Chapter - III

RESULTS AND DISCUSSIONS
REFERENCES


The performance and usefulness of sputter deposited MoO₃ thin films mainly depend on the sputter process parameters such as oxygen partial pressure, substrate temperature, substrate bias, sputtering power and the distance between the target and substrate maintained during the deposition of the films. Proper choice of the deposition parameters is very crucial in obtaining stoichiometric, crystalline films with fine structure, electrical and optical properties. Hence a systematic procedure was adopted in the preparation of MoO₃ films using dc magnetron sputtering technique and the results achieved on the deposited films were presented.

3.1 Preparation of molybdenum oxide films

In the present study, molybdenum oxide films were deposited on glass and crystalline silicon (111) substrates using dc reactive magnetron sputtering under different oxygen partial pressures, substrate temperatures, substrate bias and sputtering powers. The influence of deposition parameters such as oxygen partial pressure, substrate temperature, substrate bias and sputtering power on the physical properties of MoO₃ films were systematically studied and the results were reported.

3.2 Physical properties of magnetron sputtered MoO₃ films

The deposition parameters maintained during the preparation of MoO₃ films are given table. 3.1.

<table>
<thead>
<tr>
<th>Table 3.1 Deposition parameters of the MoO₃ films</th>
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<tr>
<td>Sputter target</td>
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<tr>
<td>Target to substrate distance</td>
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<tr>
<td>Ultimate pressure ( (P_u) )</td>
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<tr>
<td>Sputter pressure ( (P_s) )</td>
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<tr>
<td>Oxygen partial pressure ( (pO_2) )</td>
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<td>Substrate temperature ( (T_s) )</td>
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<td>Substrate bias voltage ( (V_b) )</td>
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<td>Sputtering power ( (S_p) )</td>
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The magnetron sputtered molybdenum oxide films were characterized for the chemical binding configuration, core level binding energies, crystallographic structure and surface morphology, electrical and optical properties. Fourier transform infrared spectroscopy (FTIR) was used to study the chemical binding configuration of the films formed on single crystal silicon substrates. X-ray photoelectron spectroscopy (XPS) was utilized to determine the core level binding energies of the films. X-ray diffraction (XRD) was used to analyze the crystallographic structure of the films. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were employed to analyze the surface morphology of the deposited films. The dc electrical conductivity measurements on the films were carried by using the standard technique. UV-Vis-NIR spectrophotometer was employed to record the optical transmittance and reflectance of the films and reported the results in the present chapter.

3.2.1. **Influence of oxygen partial pressure on the physical properties of MoO$_3$ films**

In order to understand the sputtering process involved during the deposition of MoO$_3$ films, the glow discharge characteristics of the magnetron cathode of molybdenum was studied to fix the approximate sputter conditions for preparation of molybdenum oxide films.

**Glow discharge characteristics**

Glow discharge characteristics of the molybdenum target under various oxygen partial pressures were carried out at a constant cathode power of 5.7 W/cm$^2$. Figure 3.1 shows the variation of molybdenum cathode potential on the oxygen partial pressure. Initially the cathode potential increased from 490 to 567 V with the increase of oxygen partial pressure from $7 \times 10^{-5}$ to $1 \times 10^{-4}$ mbar. As the oxygen partial pressure increased to $4 \times 10^{-3}$ mbar the cathode potential decreased to a value of 486 V. At low oxygen partial pressures the reduction in the ionization collision led to an increase in the cathode potential to maintain the constant cathode current. The decrease of cathode potential at higher oxygen partial pressures was attributed to the oxidation of molybdenum target. The oxidized molybdenum target has higher
secondary electron emission coefficient than the molybdenum target, hence low cathode potential is required to achieve the same cathode current [1]. Such a dual nature of variation in the cathode potential with the oxygen partial pressure was also observed in reactive magnetron sputtering of metallic target of tantalum [2] in the presence of reactive gas of oxygen during the formation of tantalum oxide films in dc reactive magnetron sputtering.

![Figure 3.1 Variation of molybdenum target potential with the oxygen partial pressure](image)

**Figure 3.1 Variation of molybdenum target potential with the oxygen partial pressure**

In order to study the influence of oxygen partial pressure on the physical properties, the MoO₃ films were formed under various oxygen partial pressures in the range of $8 \times 10^{-5} - 8 \times 10^{-4}$ mbar at a fixed substrate temperature of 473 K. Figure 3.2 shows the dependence of deposition rate of the MoO₃ films on the oxygen partial pressure. The deposition rate of the films formed at low oxygen partial pressure of $8 \times 10^{-5}$ mbar was 19.2 nm/min. The deposition rate gradually increased to 23.5 nm/min with the increase of oxygen partial pressure to $2 \times 10^{-4}$ mbar. Further increase of oxygen partial pressure to $8 \times 10^{-4}$ mbar the deposition rate decreased to
14.2 nm/min. The initial increase in the deposition rate of the films with the increase of oxygen partial pressure was due to the increase of the sputtering power since the cathode potential increased with the increase of oxygen partial pressure. The decrease of deposition rate at higher oxygen partial pressures were related to the chemical reaction between the target surface and the reactive gas of oxygen [3]. This chemical reaction led to the formation of oxide layer on the target surface and in turn reduced in the deposition rate [4]. Scarminio et al. [5] also observed the similar behaviour of increase in the deposition rate at lower oxygen partial pressures in rf sputtered molybdenum oxide films.

The core level binding energies and oxidation states present in the MoO$_3$ films were analyzed using the X-ray photoelectron spectroscopy. Figure 3.3 shows the survey scan of the MoO$_3$ film formed at the oxygen partial pressure of 2x10$^{-4}$ mbar. The peak observed at about 531 eV related to the core level binding energy of...
oxygen O 1s and the peaks located at about 412 and 395 eV were the molybdenum Mo 3P\(_{1/2}\) and Mo 3P\(_{3/2}\) respectively. The peak situated at 283 eV related to the carbon C 1s due to the contamination of carbon on the surface of the films since exposed to the atmosphere. The C 1s peak was disappeared when the films were sputter etched by argon ion bombardment for 5 minutes in the XPS system. The peaks observed around 232 and 235 eV were the doublet of Mo 3d. The peaks seen

![XPS survey spectrum of MoO\(_3\) film formed at an oxygen partial pressure of 2x10\(^{-4}\) mbar](image)

Figure 3.3 XPS survey spectrum of MoO\(_3\) film formed at an oxygen partial pressure of 2x10\(^{-4}\) mbar

at about 65 and 35 eV were the core levels of Mo 4s and Mo 4p respectively. The peaks located at about 22 and 5 eV related to the O 2s and Mo 4d respectively. The narrow scan spectra of the Mo 3d doublet core levels of the films formed at different oxygen partial pressures are shown in figure 3.4. The core level binding energy of Mo 3d\(_{5/2}\) decreased from 232.69 to 231.87 eV with the increase of oxygen partial pressure from 8x10\(^{-5}\) to 8x10\(^{-4}\) mbar. Similarly, the core level binding energy of Mo 3d\(_{3/2}\) peak energy was also decreased from 235.80 to 235.07 eV with the increase of oxygen partial pressure from 8x10\(^{-5}\) to 8x10\(^{-4}\) mbar. The line shape of the core level spectrum of the films formed at 8x10\(^{-5}\) mbar was asymmetric indicated the presence of mixed oxidation states of Mo\(^{5+}\) and Mo\(^{6+}\) in MoO\(_3\) films. By employing the
deconvolution technique the best fit of the Gaussian curves was obtained. The films formed at oxygen partial pressure of $2 \times 10^{-4}$ mbar showed the symmetric peaks of Mo 3d with the core level binding energy of Mo 3d$_{5/2}$ at 232.49 eV and Mo 3d$_{3/2}$ of 235.64 eV with the spin orbit splitting of 3.15 eV indicated the characteristic of Mo$^{6+}$ oxidation of MoO$_3$ [6]. The films formed at higher oxygen partial pressure of $8 \times 10^{-4}$ mbar showed six deconvoluted Gaussian peaks. The core level binding

