Optical, structural and photoelectron spectroscopic studies on amorphous and crystalline molybdenum oxide thin films

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Received 5 December 2003; accepted 19 December 2003

Abstract

Optical, structural and electronic properties of amorphous and crystalline molybdenum oxide thin films have been investigated. As-deposited amorphous films got crystallized into a layered orthorhombic phase on annealing at 350°C. Refractive index (n) and extinction coefficient (k) of as-deposited films and films annealed at 150°C, 240°C and 350°C have been calculated using reflectance and transmittance data. Spectral dependence of absorption coefficient has been explained on the basis of charge transfer transition mechanism. Optical band gap of amorphous MoO$_3$ is 3.16 eV and it has increased by 0.11 eV on crystallization. XPS core level analysis reveals the presence of Mo$^{4+}$, Mo$^{5+}$ and Mo$^{5+}$ oxidation states in amorphous films, proving oxygen deficiency in as-deposited films. Same studies on crystalline films show the presence of only Mo$^{6+}$ states. Valence band spectrum of amorphous films reveal emission from Mo$4d$ levels, which is absent in crystalline films. Complete correlation is seen between the optical properties and XPS data.

Keywords: Optical properties; Electronic properties; Core level spectra; Valence band spectra; Energy band diagram

1. Introduction

The phenomenon of electrochromism has been successfully employed during the last three decades to fabricate variety of devices. Recently, there has been an upsurge
of interest in this phenomenon particularly to develop large-area devices namely: dynamic windows to control the solar energy flow into the buildings [1] and infrared emissivity modulators for spacecraft enclosures [2]. The primary component of these devices is the electrochromic material, which exhibits significant changes in its optical properties on ion intercalation. Number of electrochromic materials like WO$_3$, MoO$_3$, CoO$_2$, V$_2$O$_5$ have been reported in literature [3]. Optical properties of electrochromic films, both intercalated and unintercalated, have extensively been investigated and explained based on three mechanisms: color center model [4], inter-valence charge transfer model [5] and small polaron model [6]. A common feature of all these models is the existence of reduced oxidation states of metal ions of the host, whose density play an important role in determining stability, switch-ability and maximum change in optical properties [7]. To establish the suitability of MoO$_3$ as an electrochromic (EC) material it is essential to study and understand the absorption mechanism and its dependence on the crystalline state. Thermal annealing at suitable temperature can vary the state of crystallinity. The optical absorption mechanisms prevailing in unintercalated films can be extended to explain coloration in intercalated films. In majority of the cases optical properties have been investigated after intercalating with monovalent ions (H$^+$, Li$^+$, Na$^+$ and K$^+$), etc.

The aim of the present work is to: (i) investigate the effect of oxygen deficiency on the electronic and optical properties of unintercalated amorphous MoO$_3$-$_x$ thin films; (ii) model the band diagrams of both amorphous and crystalline MoO$_3$ thin films based on XPS studies; (iii) investigate the correlation between optical absorption processes and XPS data.

2. Experimental

Thin films of molybdenum oxide were deposited on cleaned float glass and ITO-coated glass substrates by thermal evaporation under high vacuum (4 x 10$^{-6}$ mbar). Film thickness was measured with Talystep (Taylor Hobson make) and Optical Nanoscope. Annealing was carried out in air, using programmable furnace with temperature accuracy of 1°C. Annealing duration, specimen heating and cooling rates were maintained constant at 60min, 10°C/min and 2°C/min, respectively. Structural studies of films were carried out using Rigaku X-ray diffractometer with Glancing angle X-ray diffraction (GAXRD) attachment (Geiger flex-D/Max-RB-RU200). Resonance absorption of films was measured in reflectance mode using FTIR (Perkin-Elmer Model BX2) spectrophotometer. The instrument resolution was fixed at 4 cm$^{-1}$ and the number of spectra for one measurement was 256 cycles. Optical reflectance ($R$) and transmittance ($T$) data were measured using a Hitachi (model 330) double-beam spectrophotometer. Photoelectron spectroscopic studies were carried out on Perkin-Elmer Model PHI 1257 spectrometer, with dual anode Mg/Al 25 kV X-ray source, of power 150W. The radiation used for the present study was Al K$_\alpha$ radiation. The resolution of the instrument was 0.2 eV. Probing X-ray photons were incident at an angle of 45° to the substrate normal and the axis of rotational hemispherical analyzer was parallel to the substrate normal.
3. Results and discussions

