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Electrosynthesis of Electrochromic Molybdenum Oxide Thin Films with Rod-Like Features

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Structure tailoring of electrodeposited Mo (IV)-oxide thin films by thermal oxidation in ambient air to obtain electrochromic Mo (VI)-oxide thin films was exploited for the first time by novel route. Electrosynthesis of Mo (IV)-oxide thin films on Fluorine-doped SnO_2 conducting glass (10-20 Ω/) substrates were carried from aqueous alkaline solution of ammonium molybdate at room temperature. The physical characterization of as-deposited films showed the formation of hydrous and amorphous MoO_2. Scanning electron microscopy pictures and x-ray diffraction of air-annealed films clearly revealed a rod-like morphology and orthorhombic α-MoO_3 phase. Samples exhibited pronounced cathodic electrochromism.

Keywords: Molybdenum Oxide; Electrodeposition; thin films; Annealing; Structural, Optical and Electrochromic Properties

1. INTRODUCTION

A technological progress for the power saving options for intellectual architecture of buildings demand the search for new electrochromic materials and enhancement in the properties of existing materials by variety of techniques.

A layered oxygen deficient orthorhombic MoO_3 (α-phase) and monoclinic MoO_3 (β-phase) are found to exhibit optical switching upon thermal, photo or electric excitations. This optical modulation (colouration/bleaching) is effectively used in many applications like smart windows, antidazzling coatings and display devices [1-3]. Thus the synthesis of large area Mo-oxide thin films by an economical route and the structure tailoring of deposited material for the end application seems to be of prime importance.

MoO_2 exhibits monoclinic rutile structure built from infinite chains of edge sharing distorted MoO_6 octahedra held together by weak Van der Waal's forces. It is quite difficult to prepare stable stoichiometric MoO_2 in thin film form owing to the difficulties in maintaining oxygen partial pressure during reactive process. MoO_3 on the other hand is a very promising and stable molybdenum oxide for the electrochromic applications.

The reason for pronounced electrochromism in MoO_3 is related to its oxygen deficient defect perovskite structure (α and β phases) providing suitable conduits for intercalation and deintercalation of ions, existence of polyvalent oxidation states and the electronic band structure providing near infrared absorption upon electric excitation, leading to bluish colouration.

Thermal oxidation of metallic Mo is a comparatively simple technique for making Mo-oxide thin films of surprisingly high quality owing to the lattice matching between film and substrate. Vacuum evaporation in reactive condition is most extensively used method to deposit Mo-oxide thin films. Density of the deposit was about 80% compared to orthorhombic bulk MoO_3 and is independent of film thickness. High resolution TEM showed that as-evaporated amorphous thin films were consisted of nanostructures of about 1.5nm [4]. Thin films prepared by evaporation of Mo source in presence of N, N-dimethylformamide [5] exhibited grains ranging from 100 to 190 nm. Mo-oxide thin films prepared by sputtering techniques in ($Ar+O_2$) atmosphere are amorphous when deposited onto water cooled substrates [6] and polycrystalline when deposited on to substrates [7] at about 200^{o}C. Thin films prepared by chemical and electrochemical routes were also amorphous in nature requiring higher temperature oxidizing conditions [8-10] for conversion to polycrystalline MoO_3.

Thus in most of the physical, chemical and electrochemical methods employed to deposit Mo-oxide thin films on transparent substrates, the resulting deposits were oxygen deficient and amorphous or microcrystalline in nature. Hence post deposition treatments are essential for structural transformation suitable for end application. Thermal oxidation in ambient air is the most convenient and simple post deposition treatment used. However, proper care must be taken to retain adherence and surface morphology and to avoid formation of powdery film.

Cathodic reduction of molybdate from aqueous alkaline bath to deposit thin films of hydrous MoO_2 and the structural and optical properties of electrodeposited MoO_2 thin films are reported by us [11]. In the present investigation structural, optical and electrochromic properties of electrodeposited MoO_2 thin films subjected to annealing in an ambient air were studied.

2. EXPERIMENTAL PART

An aqueous 0.05M ammonium molybdate bath (pH = 9) was prepared by dissolving appropriate weight of AR grade MoO_3 powder in a few cc of warm ammonia (NH_3) and then diluted to desired volume with double distilled water. The fluorine doped tin oxide (FTO) coated conducting glass was used as a substrate for electrodeposition of MoO_2 thin films. These conducting uniform glasses having a sheet resistance of 10-20 Ω/∈ and about 95% transparency were prepared using conventional home-made spray pyrolysis technique. The cathodic electrodeposition of MoO_2 was carried on to FTO coated glass under optimized bath conditions [11], for different deposition times, in galvanostatic mode at 1 mA/cm^2 current density. In order to obtain adherent deposits, the FTO glass substrates were dipped for a few seconds into sulphochromic acid and then rinsed with double distilled water.

