Substrate Temperature Influenced Physical and Electrochromic Properties of MoO3 Thin Films

S. Subbarayudu*, V. Madhavi, S. Uthanna
Department of Physics, Sri Venkateswara University, Tirupati - 517 502, India
'srsuguru.phy@gmail.com; madhuvphysics@gmail.com; uthanna@rediffmail.com

Received 24 June, 2013; Revised 4 February, 2014; Accepted 3 March, 2014; Published 20 June, 2014
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Abstract:
Molybdenum oxide (MoO3) films were deposited on glass and silicon substrates by sputtering of molybdenum target at different substrate temperatures in the range 473-573 K at a constant oxygen partial pressure of 4x10^-4 mbar employing RF magnetron sputtering technique. The effect of substrate temperature on structural, morphological, electrical and optical properties of the MoO3 films was systematically studied. X-ray diffraction studies revealed that the films formed at 303 K were amorphous in nature, while those deposited at substrate temperature 473 K were orthorhombic MoO3 with crystallite size of 27 nm and the crystallinity increased with increase of substrate temperature. The scanning electron micrographs of the films deposited at 303 K were of fine grain structure in amorphous background and the films formed at 523 K contained the grains with shape of platelets piled one over the other with size of about 1 μm. Fourier transform infrared transmittance spectra exhibited the characteristic vibration modes of MoO3. The electrical resistivity of the films decreased with increase of substrate temperature due to partial filling of oxygen ion vacancies. The optical band gap and refractive index of the films increased with the increase of substrate temperature. The MoO3 films formed at substrate temperature of 523 K exhibits high optical modulation of 22% and coloration efficiency of 30 cm²/C.

Keywords: Molybdenum Oxide Films; RF Magnetron Sputtering; Substrate Temperature; Structural; Electrochromic Properties

Introduction
Transition metal oxides are semiconductors and have many technological applications in different fields such as lithium secondary batteries, display devices, optical smart windows, low cost electrochromic devices and gas sensors [Granqvist 1995, Julien 1994]. Molybdenum oxide (MoO3), one among the transition metal oxides, exhibits interesting structural, chemical and optical properties. An orthorhombic α-phase MoO3 layered structure is potential for lithium batteries and optical smart windows [Li et al. 2006]. Molybdenum oxide is good electrochromic material since it has oxygen deficient perovskite structure (α- and β-phases) which is suitable for intercalation and de-intercalation due to polyvalent oxidation states, which leads to bluish coloration. It also exhibits photo- and gasochromic (coloration) effects by virtue of which the material is of potential for the development of electronic display devices [Patil et al. 2008, Prasad et al. 2003, Scarminio et al. 1997]. Nanocrystalline MoO3 films also find applications in nanodevices and nanosensors [Patzke et al. 2004, Taurino et al. 2006]. It is a promising candidate for a back contact layer for cadmium telluride solar cells in superstrate configuration due to its high work function, which reduces the contact barrier [Gretener et al. 2013]. Various physical thin film deposition techniques such as electron beam evaporation [Sabhapathi et al. 1995, Sivakumar et al. 2007], pulsed laser deposition [Ramana et al. 2007, Ramana et al. 2006], thermal evaporation [Sain et al. 2005 Yang et al. 2009] and sputtering [Okumu et al., 2006, Mahamed et al. 2007, Uthanna et al. 2010, Srinivasa Rao et al. 2009, Navas et al. 2009], and chemical methods such as spray pyrolysis [Boudaoud et al. 2006, Martinez et al. 2013], electrodeposition [Patil et al. 2006], sol-gel process [Dhanasankar et al. 2011, Fan et al. 2011] and chemical vapor deposition [Itoh et al. 2008] were used for the growth of MoO3 films. Magnetron sputter deposition is an industrially practiced technique for deposition of oxide films. The physical properties of the sputter
deposited MoO₃ films depend critically on the sputter parameters such as oxygen partial pressure, substrate temperature, sputter power, sputter pressure and post-deposition heat treatment. In our earlier investigation, α-phase MoO₃ films were grown by thermal oxidation of DC magnetron sputtered metallic molybdenum films and their electrochemical and electrochromic properties were studied[Madhavi et al. 2013]. In the present investigation, thin films of MoO₃ were formed by RF magnetron sputtering technique at different of substrate temperatures and study their structure, surface morphology, electrical and optical properties. The electrochromic response of the MoO₃ films was studied and reported.