The physical color of as-deposited films is light blue, which becomes dark blue on annealing at 150°C in air for 1h and colorless when the annealing temperature is increased to 350°C. X-ray diffractogram of as-deposited films and those of annealed at 150°C, 240°C and 350°C are shown in Fig. 1. As-deposited and 150°C-annealed films show an amorphous nature as no diffraction peak is seen in the respective diffractogram (curves a and b). The presence of low-intensity peaks in the diffractogram of films annealed at 240°C (curve c) indicates onset of crystallization. High-intensity peaks in diffractogram of films annealed at 350°C (curve d) reveal the completeness of crystallization process. The d-values calculated using XRD data (curve d in Fig. 1) are given in Table 1. Comparison of experimentally calculated d-values with JCPDS data (File No. 35-609) reveals the formation of layered orthorhombic phase. Lattice parameters, estimated using the d-values data given in Table 1 are \( a = 4.13 \text{ Å}, \) \( b = 14.04 \text{ Å} \) and \( c = 3.577 \text{ Å} \).

The IR reflectance \( (R) \) of as-deposited films and those annealed at 150°C, 240°C and 350°C, measured in 1000-450 cm\(^{-1}\) spectral region, are shown in Fig. 2, curves...
Table 1
Calculated d-values of crystallized films compared to standard d-values of orthorhombic (MoO$_3$) phase

<table>
<thead>
<tr>
<th>S.no.</th>
<th>d-Values from XRD data</th>
<th>JCPDS data corresponding to layered orthorhombic: MoO$_3$ phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Films annealed at 240°C (Å)</td>
<td>Films annealed at 350°C (Å)</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>7.622</td>
</tr>
<tr>
<td>2</td>
<td>7.020</td>
<td>7.020</td>
</tr>
<tr>
<td>3</td>
<td>3.966</td>
<td>3.966</td>
</tr>
<tr>
<td>4</td>
<td>3.815</td>
<td>3.815</td>
</tr>
<tr>
<td>5</td>
<td>3.490</td>
<td>3.490</td>
</tr>
<tr>
<td>6</td>
<td>3.276</td>
<td>3.276</td>
</tr>
<tr>
<td>7</td>
<td>3.119</td>
<td>3.122</td>
</tr>
<tr>
<td>8</td>
<td>—</td>
<td>3.006</td>
</tr>
<tr>
<td>9</td>
<td>—</td>
<td>2.704</td>
</tr>
<tr>
<td>10</td>
<td>—</td>
<td>2.657</td>
</tr>
<tr>
<td>11</td>
<td>2.325</td>
<td>2.325</td>
</tr>
<tr>
<td>12</td>
<td>—</td>
<td>1.975</td>
</tr>
<tr>
<td>13</td>
<td>—</td>
<td>1.850</td>
</tr>
<tr>
<td>14</td>
<td>—</td>
<td>1.663</td>
</tr>
</tbody>
</table>

a, b, c and d, respectively. Since the measured transmittance (T) is negligible in this spectral region, mainly due to the highly reflecting ITO layer beneath the MoO$_3$ film, 100-R quantity is presumed to represent absorption at the corresponding wave number. The R spectrum of as-deposited film and films annealed at low temperatures (≤240°C) do not show sharp resonance absorption peaks, except for one broad minimum at 638 cm$^{-1}$. The absence of sharp peaks is attributed to the wide range of bond angles and bond lengths present in amorphous films. The reflectance of films annealed at 350°C does show sharp absorption peaks at 988, 808 and 536 cm$^{-1}$. Peak at 988 cm$^{-1}$ is due to terminal Mo = O bond, which is an indicator of layered orthorhombic MoO$_3$ phase [8]. Absorption at 808 cm$^{-1}$ is due to stretching mode vibration of bridging oxygen in Mo-O-Mo [8]. The absorption at 536 cm$^{-1}$ is due to the bending mode vibration of Mo-O-Mo entity, when O ion is shared by three Mo ions [9].