The film thickness was determined by surface profiler (Ambios, XP-1 model). These films were annealed in an ambient air at 450^{o}C in an electric furnace with an accuracy of ± 5^{o}C. X-ray diffraction was carried on Philips PW-3710 diffractometer with Cu-kα radiation. SEM pictures were recorded on JEOL-JSM 6360 model. Optical absorption/transmission was carried out in the range 350 to 850 nm with Hitachi-330 UV-VIS-NIR spectrophotometer.

The Mo-oxide thin films were coloured and bleached in a 0.1N H_2SO_4 electrolyte by applying a step potential between 0 to –0.5 V and from 0 to +0.5 V vs. SCE for appropriate time to achieve maximum colouration and bleaching. The optical transmittance spectra of the coloured and bleached samples were recorded in the wavelength range 350 to 850 nm.

3. RESULTS AND DISCUSSION

As-deposited electrosynthesized thin films under optimized conditions were well adherent to the FTO substrates and were transparent brown. Upon annealing in an ambient air the brown coloured films turned into pale white films. It was seen that the crystallization process begins with the formation of β-MoO_3 phase, followed by formation of mixed β and α-MoO_3 phases. A polymorphic transition from monoclinic-β phase to orthorhombic-α-MoO_3 phase is seen beyond 400 ^{o}C. Thus annealing temperature was fixed at 450°C to yield purely α-MoO_3 phase.

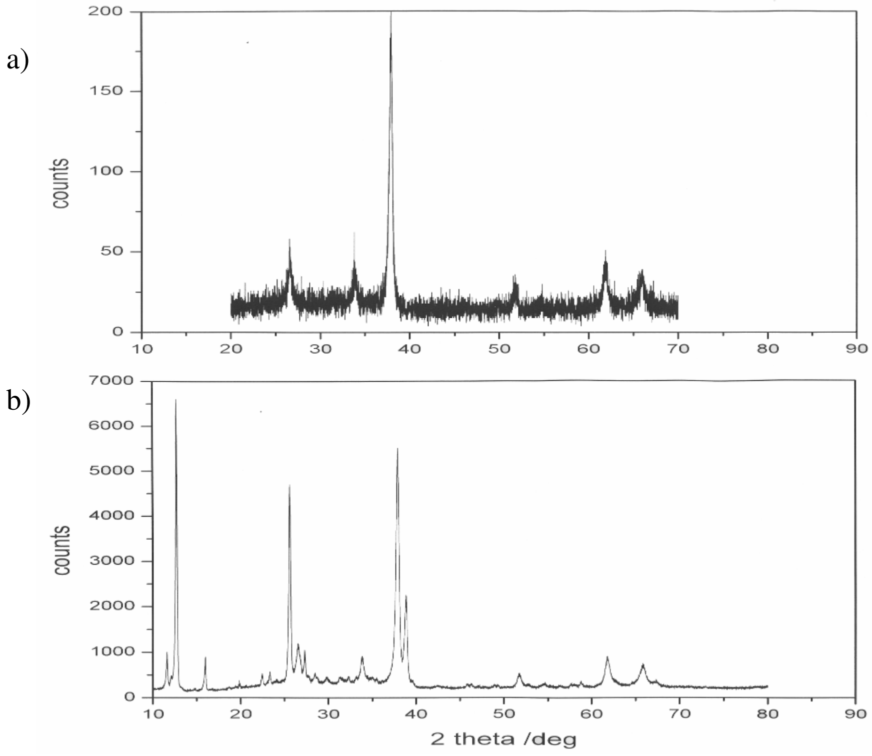

Figure 1. XRD patterns of (a) as-deposited and (b) air-annealed samples. Annealing temperature and time were 450^{o}C and 1 hr. respectively.

The X-ray diffraction patterns recorded over 10^o to 100^o of, a) as-deposited film and b) annealed in an ambient air at 450^{o}C for 1 hour are as shown in fig.1. All the peaks in the spectrum of as-deposited film correspond to the FTO substrate. Hence X-ray amorphous nature of as-deposited Mo-oxide films was confirmed by absence of any new peak. The X- ray diffraction analysis of air-annealed sample (fig.1b) clearly revealed the formation of polycrystalline orthorhombic α-MoO_3. In addition to three dominant planes, shown in figure, some minor peaks along (110), (021), (140), (150), (161), (251) and (270) corresponding to MoO_3 phase were observed. The *d* values of the observed reflections were compared with the standard *d* values from JCPDS cards (05-508 and 35-609). The lattice constants evaluated for orthorhombic α-MoO_3 unit cell are, a = 3.965 Å, b = 13.5 Å and c = 3.73 Å. These values are in good agreement with literature data [12]. The grain size was determined to be about 125 nm using Scherrer's formula.