**Experimental**

**Preparation And Characterization Of Moo₃ Thin Films**

MoO₃ thin films were deposited onto glass and silicon substrates held at different temperatures in the range 303-573 K by sputtering of pure metallic molybdenum target in oxygen and argon gas mixture using reactive RF magnetron sputtering technique. Metallic molybdenum target (99.999% pure) with 50 mm diameter and 3 mm thickness was used for sputtering. The sputter chamber was evacuated by employing diffusion pump and rotary pump combination to achieve base pressure of 4x10⁻⁶ mbar. Pressure in the sputter chamber was measured with digital Pirani – Penning gauges. After achieving base pressure of 4x10⁻⁶ mbar, oxygen gas was admitted into the sputter chamber to the pressures in the range from 8x10⁻⁵ mbar to 8x10⁻⁴ mbar. Later, argon gas was admitted to the sputter pressure of 4x10⁻² mbar. The required quantities of oxygen and argon gases were admitted into the sputter chamber through fine controlled needle valves followed by Aalborg mass flow controllers (Model GFC 17). RF power of 150 W was supplied to the sputter target using RF power generator (Advance Energy Model ATX-600 W) for deposition of MoO₃ films. The sputter parameters fixed during the growth of the MoO₃ films are given in table 1.

The deposited MoO₃ films were characterized by studying their chemical composition, crystallographic structure and surface morphology, chemical binding configuration, electrical and optical properties. The thickness of the deposited films was measured with a mechanical Veeco Dektak (Model 150) depth profilometer. The chemical composition of the films was analysed with energy dispersive X-ray Analysis (Oxford instruments Inca Penta FETx3) attached to a scanning electron microscope (Carl Zeiss, model EVO MA15). The crystallographic structure of the films was determined by using X-ray diffractometer (Bruker D8 Advance Diffractometer) with copper Ka radiation with wavelength of λ = 0.15406 nm. The X-ray diffraction profiles were taken for a 2θ range between 10 and 60° in steps of 0.05°. The surface morphology of the films was analysed with scanning electron microscope (Hitachi SEM Model S-400). The chemical binding configuration of the films formed on silicon substrates was analyzed with Fourier transform infrared spectrophotometer (Nicolet Magana IR 750) and recorded the optical transmittance in the wavenumber range 400–1500 cm⁻¹. The electrical resistivity of the films was measured with four point probe method. The optical transmittance of the films formed on glass substrates was recorded using UV-Vis-NIR double beam spectrophotometer (Perkin-Elmer Spectrophotometer Lambda 950) in the wavelength range 300 - 1500 nm.

**Results And Discussion**

In order to optimise the oxygen partial pressure for the growth of the films, the MoO₃ films were deposited at different oxygen partial pressures in the range 8x10⁻⁴ - 8x10⁻³ mbar. The chemical composition of the deposited films was determined by using EDAX. Figure 1 shows the representative energy dispersive X-ray analysis spectrum of the film formed a oxygen partial pressure of 4x10⁻⁴ mbar. The spectrum contained the characteristic constituent of molybdenum and oxygen in the films. The chemical constituents present in the films formed at different oxygen partial pressures are shown in table 2.

It is seen from the table that the films formed at low oxygen partial pressure of 8x10⁻⁵ mbar contained less quantity of oxygen than the required to form compound of MoO₃. As the oxygen partial
pressure increased to $4 \times 10^{-4}$ mbar the films exhibited
the atomic ratio of 3.02 : 1. It revealed that the oxygen
partial pressure of $4 \times 10^{-4}$ mbar is an optimum to
produce nearly stoichiometric MoO$_3$ films. Hence an
oxygen partial pressure of $4 \times 10^{-4}$ mbar was fixed to
form the films at different substrate temperatures in
order to investigate their physical properties.

![FIG. 1 EDAX SPECTRUM OF MoO$_3$ FILM FORMED AT OXYGEN
PARTIAL PRESSURE OF 4x10$^{-4}$ mbar](image)

**TABLE 2 CHEMICAL COMPOSITION OF MoO$_3$ FILMS FORMED AT
DIFFERENT OXYGEN PARTIAL PRESSURES**

<table>
<thead>
<tr>
<th>$pO_2$ (mbar)</th>
<th>Mo (at %)</th>
<th>O (at %)</th>
<th>Mo / O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8 \times 10^{-5}$</td>
<td>79.2</td>
<td>20.8</td>
<td>3.80</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>76.4</td>
<td>23.6</td>
<td>3.23</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>75.2</td>
<td>24.8</td>
<td>3.03</td>
</tr>
</tbody>
</table>

**Deposition Rate**

Substrate temperature has significant influence on the
thickness of the deposited MoO$_3$ films. The thickness
of the deposited films was in the range 1.94 - 2.29 μm.
Figure 2 shows the dependence of deposition rate on
the substrate temperature of the MoO$_3$ films.