The visible and near-infrared T and R of as-deposited and films annealed at various temperatures are shown in Figs. 3a and b, respectively. Typical spectral variation in R and T is nearly similar in all cases: the T value drops steeply at x 400 nm wavelength indicating a strong absorption due to band-to-band transition and also shows a broad minimum at 900 nm in all cases. It is experimentally confirmed that this minimum is not due to interference effect, as its spectral location remains unchanged on varying film thickness. Optical constants: refractive index (n) and extinction coefficient (k), have been calculated using R and T data given in Figs. 3a and b for all cases and the same are shown in Fig. 4. No significant changes have been observed in n at higher wavelengths with changing annealing temperatures. However, it varies sharply near the band edge. The k values of all
films show a peak between 900 and 1100 nm. Calculated $n$ and $k$ values, excepting the observed peaks in $k$ at 1000 nm, are in good agreement with the data reported in literature [10].

The spectral dependence of optical absorption coefficient $a \ (= 4pk/l)$ of all films is shown in Fig. 5. A broad maximum between 500 and 1100 nm wavelength range (2.5 - 0.73 eV) is observed in all cases. The band gap ($E_g$) is estimated using $(ahe)^2$ vs. $(hv-E_g)$ plots (Fig. 6) since the high a values ($> 10^4$) confirms the existence of direct
Fig. 3. Spectral variation of transmittance (T) and reflectance (R) of as-deposited films (—J—) and films annealed at 150°C (—•—), at 240°C (—D—) and at 350°C (—*—).

band gap. The calculated $E_g$ values are 3.27 and 3.16eV for crystalline and amorphous films, respectively. The broad absorption peak, observed in case of as-deposited films between 0.75 and 2.5 eV, is found to be a combined effect of two
absorption peaks which becomes more clear with increasing annealing temperatures (Fig. 5). Therefore, using deconvolution technique the combined peak has been resolved into two Gaussian peaks labeled "1" and "2" as shown in Fig. 5. With increasing annealing temperature the position of peak 1 shift from 1.62 to 1.72 eV and that of peak 2 remains unchanged at 1.25 eV. The existence of these absorption peaks and their peak heights variation with annealing temperature is related to the reduced oxidation states of Mo as explained later.

In order to know the sources for the above-described absorption peaks, photoemission studies (XPS) were carried out on amorphous (as-deposited) and crystalline (annealed at 350°C) films. The measured core level (CL) spectrum and valence band (VB) spectrum of as-deposited films are shown in Figs. 7a and b, respectively. The line shape of measured CL spectrum (Fig. 7a) is highly asymmetric indicating the presence of mixed oxidation states of Mo. Using deconvolution technique, the best fit has been obtained by resolving the spectrum into six overlapping Gaussian peaks labeled as A, A', B, B', C and C', where A, B, C represent Mo3d_{5/2} level of Mo in +6, +5 and +4 oxidation states, respectively. The primed peaks represent 3d_{3/2} levels of the corresponding oxidation states of Mo. The binding energies of all peaks are given in Table 2 along with the reported data, which
are in good agreement with the reported values [11]. The VB spectrum of as-deposited film (Fig. 7b) shows strong photoemission peaks at 2.43, 7.3 and 23.6 eV. Based on the reported data these are attributed to the electron emission from bands formed from Mo4d, O2p and O2s orbitals, respectively [12]. Marginal overlapping of wave functions of Mo4d and O2p orbitals is also evident from this spectrum. The low intensity of the emission peak at 2.43 eV indicates that the Mo4d levels are partially occupied. The effective occupancy ratio of Mo4d levels to O2p states is calculated using an expression given below [11]:

