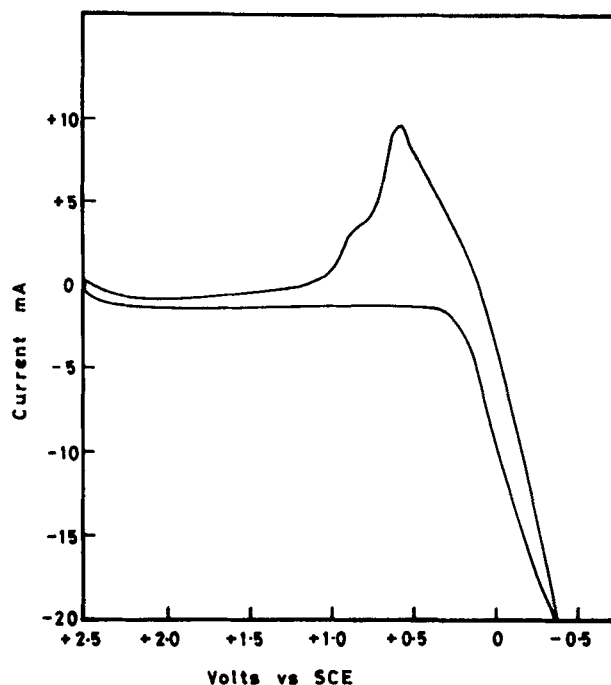
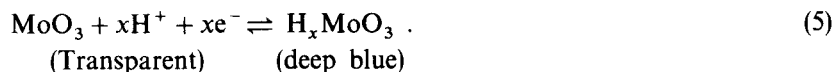


Figure 4. Cyclic-voltammogram of electrochromic cell formed with MoO₃ film.

4. Conclusions

Semiconducting molybdenum oxide thin films were deposited by spray pyrolysis technique on to the glass substrates. Films were polycrystalline in nature with hexagonal phase. The optical band gap energy (direct) was 2.9 eV. Values of activation energies were 0.29 and 0.19 eV for high and low temperature regions respectively. The as-deposited films were transparent and switched to a deep blue on application of about + 0.25 V (SCE) thereby exhibit electrochromism.

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