![Figure 3.4 XPS core level binding energy spectra of Mo 3d of MoO$_3$ films formed at different oxygen partial pressures](image)


energies achieved in the films formed at different oxygen partial pressures are given in table 3.2. The spin orbit splitting of the films formed at an oxygen partial pressure of $2 \times 10^{-4}$ mbar was in good agreement with the values reported in MoO$_3$ films [7]. It is seen from the table that the films formed at low oxygen partial pressure of $8 \times 10^{-5}$ mbar contained the Mo$^{6+}$ and Mo$^{5+}$ oxidation states indicated the presence of mixed phase of MoO$_3$ and MoO$_{3-x}$. 
Table 3.2 Core level binding energies of various oxidation states of Mo and O 1s in the MoO₃ films

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<tr>
<th>Oxygen partial pressure (mbar)</th>
<th>Binding energy (eV)</th>
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<tr>
<td></td>
<td>Mo 3d₅/₂</td>
</tr>
<tr>
<td></td>
<td>Mo⁶⁺ Mo⁵⁺ Mo⁴⁺</td>
</tr>
<tr>
<td>8x10⁻⁵</td>
<td>232.69 231.60 ---</td>
</tr>
<tr>
<td>2x10⁻⁴</td>
<td>232.49 --- ---</td>
</tr>
<tr>
<td>8x10⁻⁴</td>
<td>231.87 230.86 232.98</td>
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The presence of mixed phase was due to the insufficient oxygen in the sputter chamber during deposition of the films. Further increase of oxygen partial pressure of 2x10⁻⁴ mbar showed only the Mo⁶⁺ oxidation state indicated the formation of nearly stoichiometric MoO₃ films. At higher oxygen partial pressure of 8x10⁻⁴ mbar the films contained the Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺ oxidation states indicating once again the coexistence of MoO₃, MoO₃ₓ and MoO₂ phases. The core level binding energy of pure oxygen (O 1s) peak was 531.0 eV. The core level binding energy value of the films decreased from 530.44 to 529.77 eV with the increase of oxygen partial pressure from 8x10⁻⁵ to 8x10⁻⁴ mbar respectively as shown in fig. 3.5. The decrease in the binding energy of O 1s with the increase of oxygen partial pressure was attributed to the bonding of oxygen with molybdenum to form molybdenum oxide [8]. It revealed that the films formed at an oxygen partial pressure of 2x10⁻⁴ mbar were stoichiometric with single phase of MoO₃.
Figure 3.5 XPS core level binding energy spectra of O 1s of MoO₃ films formed at different oxygen partial pressures

The Fourier transform infrared transmittance spectra of MoO₃ films deposited at different oxygen partial pressures are shown in figure 3.6. FTIR spectrum of the MoO₃ films formed at an oxygen partial pressure of 8x10⁻⁵ mbar showed an absorption band between 500 and 1000 cm⁻¹. The broad band the band observed at 558 cm⁻¹ was due to the transverse optical (TO) vibration of Mo-O-Mo [9] and the band at 695 cm⁻¹ was the characteristic bridging of Mo-O-Mo of Mo⁵⁺ [10]. It revealed that the existence of the band at 695 cm⁻¹ at oxygen partial pressure of 8x10⁻⁵ mbar was due to the formation of substoichiometric MoO₁ₓ films. When oxygen partial pressure increased to 2x10⁻⁴ mbar, the film showed the absorption bands at 586, 838 and 1002 cm⁻¹ and a shoulder at 894 cm⁻¹. The band observed at 586 cm⁻¹ was the transverse optical vibrations of Mo-O-Mo. The band seen at 838 cm⁻¹ was attributed to the Mo-O stretching mode, 894 cm⁻¹ was connected to bridging of Mo-O-Mo in Mo⁶⁺ and 1002 cm⁻¹ related to the stretching vibration of O=Mo of the α-phase MoO₃ [11]. The presence of characteristic peaks indicated that the molybdenum oxide films formed were stoichiometric and in orthorhombic...
α-phase. With increase of oxygen partial pressure to $8 \times 10^{-4}$ mbar the intensity of broad absorption band decreased. In addition to this, transverse optical vibrational mode of MoO$_3$ band at 553 cm$^{-1}$ along with the terminal and stretching vibrations of O=Mo respectively at 836 and 1001 cm$^{-1}$ present in the films. These studies also confirmed that the oxygen partial pressure of $2 \times 10^{-4}$ mbar is an optimum to produce the films with stoichiometric α-phase of MoO$_3$.

Crystallographic structure of the films was analyzed by the X-ray diffraction. XRD profiles of the MoO$_3$ films deposited at different oxygen partial pressures are shown in figure 3.7. The presence of diffraction peaks revealed that the films were polycrystalline in nature. The films formed at low oxygen partial pressure of $8 \times 10^{-5}$ mbar showed the diffraction peaks at 2θ = 12.80, 23.05, 25.70 and 39.05° were related to the (020), (011), (040) and (060) reflections of MoO$_3$. Peak observed at 38.70° correspond to (111) reflection of unoxidised molybdenum. It revealed that the films formed at low oxygen partial pressure of $8 \times 10^{-5}$ mbar contained molybdenum oxide along with unoxidised molybdenum. The presence of elemental molybdenum along with molybdenum oxide at low partial pressure of oxygen was due to the availability of insufficient oxygen in the sputtering chamber to react with molybdenum species at the time of sputtering. The presence of (020), (040) and (060) reflections related to α-phase of MoO$_3$, while the (011) reflection connected to the β-phase of MoO$_3$ [12]. Hence the coexistence of mixed crystallographic phases of α- and β-MoO$_3$ along with elemental molybdenum were achieved at lower oxygen partial pressure of $8 \times 10^{-5}$ mbar. When oxygen partial pressure increased to $2 \times 10^{-4}$ mbar, the films showed only the (0k0) reflections indicated the single phase orthorhombic α-phase MoO$_3$. With increase of oxygen partial pressure to $8 \times 10^{-4}$ mbar the presence of (200) reflection along with (0k0) reflections indicated once again the coexistence of α- and β-phase of MoO$_3$. Such a change of phase in MoO$_3$ was also noticed with the oxygen partial pressure in pulsed laser deposited films [13]. In contrast to this, Mohamed et al. [4] observed the polycrystalline to amorphous transformation with the increase of oxygen partial pressure in dc magnetron sputtered films.
Figure 3.6 FTIR spectra of MoO$_3$ films formed at different oxygen partial pressures
From the XRD studies it revealed that the oxygen partial pressure of $2 \times 10^{-4}$ mbar is an optimum to produce single phase orthorhombic $\alpha$- phase MoO$_3$ films. The evaluated lattice parameter of the MoO$_3$ films deposited at oxygen partial pressure of $2 \times 10^{-4}$ mbar was $a = 0.402$ nm, $b = 1.388$ nm and $c = 0.369$ nm. Scarminio et al. [5] also reported that the films deposited by rf sputtering at low oxygen partial pressures exhibited the metallic behaviour and with the increase of oxygen partial pressure the films were transformed into stoichiometric MoO$_3$.

The surface morphological studies of the sputtered MoO$_3$ thin films were carried out by using atomic force microscopy and scanning electron microscope. AFM images of the MoO$_3$ films deposited at different oxygen partial pressures are shown in figure 3.8. The AFM images demonstrated that the MoO$_3$ films were homogenous and uniform. The MoO$_3$ film deposited at low oxygen partial pressure of $8 \times 10^{-5}$ mbar showed the uniform and needle like structure of various sizes. The size of initially formed nuclei would be small when films deposited at low oxygen partial pressure of $8 \times 10^{-5}$ mbar. When oxygen partial pressure increased to $2 \times 10^{-4}$

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Figure 3.7 X-ray diffraction profiles of MoO$_3$ films deposited at different oxygen partial pressures
mbar, the film showed columnar growth combined with the large needle like grains.
At this oxygen partial pressure large size grains were observed. Further increase of
oxygen partial pressure to $8 \times 10^{-4}$ mbar, the films with rare small grains were
observed. The root means square surface roughness of the films increased from 1.36
to 7.40 nm with the increase of oxygen partial pressure from $8 \times 10^{-5}$ to $8 \times 10^{-4}$ mbar.
The morphology of the MoO$_3$ films significantly varied with different oxygen partial
pressures attributed to ion bombardment during sputtering deposition.