$$\frac{h_d}{h_p} = \left(\frac{I_{4d}/I_{2p}}{n_{4d}/n_{2p}}\right)$$

where $I_{4d}/I_{2p}$ and $n_{4d}/n_{2p}$ are the ratios of integrated intensities, occupancy and sensitivity factors corresponding to Mo4d and O2p orbitals. The effective occupancy ratio ($n_{4d}/n_{2p}$), calculated using standard values of sensitivity ratio ($s_{4d}/s_{2p}$) and the experimentally recorded $I_{4d}/I_{2p}$ ratio, is 0.15. Assuming that the O2p levels are fully occupied, the number of electrons in 4d orbital per Mo atom is 2.7, which suggests a significant covalent character of Mo-O bond i.e. it is not completely ionic.

The CL spectrum and VB spectrum of annealed films are shown in Figs. 8a and b, respectively. The CL spectrum consists of two perfect Gaussian peaks located at 232.6 and 235.8 eV, which are labeled as A and $A^0$ in Fig. 8a. These peaks are due to the spin-orbit split Mo3d levels ($3d_{3/2}$ and $3d_{5/2}$). Comparing these peaks parameters viz. energy separation, relative intensities and respective FWHM with the standard
Fig. 7. (a) Core Level spectrum of as-deposited films recorded using Al K$_\alpha$ radiation. The labels A, B and C represent Mo3d$_{5/2}$ levels of Mo$^{+6}$, Mo$^{+5}$ and Mo$^{+4}$ oxidation states. The primed peaks represent 3d$_{3/2}$ levels of the corresponding oxidation states of Mo. (b) XPS valence band spectrum of as-deposited MoO$_{3-x}$ films. The emissions peaks at 2.43, 7.3 and 23.6eV are due to Mo4d, O2p and O2s bands, respectively.

Table 2
Core level binding energy values of various oxidation states of Mo present in as-deposited films compared to the values of corresponding states reported in literature

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Peak label</th>
<th>Oxidation state</th>
<th>Binding energy (eV) (experimentally obtained)</th>
<th>Binding energy (eV) (reported values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>+ 6</td>
<td>232.4</td>
<td>232.6</td>
</tr>
<tr>
<td>2</td>
<td>A’</td>
<td>+ 6</td>
<td>235.6</td>
<td>235.8</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>+ 5</td>
<td>230.3</td>
<td>231.2</td>
</tr>
<tr>
<td>4</td>
<td>B’</td>
<td>+ 5</td>
<td>233.5</td>
<td>234.3</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>+ 4</td>
<td>229.8</td>
<td>229.8</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>+ 4</td>
<td>233.0</td>
<td>233.0</td>
</tr>
</tbody>
</table>

data [13] for Mo-O system, establishes conclusively that in crystalline films Mo is present predominantly in Mo$^{+6}$ state. Hence on annealing in air, MoO$_{3-x}$ films not only get crystallized but also become nearly stoichiometric with a Mo:O ratio of
Fig. 8. (a) Core level spectra of crystalline MoO$_3$ film showing the presence of Mo$^{+6}$ oxidation states only. (b) Valence band spectra of crystalline MoO$_3$ thin film with peaks representing emissions from Mo4d, O2p and O2s levels at 7.2 and 22.3 eV.

Absence of the emission peak observed in case of as-deposited films at 2.43 eV is clearly seen. Thus from XPS studies it can be concluded that as-deposited films contain reduced oxidation states that are closely related to oxygen vacancies in films. These vacancies are created during deposition of MoO$_3$ films. It is reported that electrons trapped in such oxygen vacancies create Mo$^{+4}$ and Mo$^{+5}$ states [14]. Annealing in air eliminates a major fraction of these vacancies as oxygen deficiency decreased.