The deposition rate of the films formed at room
temperature (303 K) was 16.2 nm/min. As the substrate
temperature increased from 473 K to 523 K, the
deposition rate increased from 18.5 nm/min to 19.1
nm/min respectively. Due to the films formed at
higher substrate temperature of 573 K, there was a
slight decrease in the deposition rate to 18.3 nm/min. It
is noted that the formation of oxide phase during
reactive sputtering occurs almost nearly substrate
surface where the rate of reaction increases with
increase of substrate temperature, hence leading to the
higher deposition rate. Further increase of substrate
temperature to 573 K resulted in a slight decrease in
the deposition rate to 16 nm/min. The decrease of
deposition rate at higher substrate temperatures may
be due to the balance between the number of sputtered species arriving on the substrate surface and
the species leaving from the substrate surface due to
the re-evaporation of the deposited film hence
decrease in the deposition rate.

![FIG. 2 VARIATION IN THE DEPOSITION RATE OF MoO$_3$ FILMS
WITH SUBSTRATE TEMPERATURE](image)

**Structural Studies**

Figure 3 shows the X-ray diffraction profiles of MoO$_3$
films formed at different substrate temperatures. The
films deposited at room temperature didn’t contain
the characteristic diffraction reflections of MoO$_3$,
which revealed that the grown films were of X-ray
amorphous. The films grown at substrate temperature
of 473 K showed the diffraction peaks at $2\theta = 12.8^\circ$ and
$26.3^\circ$. These peaks were related to the (020) and (040)
reflections of orthorhombic $\alpha$- phase MoO$_3$. The
presence of (020) reflections revealed the growth of
layer structured $\alpha$- phase MoO$_3$.

![FIG. 3 XRD PROFILES OF MoO$_3$ FILMS DEPOSITED AT
DIFFERENT SUBSTRATE TEMPERATURES](image)
The films formed at the substrate temperature of 523 K showed the diffraction peaks at $2\theta = 12.9^\circ$ related to the (020) reflection, $27.8^\circ$ connected to (021) reflection and $43.2^\circ$ for the (141) reflections of $\alpha$-phase MoO$_3$ [JCPDS Code No. 76 – 1003]. It is noted that the (040) reflection was disappeared at substrate temperature of 523 K. The intensity of diffraction peaks increased with increase of substrate temperature revealed the improvement in the crystallinity of the films. Due to the further increase of the substrate temperature to 573 K, the decrease in the intensity of diffraction peaks indicated the decrease in the crystallinity of the films. The decrease in the crystallinity at higher substrate temperature of 573 K may be due to the higher surface mobility of adatoms on the substrate which was thermally induced, hence the reduction in the crystallinity of the deposited MoO$_3$ films. In the literature, Bouzidi et al. [2003] achieved $\alpha$-phase MoO$_3$ films by spray pyrolysis in the substrate temperatures range 523 - 573 K. Such a layered structured MoO$_3$ films were achieved by Martinez et al. [2013] at substrate temperature range from 473 to 673 K by spray deposition. It is noted that Sivakumar et al. [2007] obtained $\alpha$-phase MoO$_3$ films at low substrate temperature of 473 K in electron beam evaporation. Yang et al. [2009] found that the mixed $\alpha$- and $\beta$- phase MoO$_3$ films in electron beam deposition. It was clearly indicated that the grown crystallographic structure of the MoO$_3$ films mainly depends on the substrate temperature and the method of film growth.

