CHAPTER-V

ELECTROCHROMIC PROPERTIES OF SPRAYED MOLYBDENUM OXIDE THIN FILMS

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5.1 INTRODUCTION

This chapter includes electrochromic properties of sprayed molybdenum trioxide films. Electrochemical measurements were made with cyclic-voltammetry and chronoamperometry techngiues. Films after colouration were characterized for their structural and optical properties.

5.2 EXPERIMENTAL

5.2.1 CYCLIC VOLTAMMETRY AND CHRONOAMPEROMETRY

Molybdenum trioxide films deposited on F.T.O. coated glass substrates were used for electrochromic measurements. A simple electrochromic (EC) cell has been prepared for the study of EC characteristics. It consists of two F.T.O coated glass plates (10-50 hm/d). One plate has been deposited with the MoO3, which acts as a working electrode and other plate as a counter electrode. Saturated calomel electrode (SCE) was a reference electrode and 0.1 N H_2SO_4 was an electrolyte. The configuration of the cell was F.T.0/0.1 N H₂SO₄/MoO₃/F.T.O. The electrochemical characteristics were determiend by using cyclic voltammogram (CV) and chronoamperometry CV was taken with EG and G model 362 potentiostat and X-Y recorder model RE0091. CV for the cell with amorphous $(a-MoO_3)$ and polycrystalline $(p-MoO_3)$ films were recorded at different scan rates ranging from 20 to 500

mV/Sec. The experimental set up is shown in Fig.5.1. For chronoamperometric characterization, different voltages were applied between working and counter electrodes and the variation of electrical current through the cell with time was studied.

5.2.2 X-RAY ANALYSIS

X-ray diffraction patterns of fully coloured and as prepared films were recorded with Philips PW-1710 diffractometer using CuK_{α} radiation. The polycrystalline film is analysed after colouration. The as depostied films were fully coloured by applying 1 V for about 40 seconds and withdrawned from electrolyte. These films were characterized by XRD.

5.2.3 OPTICAL ABSORPTION SPECTROSCOPY

Optical density measurements were taken with spectrophotometer Hitachi 330, in the wavelength range 350 to 850 nm. The polycrystalline and amorphous films were subjected to optical absorption. The as deposited and coloured films were studied by optical absorption technique.

5.2.4 SPECTRAL TRANSMITTANCE

Spectral transmittance of the EC cell was studied with arrangement shown in Fig.5.2. For this, the cell was filled with an electrolyte of 1 N H_2SO_4 in glycerol (1:10) and it is illuminated by light wave of wavelengths varying from 350 to 700 nm to pass through the working electrode.



Fig.5.1 : Experimental Set up of Cyclic Voltammogram



Fig.5.2 : Schematic of Electrochromic Cell CE- Counter Electrode, RE-Reference Electrode, WE-Working Electrode, E-Electrolyte,

ECF-Electrochromic Film.

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The transmitted light was detected by the selenium photodetector.

5.3 RESULTS AND DISCUSSION

5.3.1 CYCLIC VOLTAMMETRY

In cyclic voltammetry a voltage between the working electrode and the counter electrode is sweft back and forth between the two set points, and the electrical currents with ion intercalation/deintercalation associated are measured. The technique can be used gualitatively to give a 'fingerprint" of electrochemical process, to trace reversible and irreversible effects, and to ascertain voltage levels that yield stable operation as well as qualitatively densities involved to measure charge in the intercalation/deintercalation processes.

MoO₃ deposited on F.T.O. coated glass substrates maintained at 250°C and 350°C were used for the EC characterization. Figs.5.3 and 5.4 show cyclic voltammograms of the cell prepared with amorphous and polycrystallkne MoOg films. In cyclic voltammogram a voltage between working electrode and counter electrode is varied between+2.5 V and -0.4 V(SCE) with 200 mV/S scan rate in 0.1 N H₂SO₄ electrolyte and current density associated with ion intercalation/deintercalation were measured for five successive cycles. In both the cases when a voltage of about +250mV(SCE) is applied, cathodic current flows and the film



Fig.5.3 : Cyclic Voltammogram of an EC cCell with Amorphous MoO_3 Film. Scan Rate 200 mV/sec.



Fig. 5.4 : Cyclic Voltammogram of an EC Cell with Polycrystalline MoO_3 Film. Scan Ratre 200 mV/sec.

rapidly switched from transparent to a deep blue, indicating that H^+ ions are intercalated in MoO₃ as it is being reduced. Anodic (bleaching) current starts $\approx +500$ mV (SCE) after reversal of potetial scan. The electrochromic electrode (working electrode) is reoxidized and deintercalates H^+ . The electrical currents associated with ion intercalation/deintercalation for the cell with polycrystalline films were larger than that of cell with amorphous films. Both the films exhibit good electrochromic property.