SEM images of the MoO$_3$ films deposited at different oxygen partial
pressures are shown in figure 3.9. The SEM images clearly showed that the MoO$_3$
films were homogenous, crack free surfaces and uniform. It is evident from the
micrographs that the oxygen partial pressure strongly influenced the surface
morphology of the MoO$_3$ films. MoO$_3$ films deposited at oxygen partial pressure of
$8 \times 10^{-5}$ mbar were identified with the presence of MoO$_3$ phase grains uniformly
covered on the surface of the substrate. The shape of the grains was more or less
needle or thin long bars which attributed to the growth of secondary phase. This may
be attributed due to less oxidation of molybdenum and led to co-existence of
different phases. It was also identified from the XRD patterns. When oxygen partial
pressure increased to $2 \times 10^{-4}$ mbar, the film showed granular structure and arranged
one over the other which confirmed the layered structure.

Figure 3.10 shows the variation of electrical conductivity of MoO$_3$ films with
the oxygen partial pressures. It was observed that the electrical conductivity
decreased with the increase of oxygen partial pressure. The films formed at low
oxygen partial pressure of $8 \times 10^{-5}$ mbar showed high electrical conductivity of $4 \times 10^{-5}$
$\Omega^{-1} \text{cm}^{-1}$ due to the presence of metallic molybdenum along with MoO$_3$. The films
formed at oxygen partial pressure of $2 \times 10^{-4}$ mbar exhibited the electrical
conductivity of $1.2 \times 10^{-5}$ $\Omega^{-1} \text{cm}^{-1}$. The low electrical conductivity of $1.6 \times 10^{-6}$ $\Omega^{-1} \text{cm}^{-1}$
was achieved at high oxygen partial pressure of $8 \times 10^{-4}$ mbar. Low value of electrical
conductivity at high oxygen partial pressure of $8 \times 10^{-4}$ mbar might be due to the
slight excess of oxygen in the films. Decrease in the electrical conductivity with the
increase of oxygen partial pressure was attributed to the partial filling of oxygen ion
vacancies in the films [14]. The achieved electrical conductivity of the films formed
Figure 3.8 AFM micrographs of MoO$_3$ films formed at different oxygen partial pressures:

(a) $8 \times 10^{-5}$ mbar, (b) $2 \times 10^{-4}$ mbar and (c) $8 \times 10^{-4}$ mbar
Figure 3.9 SEM micrographs of MoO$_3$ films formed at different oxygen partial pressures:
(a) 8x10$^{-5}$ mbar, (b) 2x10$^{-4}$ mbar and (c) 8x10$^{-4}$ mbar
at oxygen partial pressure of $2 \times 10^{-4}$ mbar was higher than the electron evaporated films [15].

![Graph showing variation of electrical conductivity of MoO$_3$ films with oxygen partial pressure](image)

**Figure 3.10 Variation of electrical conductivity of MoO$_3$ films with the oxygen partial pressure**

The optical transmittance spectra of the MoO$_3$ films formed at different oxygen partial pressures are shown in figure 11. The optical transmittance is high in the visible region and increased from 48 to 85% with the increase of oxygen partial pressure from $8 \times 10^{-5}$ to $8 \times 10^{-4}$ mbar respectively. The optical transmittance of the films formed at low oxygen partial pressure of $8 \times 10^{-5}$ mbar was low due to the formation of substoichiometric MoO$_3$ films with the characterization of the blue colour due to the oxygen ion vacancies [16]. The presence of nonreactive molybdenum along with MoO$_3$ acts as scattering centers of light and thus the decrease in the transmittance of the films. As the oxygen partial pressure increased to $2 \times 10^{-4}$ mbar, the transmittance of the films increased since the oxygen ion vacancies tends to disappeared and hence the composition of the films approached to the stoichiometric MoO$_3$. The films formed at oxygen partial pressure
≥ $2 \times 10^{-4}$ mbar were transparent indicated the stoichiometric molybdenum oxide along with the substoichiometric behavior [5]. In this region the oxide films were formed by sputtering of molybdenum oxide generated at the target surface [17]. A sharp absorption edge was observed in the range of 350 - 450 nm. The optical absorption edge of the films shifted markedly towards lower wavelength side with the increase of oxygen partial pressure. Figure 3.12 shows the representative optical transmittance and reflectance spectra of MoO$_3$ films formed at oxygen partial pressure of $1 \times 10^{-4}$ mbar. The optical absorption coefficient ($\alpha$) of the films was calculated from the optical transmittance data where the reflection losses were taken into account. The optical band gap of the films was evaluated from the Tauc plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$). Figure 3.13 shows the plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of MoO$_3$ films formed at different oxygen partial pressures. The optical band gap of the MoO$_3$ films increased from 2.96 to 3.26 eV with the increase of oxygen partial pressure from $8 \times 10^{-5}$ to $8 \times 10^{-4}$ mbar.
The low value of optical band gap of the films formed at low oxygen partial pressures was due to the formation of substoichiometric films. It was also reported that the optical band gap increased from 2.80 to 3.16 eV with the increase of oxygen flow rate from 1.65 – 8.00 sccm in the rf reactive sputtered films [5]. In the present investigation, the stoichiometric films deposited at an oxygen partial pressure of 2x10⁻⁴ mbar showed the optical band gap of 3.16 eV. It is in good agreement with the reports of pulsed laser deposited [6,8] and dc magnetron sputtered [18] films where the grown films were α- phase of MoO₃. Boudoud et al. [19] achieved a high optical band gap of 3.35 eV in spray deposited films. The polycrystalline α- MoO₃ powder optical band gap was 3.2 eV [12] while the band gap of β- MoO₃ was 2.83 eV [20]. Low optical band gap of 2.60 – 2.70 eV was also achieved in dc magnetron sputtered [21] and rf sputtered [22] films due to the formation of β- phase MoO₃. The refractive index of the films was determined from the optical transmittance interference data using Swanepoel’s envelope method [23]. Figure 3.14 shows the wavelength dependence of refractive index of MoO₃ films formed at different
Figure 3.13 Plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of MoO$_3$ films deposited at different partial pressures

Oxygen partial pressures. In all the films the refractive index decreased with the increase of wavelength. The refractive index of MoO$_3$ films (at the wavelength of 500 nm) increased from 2.01 to 2.13 with the increase of oxygen partial pressure from $8 \times 10^{-5}$ to $8 \times 10^{-4}$ mbar. The low value of refractive index of 2.01 in the case of the films formed at low oxygen partial pressure of $8 \times 10^{-5}$ mbar was due to the presence of unoxidised molybdenum along with the MoO$_3$. The increase in the refractive index at higher oxygen partial pressures was due to the formation of single phase MoO$_3$ and the increase in packing density of the films. The achieved refractive index values are in good agreement with the reported values of dc magnetron sputtered [22] and electron beam evaporated [16] films.

The studies on the influence of oxygen partial pressure on the physical properties of the MoO$_3$ films revealed that the single phase $\alpha$– MoO$_3$ with electrical conductivity of $1.2 \times 10^{-5} \ \Omega^{-1} \ \text{cm}^{-1}$ and optical band gap of 3.16 eV were obtained at an oxygen partial pressure of $2 \times 10^{-4}$ mbar. Hence oxygen partial pressure of $2 \times 10^{-4}$ mbar was fixed for the films formed at different substrate temperatures, sputtering powers and substrate bias voltages to study the influence of these parameters on the physical properties.
3.2.2 Influence of substrate temperature on the physical properties of MoO$_3$ films

In order to study the influence of substrate temperature on the physical properties of MoO$_3$ films, the films were deposited under different substrate temperatures in the range 303 - 623 K under at the optimized oxygen partial pressure of 2$\times$10$^{-4}$ mbar. The effect of substrate temperature on the structural, electrical and optical properties was systematically studied to optimize the substrate temperature to produce the crystalline MoO$_3$ films. The dependence of the deposition rate of MoO$_3$ films on the substrate temperature is shown in figure 3.15. When substrate temperature increased from 303 to 523 K, the deposition rate of the films increased from 21.45 to 23.62 nm/min. The initial increase of deposition rate at lower substrate temperature was attributed to the lower adatom mobility on the substrate surface. Further increase of substrate temperature above 523 K, the deposition rate started to decrease and reached to a minimum value of 22.56 nm/min at a substrate temperature of 623 K.
Substrate temperature (K)

Figure 3.15 Dependence of deposition rate of MoO$_3$ films with the substrate temperatures

The decrease of deposition rate at higher substrate temperatures may be due to the balance between the number of atoms arriving on the substrate and the atoms leaving from the substrate surface which resulted re-evaporation of the films hence of lower deposition rate [24].