The crystallite size ($L$) of the films was calculated from the X-ray diffraction peaks of (020) by using Debye - Scherrer’s relation [Cullity, 1974]

$$L = \frac{0.89\lambda}{\beta \cos\theta} \quad \text{(1)}$$

where $\lambda$ is the wavelength of the X-rays (0.15406 nm), $\beta$ the full width at half maximum of diffraction intensity measured in radians and $\theta$ the diffraction angle. Figure 4 shows the variation of crystallite size of MoO$_3$ films with substrate temperature. The full width at half maximum of the peak (020) in the films decreased from $0.20^\circ$ to $0.14^\circ$ with increase of substrate temperature from 473 K to 523 K respectively. In terms of the further increase of substrate temperature to 573 K, it increased to $0.19^\circ$. The crystallite size of the MoO$_3$ films deposited at substrate temperature of 473 K was 27 nm. As the substrate temperature increased to 523 K, the crystallite size increased to 62 nm. At higher substrate temperature of 573 K, the crystallite size decreased to 43 nm. The crystallite size of the films increased with increase of substrate temperature up to 523 K. At 523 K, the XRD shows that intensity of (0k0) reflection is maximum, indicating the layered structure of MoO$_3$. On further increment of substrate temperature to 573 K the intensity of (0k0) reflection decreased and intensity of peaks (021) and (141) increased. It revealed that though the films at higher substrate temperature of 573 K were not of layer structured $\alpha$- phase MoO$_3$. At higher substrate temperature of 573 K, the crystallite size decreased to 43 nm due to the re-evaporation hence smaller size of crystallites was grown.

In literature, Martinez et al. [2013] reported that the crystallite size decreased from 30 nm to 10 nm with increase of substrate temperature from 423 K to 553 K respectively in the MoO$_3$ films formed by spray pyrolysis method. Fan et al. [2011] also noticed the decrease in the crystallite size from 32 nm to 25 nm with increase of substrate temperature from 573 K to 673 K in RF sputtered MoO$_3$ films.

Figure 5 shows the dependence of interplanar spacing $d_{(020)}$ on the substrate temperature of the MoO$_3$ films. It was seen from the figure that the interplanar spacing $d_{(020)}$ decreased from 0.337 nm to 0.314 nm with increase of substrate temperature from 473 K to 573 K respectively. The decrease in the interplanar spacing with increase of substrate temperature was mainly due to compressive stresses developed in the films.

The dislocation density ($\delta$) and strain ($\epsilon$) developed in the films were calculated from the crystallite size using the relations,

$$\text{Dislocation density, } \delta = 1/L^2 \quad \text{(2)}$$

Figure 6 shows the variation of dislocation density
developed in the MoO$_3$ films with substrate temperature. The dislocation density of the films deposited at substrate temperature of 473 K was $1.4\times10^{15}$ lines/m$^2$ and it decreased to $2.6\times10^{14}$ lines/m$^2$ at substrate temperature of 523 K. On further increase of substrate temperature to 573 K, the dislocation density increased to $5.4\times10^{14}$ lines/m$^2$.

\[ \text{Stress, } \sigma = Y\left(\frac{a - a_0}{2\nu a_0}\right) \quad \text{------- (3)} \]

where \( a \) is the experimentally determined lattice parameter, \( a_0 \) the bulk lattice parameter, \( \nu \) the Poisson’s ratio and \( Y \) the Young’s modulus.

The decrease in dislocation density in the films were mainly due to the enhancement in the crystallinity with increase of substrate temperature up to 523 K. At higher substrate temperature of 573 K there was an increase in the dislocation density and strain in the films.

\[ \text{Stress } (\sigma) \text{ developed in the films was estimated from lattice parameter using the relation [Eckertova, 1984].} \]

\[ \text{Stress, } \sigma = Y\left(\frac{a - a_0}{2\nu a_0}\right) \quad \text{------- (3)} \]