The amorphous MoO_3 films have many defects, while polycrystalline films are found to be somewhat porous. Therefore H⁺ can easily be intercalated through the lattice defects and trapped with electrons to form molybdenum bronze and hence to cause electrochromic effect. Vacuum evaporated amorphous and polycrystalline tungsten trioxide films also exhibited similar behaviour [1]. The colouration and bleaching process may be expressed by

 $MoO_3 + xH^+ + xe^- \longrightarrow H_xMoO_3 \qquad \dots (5.1)$

In both the cases, the peak values of the currents were found to be decreased to a smaller extent as a result of colouration-bleaching cycle.

Potential scan experiments were carried out under different scan rates. The scan rate was varied from 20 to 500 mV/sec. in 0.1 N H_2SO_4 electrolyte. The results of the potential scan are shown in Figs.5.5 and 5.6, for amorphous





a) 500 mV/sec., (b) 200 mV/sec., (c) 100 mV/sec.,
d) 50 mV/sec., (e) 20 mV/sec.

and polycrystalline MoO₃ films respectively. In both the cases, it is observed that anodic peaks shift to higher potentials with increase in potential scan rate. By plotting the anodic peak current density versus the square root of the scan rate. By shown in Fig.5.7, a nonlinear relationship is found. This may be due to the fact that, the reaction is not purely diffusion controlled. According to Faughnan [23] theory, the colouration process is shown to be caused by barrier limited current whereas the bleaching process was described as due to a space-charge limited cationic current.

5.3.2 CHRONOAMPEROMETRY

Chronoamperometry is a useful technique for studying the kinetics of ion intercalation/deintercalation [4]. The intercalation kinetics in principle is rather complicated, and several mechanisms can limit the current.

The EC cell with polycrystalline MoO₃ film was operated at constant voltages and the current during colouration and bleaching cycles were measured with respect the to time. The variation is shown in Fig. 5.8. Initially a sharp decrease in colouration current was observed and it remains steady within about 10 seconds, indicating that film is fully coloured. The current increases with increase in applied voltages, indicating that the intensity of colour depends on the negative applied voltage. On reversing the polarity of the applied voltage, the current decays more



Fig. 5.7 : Plot of Anodic Peak Current density versus Square root of Scan Rate for (a) Amorphous Film (b) Polycrystalline Film.



Fig.5.8 : Chronoamperometric characteristic of the EC cell.

rapidly until all the colour leaves the film and then more slowly to an equilibrium value. The bleaching time was about 25 seconds. Figure 5.9 shows a photograph of (i) as deposited (ii) bleached and (iii) coloured films.

5.3.3 X-RAY ANALYSIS

X-ray analysis of the electrochemically coloured film and as deposited polycrystalline film was made and shown in Fig.5.10(a and b) respectively. The XRD pattern of the as deposited film exhibits characteristic peaks of MoO₃. The XRD pattern of the coloured film is compared with that of as deposited film and given in Table 5.1.

Table 5.1 Comparision of XRD data of as deposited and coloured films

Sr.No.	For as depo Observed 'd'values A ^O	sited film I/Imax %	For coloured Observed 'd'values A ^O	film I/Imax %
1	3.4634	99.74	3.5174	99.65
2	2.3113	56.00	2.3467	53.73
3	2.3045	37.12	2.3408	40.58

It is found that the XRD peaks of the coloured film are shifted from that of as deposited MoO_3 film. This shift may be due to the formation of molybdenum bronze.



Fig.5.9 : Photograph of (a) As Deposited Film (b) Bleached Film (c) Coloured Film

102





5.3.4 OPTICAL ABSORPTION

Figure 5.11(a and b) shows a change in optical absorption spectra of the polycrystalline MoO₃ film before and after colouration. Before colouration films were almost transparent at wavelengths longer than 400 nm, while a marked increase in light absorption throughout the visible wavelength spectrum is observed for coloured film. This spectra has a broad peak with its maximum at 850 nm. The absorbance change $\triangle ABS$ was about 0.9 cm⁻¹ at this wavelength. This large increase in optical absorption is desirable for window applications. Figure 5.12 (a and b) shows optical absorption spectra of amorphous MoO3 film before and after colouration, respectively. The periodic shape of thespectrum after colouration may be due to optial interference in the film. Similar behaviour is reported for amorphous tungsten oxide films prepared by vacuum deposition method [5,6]. Before colouration, the film were almost transparent at wavelengths longer than 550 nm, while after colouration absorption density increases beyond 550 nm. This absorption change △ABS is about 0.24 cm-1 at 770 nm.

5.3.5 SPECTRAL TRANSMITTANCE

The spectral transmittance of the cell was studied in terms of the photodetected current during colouration. The photocurrent was measured in the wavelength range between 350 to 700 nm. for as deposited and colour film and shown in Fig. 5.13 a and b. After application of -0.4V film was found to be coloured and therefore the spectral transmittance was decreased.







Fig.5.12 : Optical Absorption Spectra for Amorphous Film. a) Before Colouration (b) After Colouration.



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