The XPS measurements indicated that the substrate temperature strongly influenced the stoichiometry and phase of the deposited film. The XPS core level binding energy spectra of Mo 3d doublet of the MoO$_3$ films formed at different substrate temperature was shown in figure 3.16. The core level binding energy of Mo 3d$_{5/2}$ was increased from 232.44 to 232.89 eV with the increase of substrate temperature from 303 to 623 K. The shift in the core level binding energy was 0.45 eV. Similarly the Mo 3d$_{3/2}$ peak energy was also increased from 235.57 eV to 236.01 eV with a shift of 0.43 eV. The core level spectra of Mo 3d deposited at 303 K showed the asymmetric peaks. This asymmetric nature of Mo 3d core level binding energies at low substrate temperature indicated the presence of mixed
Figure 3.16 XPS core level of Mo 3d doublet of the MoO$_3$ films formed at different substrate temperatures

oxidation states of Mo$^{5+}$ and Mo$^{6+}$ [25]. The films deposited at substrate temperature of 303 K contained core level spectra of Mo 3d at binding energies 232.44 and 235.57 eV for Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ respectively with FWHM of 1.77 eV and with the intensity ratio of Mo 3d$_{3/2}$/Mo 3d$_{5/2}$ of 2:3. These bands were asymmetric with shoulders. The broaden peaks at low substrate temperatures was attributed that the molybdenum atoms were in different coordination environments due to dominantly amorphous or with disordered structure or substoichiometric [25,26]. When the substrate temperature increased to 473 K, the films showed symmetric peaks of Mo 3d$_{5/2}$ at the core level energy of 232.5 eV and Mo 3d$_{3/2}$ at 235.6 eV which is the characteristic Mo$^{6+}$ oxidation state of MoO$_3$. Further increase of substrate temperature to 523 K the intensity of Mo 3d doublet peaks increased. The O 1s core level binding energy of MoO$_3$ films decreased from 530.29 to 530.17 eV with the increase of substrate temperature from 303 to 473 K, further increase of substrate temperature from 473 to 623 K it increased from 530.17 to 530.70 eV respectively. The increased core level binding energies of O 1s were related to the molybdenum and oxygen bonds. The core level binding energies obtained in the films deposited
at different substrate temperatures are given in Table 3.3. It is clearly showed an increase in the core level binding energies of Mo 3d doublet and O 1s with increase of substrate temperature. The existence of molybdenum in its highest oxidation state of Mo\(^{6+}\) is in good agreement with reported values [8,26]. Further increase of substrate temperature to 623 K, the intensity of Mo 3d doublet peak increased. These results indicated that the films deposited at < 473 K were substoichiometric, whereas those films deposited at substrate temperature in the range 473 – 623 K were stoichiometric. The FWHM increased from 1.66 to 1.75 with increase of substrate temperature from 303 to 623 K. Figure 3.17 shows the XPS core level valence band spectra of molybdenum oxide films deposited at different substrate temperatures. The valence band spectra of the films showed the strong X-ray photoemission peaks at about 5.47, 7.50 and 22.23 eV were related to the Mo 4d, O 2p and O 2s orbitals respectively [7,27]. The overlapping of Mo 4d and O 2p orbital is also evident from the spectra. The low intensity of the emission peak at 5.1 eV indicated the Mo 4d level was partially filled. From the XPS studies, it is clear that the films deposited at 303 K were substoichiometric MoO\(_{3-x}\) films. When substrate temperature increased \( \geq 473 \) K intensity of molybdenum peak decreased while the intensity of the peaks of O 2p increased which lead to a stoichiometric film. The MoO\(_3\) films deposited at 303 K was characterized by the

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<th>Substrate temperature (K)</th>
<th>Binding energy (eV)</th>
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<tr>
<td></td>
<td>Mo ( 3d_{5/2} )</td>
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<tr>
<td></td>
<td>Mo(^{6+}) Mo(^{5+})</td>
</tr>
<tr>
<td>303</td>
<td>232.44 231.23</td>
</tr>
<tr>
<td>473</td>
<td>232.49 ----</td>
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<tr>
<td>523</td>
<td>232.77 ----</td>
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<td>623</td>
<td>232.89 ----</td>
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Figure 3.17 XPS core level valence band spectra of MoO$_3$ films formed at different substrate temperatures

broad O 2p photoelectron peak at binding energy $\sim 7.5$ eV. Moreover, the band structure of amorphous films deposited at 303 K may be considerably different from crystalline films deposited at higher substrate temperature because of their substoichiometric composition. It was known that MoO$_{3-x}$ films formed substoichiometric oxides upon evaporation in vacuum or in a reducing atmosphere [28,29]. The departure from stoichiometry was associated with the formation of colour centers [30]. Molybdenum contained the outer electronic configuration 4d$^5$ 5s$^1$. If MoO$_3$ was considered to be completely ionic, i.e. Mo$^{6+}$ and O$^{2-}$, the valence band would consisted of O 2p states and the conduction band would be composed of empty 4d and 5s states. This was in consistent with the model proposed by Goodenough [31]. The substoichiometric amorphous material of MoO$_{3-x}$ contained the oxygen ion vacancies, which was positively charged structural defects. When substrate temperature increased from 303 to 473 K the electron distribution curve (XPS) of the film deposited at 473 K exhibited a small band near the Fermi edge, which was absent in the films deposited at 303 K. This new band appeared below
the Fermi level was attributed to the electrons trapped in positively charged anion vacancies in the amorphous oxide lattice. The thermal excitation can promote electrons from the valence band into these positively charged defects. The oxygen ion vacancies occupied by two electrons were acted as donors. Both the donor centers were formed in the crystalline molybdenum oxide.

Figure 3.18 shows the variation of energy difference of $\Delta (O\ 1s - Mo\ 3d_{5/2})$ values with substrate temperature has been used to characterize the Mo-O bonds.

![Graph showing variation of energy difference with substrate temperature](image)

**Fig. 3.18 Variation of energy difference of $\Delta (O\ 1s - Mo\ 3d_{5/2})$ values with substrate temperatures**

The electron escape depths ratio for Mo 3d and O 1s photoelectrons, $\lambda_{Mo}/\lambda_{O}$, was estimated as $\lambda_{Mo}/\lambda_{O} = \sqrt{E_{k}(Mo)/E_{k}(O)} = 1.187$, where $E_{k}(Mo)$ and $E_{k}(O)$ are the kinetic energies of the Mo 3d and O 1s photoelectrons respectively. The O 1s and Mo 3d core level spectra were not probing exactly the same region of the oxide. However in view of the relatively small difference between the scapc depths, one can assume 3d signal is included along an oxide depth similar to the O 1s signal. The $\Delta E (O\ 1s - Mo\ 3d_{5/2})$ showed the relative O-Mo chemical shifts from the principles of XPS analysis,
which should be a measure of ionicity of the bond and the charge transfer. On the other hand, the chemical shift of Mo 3d$_{3/2}$ centroid should be roughly proportional to the overall composition O/Mo of the near surface region probed by XPS. One can also say that the $\Delta E$ (O 1s- Mo 3d$_{5/2}$) is insensitive to energy reference problems such as surface charging. From the Figure it is clearly seen that with increase of substrate temperature, the binding energy for the Mo 3d doublet also shifted towards higher binding energies. It is observed from the figure 3.18, for substrate temperature less than 473 K, the energy difference remains almost near which shows the existence of 5+ and 6+ states. For substrate temperature $\geq$ 473 K, $\Delta = 297.8$ eV which showed the existence only 6+ state. These results are related to the chemical shift of Mo toward higher binding energies during the oxidation process. No chemical shift of the Mo 3d taken place before conversion of chemisorbed oxygen into oxidation state.