Surface Morphology

The surface morphology of the deposited MoO$_3$ films was analyzed with scanning electron microscope. Figure 8 shows the scanning electron microscope images of the films formed at different substrate temperatures. SEM images of MoO$_3$ films formed at room temperature (303 K) showed very smooth morphology without any fragmentation features or topographical contrast, which indicated the growth of fine grain structure in amorphous background. The average size of the grown grains were of about 150 - 200 nm. The films deposited at substrate temperature of 473 K showed the grain growth with the shape of needle or elongated thin long bar structures. The size of grown grain size was of about 800 nm long and 150 nm in diameter. At this substrate temperature, the crystallinity of the films was increased due to the coalescence of neighbour crystallites driven by thermal energy received from the substrate by heating. Further increase of substrate temperature to 523 K the growth of grains like platelets piled one over the other with size of about 1 μm to 1.5 μm. The films formed at
higher substrate of 573 K the size of the grains decreased to about 1.2 μm. In general, the MoO₃ films grew with grains in the shape of needles platelets, elongated columns and rectangular shape depend on the deposition method employed and process parameters maintained during the deposition. Hence, the observed needle and platelet shaped grains achieved at higher substrate temperatures may be due to better mobility of adatoms or molecules to promote the growth. Yang et al. [2009] noticed the grains with pearl-like structure with platelets one over the other with size varied from 0.1 μm to 4 μm at substrate temperature of 373 K while at higher temperature of 673 K the average diameter of nanocrystallites of about 0.1 μm diameter and 3.5 μm long in electron beam evaporated MoO₃ films. The grains with shape of platelets were also grown by Wu et al. [2009] in vapor transport deposited MoO₃ films. Comini et al. [2008] achieved needle like nanoparticles with size about 200-400 nm at substrate temperature of 973 K in sol-gel deposited films.

**Fourier Transform Infrared Spectroscopy**

The infrared spectroscopy gives the information about the chemical binding of the atoms in the deposited films. Figure 9 shows Fourier transforms infrared transmittance spectra of MoO₃ films formed at different substrate temperatures. The films formed at 303 K showed a broad absorption band between 600 cm⁻¹ and 1000 cm⁻¹ which is the characteristic Mo - O vibrations attributed to the wide range of bands with different angles and lengths in the amorphous nature. There were three weak absorption bands around 795 cm⁻¹, 668 cm⁻¹ and 570 cm⁻¹ related to two stretching vibration modes of Mo = O, Mo - O and one transverse optical vibrations mode of Mo - O - Mo respectively [Navas et al. 2009]. The FTIR spectra of the films formed at substrate temperature 473 K showed the absorption bands at about 990 cm⁻¹, 811 cm⁻¹, 689 cm⁻¹ and 572 cm⁻¹. The absorption band observed at 811 cm⁻¹ was attributed to the bridging vibration of Mo = O indicated the existence of Mo⁶⁺ oxidation state related to α-phase MoO₃ and 992 cm⁻¹ for stretching mode of Mo = O. Further increase of substrate temperature of 523 K, the intense absorption band observed at 567 cm⁻¹ along with weak bands at 686 cm⁻¹, 808 cm⁻¹ and 992 cm⁻¹. The absorption band seen at 567 cm⁻¹ was assigned to the bending vibration of Mo - O - Mo bond, the broader band at around 808 cm⁻¹ attributed to the binding vibrations of Mo⁶⁺ which shifted to lower wavenumber side. Nazri and Julien [1992] observed the terminal oxygen stretching mode (ν) of M = O and the bending vibrational mode of Mo - O - Mo at 988 cm⁻¹ and 687 cm⁻¹ respectively in heat treated MoO₃ films.

**Electrical Properties**

Figure 10 shows the variation of electrical resistivity of MoO₃ films with substrate temperature. The electrical resistivity of the films increased with increase of substrate temperature. The films formed at room temperature exhibited low electrical resistivity of 1.2x10³ Ωcm. The low electrical resistivity of films was due to amorphous nature and presence of oxygen ion vacancies. The electrical resistivity increased from 1.6x10⁴ Ωcm to 3.4x10⁴ Ωcm with increase of substrate temperature from 473 K to 523 K. The increase in resistivity with substrate temperature was due to the
polycrystalline nature of the films as well as filling the oxygen ion vacancies. At higher substrate temperature of 573 K the electrical resistivity further increased to 4.8x10^4 Ωcm. In the literature, Sabhapathi et al. [1995] achieved the electrical resistivity of 5x10^4 Ωcm at Substrate temperature of 573 K in electron beam evaporated MoO₃ films. Yang et al. [2009] reported the electrical resistivity of the films formed at substrate temperatures 373 K and 473 K were higher than those formed at substrate temperature of 573 K and 673 K, which was due to the presence of different phase of the structure. Yahaya et al. [1998] achieved high electrical resistivity of 3x10^6 Ωcm at substrate temperature of 373 K at 673 K respectively. Boudaoud et al. [2006] reported the electrical resistivity of 4x10^5 Ωcm in spray deposited MoO₃ films. But in vacuum evaporated MoO₃ films, the electrical resistivity decreased from 1x10^9 Ωcm to 5x10^4 Ωcm with increase of substrate temperature from 323 K to 673 K respectively. Miyata and Akiyashi [1985] reported the highest electrical resistivity of 2x10^10 Ωcm in RF magnetron sputtered films. It is noted that the electrical resistivity of the DC magnetron sputtered MoO₃ films increased from 3.3x10^9 Ωcm to 8.3x10^4 Ωcm with increase of substrate temperature from 303 K to 473 K respectively.