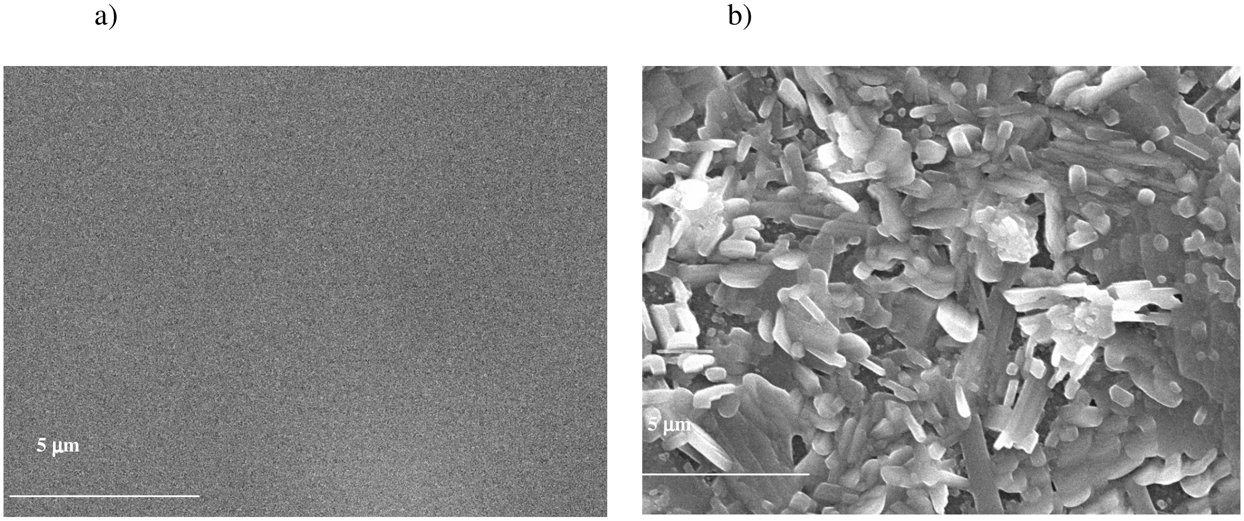

Figure 2. SEM pictures of (a) as-deposited and b) air-annealed at samples.

The scanning electron micrographs of as-deposited and air-annealed samples are shown in fig. 2 (a and b). The as-deposited sample exhibits a relatively smooth and completely covered surface before annealing, characteristic feature of an amorphous film. Air annealed thin films are crystalline and consist of elongated rod-like crystallites of several μm size. The crystallites are randomly oriented.

The optical absorption spectra of the as-deposited and air-annealed films were recorded in the wavelength range 350 to 850 nm at room temperature. The optical density was converted into absorption coefficient α using predetermined thickness values. The absorption coefficient was of the order of 10^5 cm^{-1}. A plot of $(\alpha h\nu)^2$ vs hν showed that the direct allowed transitions are responsible for optical absorption. The extrapolation of straight-line portion to zero absorption (α=0) gives the band gap energy E_g. Fig.3 (a and b) shows $(\alpha h\nu)^2$ vs hν curves for as-deposited and air annealed samples. The band gap changes from 2.83 eV to 3.03 eV. These values confirm transformation from MoO_2 to MoO_3 upon thermal oxidation. The band gap energies are in agreement with reported [13-14] values for polycrystalline thin films. The band gap variation from 2.7 eV for X- ray amorphous to 3.4 eV for ordered polycrystalline MoO_3 thin a film is widely reported [15-16].

The samples were tested for their electrochromic property and found that as-deposited MoO_2 sample do not exhibit this property, where as air-annealed MoO_3 sample exhibit pronounced cathodic electrochromism, according to following well-known reaction mechanism [17]:

$$MoO_3 + xH^+ + xe^- \Leftrightarrow HxMoO_3$$

Here air-annealed MoO_3 sample, which is originally transparent, can flip to a coloured (blue) state upon simultaneous injection of protons from electrolyte and electrons from external stimulus.