The infrared spectroscopy also provides clear evidence on the bonding of electrons in the material. Figure 3.19 shows Fourier transform infrared spectra of MoO$_3$ films deposited at different substrate temperatures. The Fourier transmittance spectra of MoO$_3$ film deposited at 303 K does not exhibit any sharp absorption bands except a broad band between 600 and 1000 cm$^{-1}$ was the characteristic Mo-O bond vibrations attributed to the wide range of bond angles and bond lengths present in amorphous nature of the films [7] along with the broad band a small band at 558 cm$^{-1}$. This band was related to the transverse optical vibrations of Mo-O-Mo. When substrate temperature increased to 473 K, bands observed at 589, 640, 770, 835 and 1001 cm$^{-1}$ were observed. The band at 835 cm$^{-1}$ was attributed to terminal bond Mo $=$ O, the bands appeared at 640 and 1001 cm$^{-1}$ are attributed to the bridging Mo-O-Mo and Mo $=$ O bonds indicated the existence of Mo$^{6+}$ [32,33] which also confirmed from XPS studies. Further increase of substrate temperature of 523 K, the intense bands were observed at 580, 890 and 1000 cm$^{-1}$. The absorption band seem at 580 cm$^{-1}$ was assigned to the bending vibrations of Mo-O-Mo bonds [34], the broader band at around 890 cm$^{-1}$ was attributed to the binding vibrations of Mo$^{6+}$ and a very sharp band at 1000 cm$^{-1}$ was indicative of the Mo=O bond for Mo$^{6+}$. With further increase of substrate temperature to 623 K, the most intense bands were observed at
586 cm$^{-1}$, 838 cm$^{-1}$ and 1002 cm$^{-1}$. The band observed at 586 cm$^{-1}$ was the transverse optical vibrations of Mo-O-Mo in the polycrystalline phase. The band observed at 838 cm$^{-1}$ was related to Mo-O stretching mode and the band at 1002 cm$^{-1}$ due to the terminal Mo = O bond. Therefore the substrate temperature of 523 K was an optimum substrate temperature to produce layered structure α-phase MoO$_3$ films.

The XRD profiles of the MoO$_3$ films deposited at different substrate temperatures are shown in figure 3.20. The films deposited at the substrate
temperature of 303 K showed the absence of peaks indicated that the films were amorphous in nature. When the substrate temperature increased to 473 K, the diffraction patterns with diffraction peaks at $2\theta = 12.8$, 25.70 and 39.05° related to the (020), (040) and (060) planes of MoO$_3$ indicated the polycrystalline nature of the films. It is to mention here that the transformation of amorphous to polycrystalline nature can also be achieved by annealing of the room temperature deposited films [35]. The presence of these diffraction planes at this temperature was related to $\alpha$-phase MoO$_3$. As substrate temperature increased to 523 K, the intensity of the diffracted planes increased and the appearance of another peak (110) with low intensity. The crystalline nature of the films was observed to be enhanced, owing to the perfect growth of $\alpha$-MoO$_3$ films. At the substrate temperature of 473 and 523 K the (0k0) peaks predominate indicated a preferential growth and suggest layered structure of the films. The layered structure of these films was characterized by a lower density columnar structure [6]. As the substrate temperature further increased to 623 K, the pattern exhibits several peaks in different
directions indicating the polycrystalline nature of MoO$_3$ films. These are in good agreement between the interplanar distances of MoO$_3$ films deposited in the range 473 – 623 K and the JCPDS file (Card No: 35- 0609) corresponding to the layered structure $\alpha$- MoO$_3$ phase. It is evident that the increase in substrate temperature favoured the growth of layered $\alpha$- MoO$_3$. The crystallite size of the films increased with increase of substrate temperature up to 523 K, and then decreased with further increase of substrate temperature. The increase in crystallite size with increase of substrate temperature was attributed to the atomic, molecular or ionic species of MoO$_3$ impinged on the substrate surface acquire a large thermal energy and hence a large mobility. As a result, a large number of nuclei formed which coalescence at higher temperature to form a uniform film with good adhesion. At substrate temperature of 623 K, the decrease in crystallite size might be due to the re-evaporation of molybdenum formed on the film surface owing to its higher vapour pressures. Bouzidi et al. [36] reported that the orthorhombic symmetry of MoO$_3$ films were obtained in the temperature range of 523 to 573 K. Sivakumar et al. [37] observed that the films having orthorhombic MoO$_3$ ($\alpha$- phase) were obtained with preferred orientation at 473 K. Hence from XRD and XPS results, it revealed that stable orthorhombic phase of MoO$_3$ films with high crystallinity was obtained at a substrate temperature of 523 K. This indicated that the films formed at the oxygen partial pressure of 2x10$^{-4}$ mbar and the substrate temperature of 523 K was layered orthorhombic $\alpha$- phase MoO$_3$ films.

AFM images of MoO$_3$ films deposited at different substrate temperatures are shown in figure 3.21. The morphology of the films significantly varied with substrate temperatures. The AFM micrograph of MoO$_3$ films deposited at 303 K showed small islands which were homogenous and uniform. The size of initially formed nuclei would be small which attributed to the substoichiometric nature as revealed by XPS and XRD. As the substrate temperature increased from 473 – 623 K, the size of the nuclei also increased. When substrate temperature increased to 623 K, grains appear to be quasi spherical nuclei in random direction is due to the polycrystalline nature which confirms from XRD studies. Such a morphological nature of MoO$_3$ films has been reported by thermal evaporated and electron beam
Figure 3.21 AFM micrographs of MoO$_3$ films formed different substrate temperature:

303 K, (b) 473 K, (c) 523 K and (d) 623 K
evaporated films [38-40]. AFM also used to measure the root mean square roughness ($R_{\text{rms}}$) of the films [41]. Figure 3.22 shows the variation of surface roughness ($R_{\text{rms}}$) and peak-to-valley roughness ($R_{p,v}$) with substrate temperature. From the figure it is observed that both $R_{\text{rms}}$ and $R_{p,v}$ values increased with increase of substrate temperature; the values of the roughness were in the range 5.70 to 64.00 nm. Though the both $R_{\text{rms}}$ and $R_{p,v}$ values are seems to be different but each value can describe more specific morphology. These results mean that the $R_{p,v}$ value describes the size of the grains and the $R_{\text{rms}}$ follow basically the uneven surface caused by the difference of domains. From AFM it has been observed that the grain size of the films was larger and the portion of (110) oriented domains was higher at higher temperatures of 623 K. Mohamed et al. [21] showed the roughness of as deposited films increased with

![Figure 3.22 Variation of surface roughness values measured by AFM at different substrate temperatures](image)

Figure 3.22 Variation of surface roughness values measured by AFM at different substrate temperatures

the increase of annealing temperature, attributed to the grain growth and to the stress which build up in the film during heating and subsequent cooling.
The scanning electron micrograph images of the MoO$_3$ films formed at different substrate temperatures are shown in figure 3.23. It is observed from the figure that the films deposited at 303 K showed very smooth morphology without any fragmentation features or topographical contrast, which indicated the fine grain structure in amorphous background. As the substrate temperature increased to 473 K, the crystallinity of the films were observed was due to the coalescence of neighboring crystallites driven by the thermal energy acquired from the heating of the substrate. The grain size of the film was about 150 nm. Further increase of substrate temperature to 523 K, the films were grown with needle or elongated thin long bar structures which showed the size of about 0.8 μm. It is quite common that the MoO$_3$ phase grown in oval, plates, needle, elongated columns, rectangular or parallel piped depending on the deposition technique and the growth conditions. Hence the observed results were attributed the needle or elongated thin long bar structures of the grains mainly due to the high substrate temperature under which the deposited molecules have better mobility to promote the growth of layers with a larger grain size which corresponds to a layered structure of MoO$_3$ films. Formation of such needle like morphology was observed by few workers [42-44]. When substrate temperature increased to 623 K, shape of the grains appears to quasi spherical in random orientation. Differences in crystalline orientation could be associated with different deposition rates, which mainly depend on deposition temperature. The migration of adatoms on surface of films is low at low temperature whereas at high substrate temperature causes the adatoms to reevaporate from the film surface. Morphological studies revealed that the films grown at substrate temperature of 523 K exhibits layered structure of MoO$_3$ films.

The microhardness of the MoO$_3$ films formed at different substrate temperature is shown in figure 3.24. The microhardness of the films formed increased from 4.9 to 12.8 GPa with the increase of substrate temperature from 303 – 623 K respectively. The low value of microhardness of the films formed at 303 K was due to the amorphous nature and the presence of oxygen ion vacancies in the films. The microhardness of the films increased to 11.2 GPa when the films formed at substrate temperature of 523 K due to the polycrystalline nature where the
Figure 3.23 SEM micrographs of MoO₃ films deposited at different temperatures:
(a) 303 K, (b) 473 K, (c) 523 K and (d) 623 K
packing density of the films increased due to the filling of oxygen vacancies and the formation of stoichiometric films. Further increase of substrate temperature to 623 K, a slight increase in the microhardness to 11.6 GPa due to improvement in the crystallinity of the films. The stress developed in the films was calculated from the XRD peak for the films formed at different substrate temperature.