**Optical Properties**

The optical absorption in the MoO₃ films was influenced by the substrate temperature. Figure 11 shows the optical transmittance spectra of MoO₃ films formed at different substrate temperatures in the range 303 - 573 K. The films formed at 303 K showed an average optical transmittance of about 60% at wavelengths higher than 600 nm. As the substrate temperature of the films increased to 523 K the transmittance of the films increased to 85%. High optical transmittance of the films formed at this substrate temperature was due to the decrease in the oxygen ion vacancies in the films. The films formed at higher substrate temperature of 573 K exhibited a decrease in the optical transmittance. The optical absorption edge of the films shifted to lower wavelength side with increase of substrate temperature up to 523 K and at higher substrate temperature of 573 K, the absorption edge shifted to red side. The red shift in the absorption edge at higher substrate temperature was due to the scattering of photons by the charge carriers.

The optical absorption coefficient (α) of the films was evaluated from the optical transmittance (T) data using the relation,

$$\alpha = - \frac{(1/t) \ln (T)}{t} \quad (4)$$

where t is the film thickness. The optical band gap (E_g) of the films was evaluated from the optical absorption coefficient using the Tauc’s relation [Tauc, 1974] assuming that the direct transitions takes place in these films.

$$\alpha h\nu = A (h\nu - E_g)^2 \quad (5)$$

The optical band gap of the films was determined from the plot of (αhν)^2 versus photon energy (hν). The extrapolation of the linear portion of plots of (αhν)^2 versus photon energy to α = 0 yield the optical band gap of the films. The optical band gap of the films increased from 2.98 eV to 3.28 eV with increase of substrate temperature from 303 K to 473 K respectively. On further increase of substrate
temperature to 523 K, the optical band gap increased to 3.34 eV, there after it decreased to 3.22 eV at higher substrate temperature of 573 K. It is to be noted in the literature that the optical band gap decreased from 2.80 eV to 2.35 eV with increase of substrate temperature from 303 K to 473 K in the MoO₃ films formed on glass substrates while those formed on FTO coated glass decrease from 2.76 eV to 2.30 eV with increase of substrate temperature from 303 K to 473 K in electron beam evaporated films [Boudaoud et al. 2006]. Sabhapathi et al. [1995] noticed such a decrease in the optical band gap with increase of substrate temperature in electron beam deposited films. Ramana and Julien. [2006] found that the optical band gap decreased from 3.35 eV to 2.81 eV with increase of substrate temperature from 303 K to 773 K in pulsed laser deposited films. Recently, Navas et al. [2009] observed the increase in the optical band gap from 3.35 eV to 3.62 eV with increase of substrate temperature from 473 K to 673 K in RF magnetron sputtered MoO₃ films. Large optical band gap value of 3.93 eV was achieved by Lin et al. [2009] in electron beam evaporated films. The optical band gap decreased for substrate temperature higher than 523 K, the oxygen vacancies occupied by electrons generate energy levels in the energy gap, which is close to valence band and act as donor centers. These oxygen vacancies which form a defect band in forbidden band are responsible for the broad-band absorption. [Deb and Chopoorian. 1996, Sian and Reddy. 2004, Yang et al. 2009].

Figure 12 shows the variation of refractive index with wavelength of MoO₃ films formed at different substrate temperatures. In general, the refractive index of MoO₃ films decreased with increase of wavelength. The refractive index of the films at 500 nm at room temperature was 2.01 and at substrate temperature of 473 K it was increased to 2.11. The low value of refractive index at 303 K was due to the low packing density because of the amorphous nature of the films. On increase of substrate temperature from 523 K to 573 K, the refractive index of the films increased from 2.13 to 2.16. The increase in the refractive index with increase of substrate temperature was due to improvement in the crystallinity and the packing density of the films. Uthanna et al. [2010] observed that the refractive index of the DC magnetron sputtered MoO₃ films increased from 2.03 to 2.10 with increase of substrate temperature from 303 K to 573 K.