The spectral dependence of a can now be explained with the help of a proposed band diagram, based on XPS results shown in Fig. 9. In MoO$_{3-x}$ the valence band edge ($E_V$) and the conduction band edge ($E_C$) lie at $-2.5$ and $+0.68$ eV, respectively, so that the difference between $E_C$ and $E_V$ is 3.18 eV, which is equal to the value observed from optical studies. In case of crystalline films $E_V$ lies at $-1.7$ eV, while $E_C$ lies at 1.56 eV making the $E_g$ equal to 3.26 eV. It is also evident from Fig. 8b that the Fermi level now appears almost at the center of the band gap indicating an improvement in Mo:O ratio.
As mentioned earlier, the charge transfer from oxygen vacancies to Mo ions creates reduced oxidation states of Mo (Mo$^{+4}$ and Mo$^{+5}$), hence these states may be considered as doubly or singularly positively charged vacancies V$^{2+}$ or V$^+$. According to Deb and Chopoorian [14] V$^{2+}$ and V$^+$ vacancies give rise to energy levels in energy gap close to $E_v$ edge and serve as acceptor states. The states corresponding to V$^+$ appear at higher energy side compared to those created by V$^{2+}$. An occupancy ratio of 2.7, estimated from XPS studies, show that a fairly good number of these states are occupied. It is also reported that such vacancies tend to cluster to form complex aggregate centers [15]. The physical proximity of these vacancies in any aggregate facilitate transfer of charges, without altering their respective densities, from higher to lower vacancy sites or in other words charge transfer from lower to higher Mo oxidation states. Such transitions occur when photons are incident as represented by the following two equations:

$$\text{Mo}^{+5}(A) + \text{Mo}^{+6}(B) + h\nu(x \text{ 1.75 eV}) \rightarrow \text{Mo}^{+6}(A) + \text{Mo}^{+5}(B),$$

and

$$\text{Mo}^{+4}(A) + \text{Mo}^{+5}(B) + h\nu\delta E (1.25 \text{ eV}) \rightarrow \text{Mo}^{+5}(A) + \text{Mo}^{+4}\delta BP.$$

The absorption peak observed at 1.75 eV (Gaussian 1 in Fig. 5) is related to the charge transfer from +5 to +6 state and the second peak at 1.25 eV due to charge transfer from +4 to +5 state. Both these absorption processes contribute to the experimentally measured minimum in $T$ at 900 nm. A decrease of this minimum (Fig. 3) in films annealed at 350°C shows that the density of vacancy states, described above, get reduced. These observations are in consistence with XPS results.
Based on the variation in the integrated area (IA) of these peaks with changing annealing temperature it is concluded that Gaussian 1 (Fig. 5) is responsible for the blue color of the films, since IA of this peak is large when the films are deep blue (150°C), and small when these are colorless (350°C).

4. Conclusions

The as-deposited films and those annealed at 150°C are amorphous, while films annealed at 240°C indicate an onset of crystallization, which is complete when the annealing temperature is raised to 350°C. Crystalline films stabilize in a layered orthorhombic structure with the unit cell dimensions of \(a = 4.13\) Å, \(b = 14.4\) Å and \(c = 3.577\) Å. Amorphous nature of as-deposited films and evidence of layered structure in crystalline films obtained FTIR studies are in good agreement with XRD results. Values of optical constants estimated from \(R\) and \(T\) data are in good agreement with those reported in literature. Optical studies reveal a broad absorption band peaking in NIR region, which is deconvoluted into two Gaussians 1 and 2, centered at 1.75 and 1.25 eV respectively. XPS core level (CL) studies reveal the presence of Mo\(^{+4}\) and Mo\(^{+5}\) oxidation states in amorphous films, while Mo\(^{+6}\) states only in crystalline films. Gaussian 1 and 2 of absorption band in the NIR region are related to charge transitions from Mo\(^{+5}\) to Mo\(^{+6}\) states and from Mo\(^{+4}\) to Mo\(^{+5}\) oxidation states, respectively.

References