The dependence of stress on the substrate temperature of MoO₃ films is shown in figure 3.25. It is seen from the figure that the internal stress of the films formed at room temperature was -430 GPa which indicated that the stress is compressive. This compressive stress decreased to -160 GPa in the case of the film formed at substrate temperature of 373 K. Further increase of substrate temperature to 473 K the stress was transformed from compressive to tensile stress and reached to a value of 5 GPa. Further increase of substrate temperature to 623 K the tensile stress slightly increased to 36 GPa. The compressive stress developed at substrate temperature up to 373 K was attributed to the lattice distortions because of amorphous nature of the films and presence of different oxidation states of MoO₃ films. The films formed at
substrate temperature $\geq 473$ K were stoichiometric and polycrystalline hence tensile stress developed. At high substrate temperature the increase of tensile stress was due to the improvement in the crystallinity of the films. The change of stress from compressive to tensile by means that the film becomes denser. Substoichiometric MoO$_3$ is known to have many phases [45,46].

Figure 3.25 Variation of stress developed in the molybdenum oxide films with different substrate temperature

The electrical properties were highly influenced by the substrate temperature maintained during the deposition of the MoO$_3$ films. Figure 3.26 shows the variation of electrical conductivity with the increase of substrate temperature. The films formed at 303 K showed high electrical conductivity of $3\times 10^4$ $\Omega^{-1}$ cm$^{-1}$ were due to the presence of excess of oxygen ion vacancies. The XRD studies revealed that the films formed at 303 K were amorphous. In general amorphous films generally of low conductivity due to fine grain structure. In the present work though the films are amorphous and the electrical conductivity was high because of the presence of oxygen ion vacancies. As the substrate temperature increased to 473 K the electrical conductivity of the films decreased to $1.2\times 10^{-5}$ $\Omega^{-1}$ cm$^{-1}$ was due to the
polycrystalline nature as well as the filling of oxygen ion vacancies hence of low conductivity. Further increase of substrate temperature to 623 K.

![Graph](image)

**Fig. 3.26 Variation of electrical conductivity of MoO₃ films with the substrate temperatures**

The electrical conductivity of the films slightly increased to $3.2 \times 10^{-5} \, \Omega^{-1} \, \text{cm}^{-1}$ due to improvement in the crystallinity and the oxygen ion vacancies formed in the films during the deposition due to the partial dissociation of the constituent element. The electrical conductivity value of $2.0 \times 10^{-5} \, \Omega^{-1} \, \text{cm}^{-1}$ achieved at substrate temperature of 523 K was in agreement with the electron beam evaporated films [43]. In order to understand the electrical conductivity in the films, the temperature dependence of electrical conductivity was studied in the vacuum in the temperature range 303 – 523 K. Figure 3.27 shows the dependence of $\log \sigma$ with the reciprocal of temperature of the films formed at different substrate temperatures. From the figure it is clear that the electrical conductivity of the films increased with the increase of temperature. The variation of electrical conductivity with temperature showed the distinct straight lines. It is also seen that the transition temperature of the straight line region shifted towards lower temperature side. The activation energies calculated from the slope of
the plots of the films at higher temperature region was varied from 0.98 to 1.30 eV while at low temperature region the activation energies were in the range 0.02 to 0.10 eV. The activation energies of the films increased with the increase of substrate temperature. It is to mention that Krishna Kumar [47] achieved the activation energies of 1.35 and 0.46 eV at high and low temperature region in thermal evaporated films, while low activation energy of 0.68 and 0.78 eV at higher temperature region in electron beam evaporated [43] and activated reactive evaporated MoO₃ films [48]. Difference in the activation energy was due to the different techniques employed and process parameters maintained during the deposition of the films.

Figure 3.28 shows the optical transmittance spectra of MoO₃ films deposited at different temperatures in the range from 303 to 623 K. It is observed from the figure that the optical transmittance of the films deposited at 303 K was low. When substrate temperature increased to 473 K the optical transmittance of the film also
increased. The increase in transmittance with the increase of substrate temperature was attributed to the decrease in density of defect centers. Further increase of substrate temperature to 523 K, a decrease in optical transmittance was observed with a slight shift in absorption edge towards to higher wavelength side. With increase of substrate temperature the optical transmittance of MoO$_3$ films decreased which attributed to the scattering of light by the charge carriers. The optical transmittance spectra of MoO$_3$ films deposited at 303 K showed significant broad band absorption around 850 nm which was due to oxygen deficiency. The absorption edge shifted towards higher wavelength side with the increase of substrate temperature. The optical band gap of the films deposited at 303 K was 3.03 eV. When substrate temperature increased to 523 K, the optical band gap of the films increased to 3.2 eV. This increase in optical band gap was attributed to the partial filling of oxygen ion vacancies [36]. Further increase of substrate temperature to 623 K the optical band gap of the MoO$_3$ films decreased to a value of 3.14 eV. The decrease in the optical band gap was attributed to the oxygen ion vacancies able
to capturing one or two electrons, the oxygen vacancies occupied by electrons acts as donor centers. These centers form a narrow donor band at about 0.3 eV below the conduction band in the band gap [49]. The optical band gap obtained at the substrate temperature of 523 K were in good agreement with the reported crystalline MoO$_3$ films [50,51].

Figure 3.29 shows the variation of photon energy of MoO$_3$ films with respect to substrate temperatures. It was observed that with increasing the substrate temperature from 303 - 523 K, the optical band gap increased from 3.03 to 3.22 eV. It decreased to 3.15 eV with further increase of substrate temperature to 623 K. The direct band gap values of the MoO$_3$ films prepared by electron beam evaporation decreased from 3.24 to 2.98 eV in the substrate temperature range 673 - 523 K [15] and between 2.80 to 2.35 eV in the range 303 - 473 K [37]. Bouzidi et al. [36] observed that when substrate temperature of 473 K the band gap was 3.3 eV, and slightly increased up to 3.34 eV for substrate temperature of about 523 K. Above this substrate temperature,
the band gap decreases to 3.14 eV of about 623 K. The refractive index of the MoO$_3$ films was determined from the optical transmittance interference data employing Swanepoel's envelope method. Figure 3.30 shows the Wavelength dependence of refractive index of MoO$_3$ films deposited at different substrate temperatures. The refractive index of the films increased from 2.03 to 2.12 with the increase of substrate temperature from 303 to 623 K.

The variation of refractive index with the substrate temperature at particular wavelength of 500 nm is shown in fig.3.31. The low refractive index of 2.03 of the films deposited at 303 K was due to the low packing density because of the amorphous nature. As the substrate temperature increased to 623 K the refractive index of the films increase due to improvement in the packing density with improved stoichiometric behaviour. Mohamed et al. [21] observed that the refractive index of the MoO$_3$ films decreased with the increase annealing temperature.
The substrate temperature dependence studies on the physical properties of MoO$_3$ films revealed that the films formed at 523 K were of polycrystalline α-phase MoO$_3$ with electrical conductivity of $2.0\times10^{-5} \ \Omega^{-1}\text{cm}^{-1}$, optical band gap of 3.22 eV and refractive index of 2.09.

![Graph showing variation of refractive index with substrate temperature](image)

Figure 3.31 Variation of refractive index of MoO$_3$ films for different substrate temperatures at $\lambda = 500$ nm

### 3.2.3 Influence of sputtering power on the physical properties of MoO$_3$ films

In order to study the influence of sputtering power on the physical properties of MoO$_3$ films, the films were deposited under different sputtering powers in the range 2.3 - 6.8 W/cm$^2$ and at fixed oxygen partial pressure of $2\times10^{-4}$ mbar, substrate temperature of 523 K and sputtering pressure of $4\times10^{-2}$ mbar.