Electrochromic Properties

Figure 13 shows the optical transmittance spectra of colored and virgin (bleached) states of the MoO₃ films formed at 303 K and 523 K. The optical modulation, (ΔT %) is the difference of transmittance Tₜ in bleached and Tₜ in colored state [(Tₜ% bleached ) – (Tₜ% colored)]. The color efficiency (η) at a particular wavelength correlated to the optical contrast can be given by the relation [Granqvist, 1995],

$$\eta = \log \left( \frac{T_b}{T_c} \right) \div \left( \frac{Q}{A} \right)$$

where Tₜ is the bleaching state transmittance, Tₜ the colored state transmittance, Q the charge inserted into the films and A the area of the films. The films formed at 303 K showed the virgin state optical transmittance of 53% where as in the colored state it decreased to 38%. The films prepared at 303 K exhibited the optical modulation (at 600 nm), ΔT = 15%. The color efficiency of these MoO₃ films was 26 cm²/C. On increasing the substrate temperature to 523 K, the optical transmittance of the virgin state was 87% and at colored state it decreased to 65% with optical modulation of 22%. The color efficiency of the MoO₃ films formed at substrate temperature 523 K was increased 30 cm²/C. Thus the optical modulation and coloration efficiency was increase with increase of substrate temperature from 303 K to 523 K. The coloration efficiency of the films deposited at 573 K decreased to 24 cm²/C. The decrease in the coloration efficiency at higher substrate temperature of 573 K may be due to the decrease in the intercalation of Li⁺ ions during the coloration process. Lin et al. [2010]
reported the coloration efficiency of 25.1 cm²/C for the films annealed at 573 K. Recently, Madhavi et al. [2013] achieved the optical modulation of 14% and coloration efficiency of 27 cm²/C in thermally oxidized MoO₃ films. Sivakumar et al. [2006] reported a maximum coloration efficiency of 30 cm²/C at the wavelength of 633 nm in the films formed at room temperature and it decreased to 14 cm²/C in the films formed at substrate temperature of 473 K, there after it increased to 22 cm²/C at 573 K in electron beam evaporated MoO₃ films. The films deposited at 523 K exhibited the better electrochromic properties which will be useful in manufacturing of electrochromism based smart windows.

The films deposited at substrate temperature of 523 K exhibited the growth of grains with shape of platelets piled one over the other about the size of 1 μm to 1.5 μm. Fourier transform infrared transmittance spectrum of the films formed at 303 K showed broad absorption band between 600 and 1000 cm⁻¹ associated with the characteristic Mo-O vibrations in the amorphous background. The films formed at 473 K exhibited the bridging and stretching vibrations of Mo=O confirmed the existence of Mo⁶⁺ oxidation state related to α-MoO₃. The electrical resistance of the amorphous MoO₃ films formed at 303 K was 1.2x10³ Ωcm and at substrate temperature of 523 K it increased to 3.4x10⁴ Ωcm due to the crystalline nature as well as filling of oxygen ion vacancies. The optical band gap of the films increased from 2.98 eV to 3.34 eV with increase of substrate temperature from 303 K to 523 K. The refractive index of the films increased with increase of substrate temperature due to improvement in the crystallinity and packing density of the films. The electro chromic performance of the films was studied on the MoO₃ films. Optical modulation of the films increased from 15% to 22% and coloration efficiency increased from 26 cm²/C to 30 cm²/C with increase of substrate temperature from 303 K to 523 K respectively.

**REFERENCES**


Julien C. M., Pistonia (Ed), Lithium Batteries; New Materials, Developments and Perspectives, Amsterdam, North Holland, 1994.


Navas, I; Vinod Kumar, R.; Lethy, K.J.; Detty, A.P.;
N. Ganesan, V.; Sathe, V. and Mahadevan Pillai, V.P.


Y. Yang, W.Y., Kim, W.G. and Rhee, S.W., “Radio frequency

**Mr. S. Subbarayudu** received his Master Degree in Physics from Sri Krishnadevaraya University, Anantapur, India during the year 1991 - 93. He is working as Assistant Professor in Physics, SBVR Degree College, Badvel, Andhra Pradesh. He is carrying out research work leading to the Degree of Doctor of Philosophy in Physics in the Department of Physics, Sri Venkateswara University, Tirupati - 517 502, Andhra Pradesh, India. Currently he is working on the preparation and characterisation of RF magnetron sputtered MoO$_3$ films for applications in gas sensors and electrochromic devices.