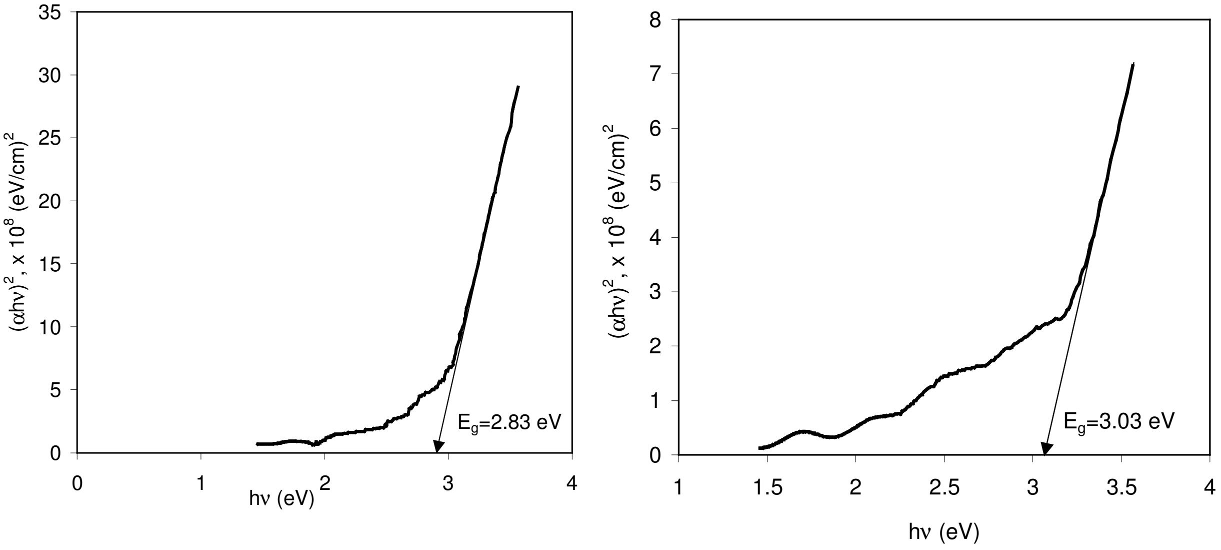

Figure 3. Variation of $(\alpha h\nu)^2$ vs. $h\nu$ for (a) as-deposited and (b) air-annealed sample.

The transmission spectrum in coloured and bleached states for the air-annealed sample is as shown in fig.4. In bleached state the film was transparent pale white with the transparency of about 80 % at 630 nm. Upon colouration the film became deep blue, confirming the absorption in near infrared region (complimentary colour). The transparency dropped to about 34 %.

The colouration efficiency (C.E.) is an important parameter related to electrochromic device application. It is defined as the ratio of change in optical density of the film in its coloured and bleached state to the corresponding intercalated or deintercalated charge density at a certain wavelength λ.

The colouration efficiency was calculated using relation,

$$C.E. = (\Delta OD / \Delta Q)_{\lambda}$$

where, $\Delta OD = \ln [T_b/T_c]$ = change in optical density at wavelength λ.

ΔQ = amount charge intercalated per unit area.

ΔOD is obtained from optical transmittance curves and ΔQ values are estimated from chronoamperometry (current-time) curves. T_b and T_c are transmittance in bleached and coloured states respectively. Maximum value of colouration efficiency is most desirable. Colouration efficiency (C.E.) of 34 cm^2/C at 630 nm was obtained. Thus the present novel route of converting electrosynthesized amorphous MoO_2 films to polycrystalline α-MoO_3 films with unique rod-like features offers a potential route of yielding electrochromic thin films with promising properties.

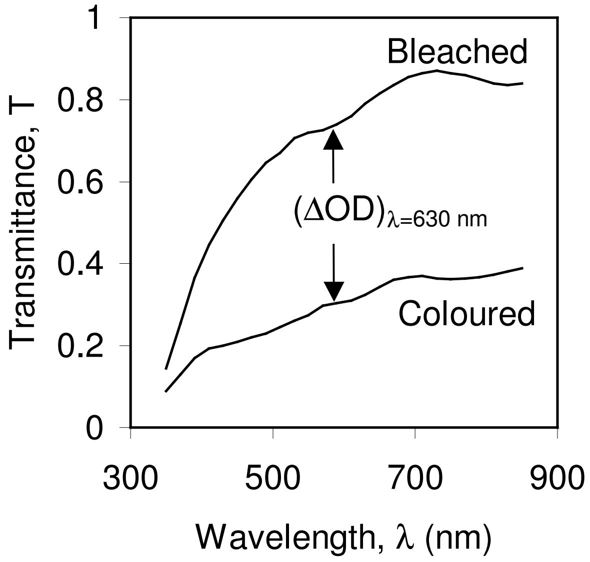

Figure 4. Transmission spectra for air-annealed sample in the bleached and coloured states. Colouration and bleaching was obtained by applying ± 0.5 V(SCE) to the electrochemical cell.

4. CONCLUSIONS

The morphological, structural and optical analysis of as-deposited, and air-annealed thin films of hydrous MoO_2 strongly suggests that the structure tailoring is possible to obtain good quality thin films of MoO_3 useful for electrochromic applications. As-deposited thin films air annealed at 450°C with α-MoO_3 phase shows pronounced electrochromic performance.

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