The X-ray photoelectron spectroscopic measurements indicated that the sputtering power also strongly influenced the stoichiometry and phase of the deposited MoO$_3$ films. The core level binding energies of the MoO$_3$ films formed at different sputtering powers are shown in figure 3.32. The films deposited at low sputtering power of 2.3 W/cm$^2$ showed the core level binding energies of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ at 232.35 and 235.49 eV respectively. The asymmetric nature of the
core level peaks of Mo 3d deposited at 2.3 W/cm² indicated the presence of mixed oxidation states due to the low sputtering yield. The deconvolution of the Mo 3d core levels yielded four Gaussian peaks due to the presence of oxidation states of Mo⁶⁺ and Mo⁵⁺. As the sputtering power increased to 5.7 W/cm² the films showed symmetric core level binding energy peaks of Mo 3d₅/₂ and Mo 3d₃/₂ at 232.77 and 235.90 eV with the spin orbit splitting of 3.13 eV.

![Figure 3.32 XPS core level binding energy spectra of Mo doublet of MoO₃ films formed at different sputtering powers](image)

The doublet of Mo 3d levels contained the area under the peaks with the ratio of 3:2 revealed the existence of molybdenum in the films in the highest oxidation state of Mo⁶⁺ that is the MoO₃. This is in agreement with the results achieved in electron beam evaporated [37] and magnetic null discharge sputtered MoO₃ films [52]. Further increase of sputtering power to 6.8 W/cm², the core level binding energies of Mo 3d shifted towards lower energy side of 232.28 and 235.43 eV. The nature of the asymmetric peaks indicated the presence of addition phases of molybdenum. The core level binding energy of O 1s increased from 530.45 to 530.54 eV with the increase of sputtering power from 2.3 to 5.7 W/cm², thereafter decreased to
530.12 eV at higher sputtering power of 6.8 W/cm². At sputtering powers less than 5.7 W/cm² less number of molybdenum atoms were sputtered from the target which effectively react with the available oxygen in the plasma resulted in the deposition of the films with high oxygen content. As the sputtering power increased to 5.7 W/cm² there was a balance between the sputtered molybdenum species and the oxygen atoms, hence the films were nearly stoichiometric. At sputtering power higher than 5.7 W/cm² the sputter rate of molybdenum was high which accelerate the effective reaction with the available oxygen and form MoO₃ along with the additional unreacted molybdenum. Similar increase of metallic content with the sputtering power was also observed in the indium tin oxide films formed by rf magnetron sputtering [53].

Fourier transform infrared spectra (FTIR) of the MoO₃ films deposited at different sputtering powers are shown in figure 3.33. The FTIR spectra of the films deposited at low sputtering power of 2.3 W/cm² showed the absorption bands at 553, 850 and 1001 cm⁻¹ with minimum intensity. The band situated at 553 cm⁻¹ related to the transverse optical vibrational mode of MoO₃ and the absorption band located at 850 cm⁻¹ connected to the terminal Mo=O bond of Mo⁵⁺. The band seen at 1001 cm⁻¹ correspond to the stretching vibration of γ(Mo-O) the oxidation state of Mo⁶⁺ which is a characteristic feature for the existence of α-MoO₃ phase. Further increase of sputtering power to 5.7 W/cm² the intense bands were observed at 580, 890 and 1000 cm⁻¹. The absorption band seen at 580 cm⁻¹ was assigned to the bending vibrations of Mo-O-Mo bonds. As the sputtering power further increased to 6.8 W/cm² a broad band with less intense peaks were observed due to deficiency of oxygen in the films.

X-ray diffraction profiles of the MoO₃ films deposited at different sputtering powers are shown in figure 3.34. The XRD spectra indicated that the crystallographic orientation of the MoO₃ films is significantly influenced by the sputtering power. The films deposited at low sputtering power of 2.3 W/cm² showed the (020), (011), (200), (040) and (060) reflections. The presence of (011) and (200) reflections was related to the β-phase of MoO₃. The occurrence of (020), (040) and
Figure 3.33 FTIR spectra of MoO$_3$ films formed at different sputtering powers
(060) reflections revealed the existence of α– phase MoO$_3$. The films formed at low sputtering power were mixed phase of α- and β- MoO$_3$. When sputtering power increased to 5.7 W/cm$^2$, the films showed only the (020), (040) and (060) reflections indicated the orthorhombic α- phase of MoO$_3$ with layered structure. Further increase of sputtering power to 6.8 W/cm$^2$, the film showed the mixed phase of α- and β- MoO$_3$ along with the presence of unreacted elemental molybdenum (111) reflections. The XRD studies revealed that the films formed at sputtering power of 5.7 W/cm$^2$ were of α- phase MoO$_3$. The crystallite size of the films increased from 44 to 57 nm with the increase of sputtering power from 2.3 to 6.8 W/cm$^2$ respectively. As the sputtering power increased the energy of sputtered particles increased. High energy condensed particles acquired high mobility on the substrate surface hence formed the larger size crystallites.

![X-ray diffraction profiles of MoO$_3$ films deposited at different sputtering powers](image)

**Figure 3.34** X-ray diffraction profiles of MoO$_3$ films deposited at different sputtering powers

Figure 3.35 shows the AFM morphology of the MoO$_3$ films deposited at different sputtering powers. It is clear from the morphologic images of the films deposited at low sputtering power of 2.3 W/cm$^2$ showed smooth structure. As the
Figure 3.35 AFM morphology of MoO$_3$ films formed at different sputtering powers:
(a) 2.3 W/cm$^2$ (b) 5.7 W/cm$^2$ and (c) 6.8 W/cm$^2$
sputtering power increased to 6.8 W/cm², the grain size of the films increased due to increase in the adatom mobility. The root mean square roughness (R_{rms}) of the MoO₃ films was determined from the AFM micrographs. It was observed that R_{rms} of the films increased from 20.3 – 64.0 nm with the increase of sputtering power from 2.3 to 5.7 W/cm². Further increase of sputtering power to 6.8 W/cm² roughnesses of the films decreased to 22 nm.

Figure 3.36 shows the scanning electron micrographs of the MoO₃ films deposited at different sputtering powers. The micrographs showed that the MoO₃ films deposited at low sputtering power contained a smoother and less dense in structure. As the sputtering power increased to 5.7 W/cm², the grain size of the films increased and the shape of the grains to be long bar needle like structures arranged one over the other attributed to the growth of layered α– phase MoO₃. Such needle like crystallites was also obtained in hot wall metal organic chemical vapour deposited [54] and dc reactive magnetron sputtered MoO₃ [42] films. The surface diffusion of the adatoms was enhanced with the momentum transfer to the growing surface resulted an increase in the grain size. The enhancement in crystallinity of the films was achieved at higher sputtering power of 5.7 W/cm² due to larger impact energy of the bombarding particles, which lead to better surface mobility. Further increase of sputtering power to 6.8 W/cm², big needle structures were appeared with distorted structure might be due to increase in shadowing effect where adatoms find thermodynamically favourable sites will decrease. The increase in the grain size was a result of bombardment to the growth surface by more energetic particles with increasing sputtering power [55].

The electrical conductivity of the films formed at different sputtering powers is shown in figure 3.37. The electrical conductivity of the MoO₃ films increased from \(8 \times 10^{-6}\) to \(1.2 \times 10^{-4} \ \Omega^{-1} \ \text{cm}^{-1}\) with the increase of sputtering power from 2.3 to 6.8 W/cm². The low electrical conductivity of \(8 \times 10^{-6} \ \Omega^{-1} \ \text{cm}^{-1}\) at low sputtering power of 2.3 W/cm² was due to low crystallinity of the films with low carrier concentration. The electrical conductivity of the films further increased with the increase of sputtering power due to the better crystallinity achieved by larger impact energy of the bombarding particles. When sputtering power increased to 6.8 W/cm²,
the electrical conductivity of the films increased sharply to $1.2 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$. It is obvious that higher electrical conductivity of the films formed at high sputtering power of 6.8 W/cm$^2$ due to the presence of metallic molybdenum along with the MoO$_3$ films as revealed by X-ray diffraction studies. The electrical conductivity achieved at the sputtering power of 5.7 W/cm$^2$ [56].

The optical transmittance spectra of the films formed at different sputtering powers are shown in the figure 3.38. It is seen from the figure that the transmittance of the films deposited at low sputtering power of 2.3 W/cm$^2$ was of about 75%. The high transmittance at low sputtering power was due to monoclinic structure revealed from XRD studies. As sputtering power increased to 6.8 W/cm$^2$, the optical transmittance of the films was decreased. The reduction in the transmittance was due to scattering of light by metallic molybdenum present along with MoO$_3$ sharp fall in the optical transmittance at shorter wavelength side resulted from the excitation of charge carriers across the optical band gap. Figure 3.39 shows the plots of $(\alpha hv)^2$.

![Graph showing variation of electrical conductivity with sputtering power](image_url)

**Figure 3.37 Variation of electrical conductivity of MoO$_3$ films with the sputtering power**
Figure 3.36 SEM morphology of MoO$_3$ films formed at different sputtering powers:
(a) 2.3 W/cm$^2$, (b) 5.7 W/cm$^2$ and (c) 6.8 W/cm$^2$
versus photon energy of the films formed at different sputtering powers. The optical band gap of the films decreased from 3.28 to 3.12 eV with the increase of sputtering power from 2.3 to 6.8 W/cm². Such a decrease in the band gap with the increase of sputtering power was achieved in dc magnetron sputtered copper oxide / copper aluminum oxide films [57]. The decrease in the optical band gap with the increase of sputtering power might be due to the creation of oxygen ion vacancies, which acts as positively charged structural defects able to capture one or two electrons. The oxygen vacancies occupied by electrons acts as donor centers which lie close to valence band, which was responsible for broad band absorption. A broad absorption band was observed in the visible region of the spectrum. The low value of optical band gap of 3.12 eV at the high sputtering power of 6.8 W/cm² was due to the presence of MoO₃ along with the elemental molybdenum. The band gap achieved at the sputtering power of 5.7 W/cm² was in good agreement with the films formed by and spray pyrolysis deposited [36] films.

![Fig. 3.38 Optical transmittance spectra of MoO₃ films](image)

**Fig. 3.38 Optical transmittance spectra of MoO₃ films**
The wavelength dependence of refractive index of the films formed at different sputtering powers is shown in figure 3.40. At a fixed sputtering power the refractive index of the films decreased with the increase of wavelength of incident radiation. The refractive index of the films at the wavelength of 500 nm decreased from 2.12 to 1.94 with the increase of sputtering power from 2.3 to 6.8 W/cm\(^2\) respectively. The low value of refractive index in the films formed at high sputtering power of 6.8 W/cm\(^2\) was due to the presence of unoxidised molybdenum or MoO\(_3\). The achieved refractive index of 2.04 at the sputtering power of 5.7 W/cm\(^2\) was in agreement with the reported values of dc magnetron sputtered [4].

![Figure 3.39 Plots of \((ahv)^2\) versus photon energy of MoO\(_3\) films](image-url)

These studies revealed that the sputtering power of 5.7 W/cm\(^2\) is an optimum to generate the single phase films of MoO\(_3\).
3.2.4 Influence of substrate bias voltage on the physical properties of MoO$_3$ films

The prime advantage of bias the substrate leads to generation of the films on unheated substrates which enable to use the temperature sensitive substrates for certain device applications. Hence in order to study the influence of substrate bias voltage on the physical properties of the MoO$_3$ films, the films were formed at room temperature under the optimized oxygen partial pressure of $2 \times 10^{-4}$ mbar and sputtering power of 5.7 W/cm$^2$ under various substrate bias voltages in the range from 0 to -150 V. Figure 3.41 shows the dependence of deposition rate of MoO$_3$ films on the substrate bias voltage. The deposition rate of the MoO$_3$ films formed on unbiased substrate was 21.3 nm/min. Deposition rate of the films increased to 23.4 nm/min with the increase of substrate bias voltage to -120 V. The increase in the deposition rate with the increase of substrate bias voltage was attributed to the negative bias attract the positively charged molecules and clusters of the sputtered species in the plasma hence increased in the thickness of the deposited film. Further
increase of substrate bias voltage to -150 V, the deposition rate start to decrease and reached the value of 22.8 nm/min. The decrease in the deposition rate at higher substrate bias voltage was due to the bombardment of positively charged particles caused the number of molecules to resputter from the film surface. Such a dependence of deposition rate on the substrate bias voltage was also noticed by Yang et al. [58] in rf sputtered indium tin oxide films. The core level binding energies and oxidation states in the deposited MoO₃ films was analyzed from the X-ray photoelectron spectroscopic studies. Figure 3.42 shows the XPS core level binding energy spectra of Mo 3d states in MoO₃ films formed at different substrate bias voltages. The films formed under unbiased substrate contained the core level binding energies of Mo 3d₅/₂ and Mo 3d₃/₂ at 232.44 and 235.58 eV respectively with spin orbit splitting of 3.14 eV. This core level spectrum showed the asymmetric shoulders due the presence of mixed oxidation states of Mo⁵⁺ and Mo⁶⁺ of molybdenum oxide.

![Figure3.41 Dependence of deposition rate of MoO₃ films on the substrate bias voltage](image)

Figure 3.41 Dependence of deposition rate of MoO₃ films on the substrate bias voltage
It indicated that the films formed under unbiased condition were substoichiometric [25] with the presence of mixed phase of MoO3 and MoO3-x. The films formed at substrate bias voltage of -90 V, the spectrum also exhibited the asymmetric peaks of Mo 3d5/2 and Mo 3d3/2 at binding energy of 232.65 and 235.83 eV respectively. Further, increase of substrate bias voltage to -120 V, the symmetric peaks of Mo 3d5/2 and Mo 3d3/2 were observed with the core level binding energies of 232.75 and 235.94 eV respectively, with the spin orbit spitting of 3.19 eV, which is the characteristic of Mo6+ oxidation state of MoO3 as observed in electron beam evaporated films [59]. At higher substrate bias voltage of -150 V the core level binding energy peaks showed again the mixed phase of MoO3 and MoO3-x. The core level of O 1s also shifted towards lower core level binding energy side from 530.29 to 530.05 eV with the increase of substrate bias voltage from 0 to -120 V respectively thereafter increased to 530.18 eV at higher substrate bias voltage of -150 V. It revealed that the films formed at substrate bias voltage at -120 V were single phase with the existence of Mo6+ oxidation state of MoO3.

Figure 3.43 shows the Fourier transform infrared spectra of the MoO3 films formed at different substrate bias voltages. The FTIR transmission spectrum showed absorption broad band between 600 and 1000cm⁻¹ was the characteristic of Mo-O band vibrations attributed to the existence of wide range of band angles and band lengths of the amorphous nature of the films and a small band observed at 556 cm⁻¹ was assigned to the transverse optical vibration mode of Mo-O-Mo [60]. The films formed at substrate bias voltage of -90 V showed the absorption bands at 585, 690, 832 and 998 cm⁻¹. The bands situated at 585 and 690 cm⁻¹ were related to the transverse optical vibration mode of Mo-O-Mo, the bridging of Mo-O-Mo in Mo5+ oxidation state [61]and at 832 cm⁻¹ was attributed to the terminal Mo=O. The band seen at 998 cm⁻¹ was the terminal of Mo=O indicated the existence of Mo6+ oxidation states [62]. It revealed that the films formed at substrate bias voltage of -90 V were of polycrystalline with the coexistence of Mo6+ and Mo5+ oxidation states in the form of MoO3 and MoO3-x.
Figure 3.42 XPS core level binding energy spectra of Mo 3d of MoO₃ films formed at different substrate bias voltages.

With increase of substrate bias voltage to -120 V intense bands observed at 583, 840 and 1001 cm⁻¹ indicated that the films were of layered structure with orthorhombic α- phase of MoO₃ in the Mo⁶⁺ oxidation state. Further increase of substrate bias voltage to -150 V there was a decrease in the intensity of the bands.

Figure 3.44 shows the X-ray diffraction profiles of the films formed at different substrate bias voltages. The films formed under unbiased condition showed a broad band without the presence of any diffraction reflections indicated the films were in amorphous nature. The films prepared at the substrate bias voltage of -90 V showed the reduction in the intensity of the broad band with the presence of different peaks at 2θ = 12.62, 23.02, 25.5 and 38.9° related to the (020), (011), (040) and (060) reflections of MoO₃ indicated the films were in polycrystalline nature. The exhibited (0k0) reflections correspond to α- phase MoO₃, while the (011) reflection with low intensity related to the β- phase of MoO₃. Hence the amorphous films could be crystallized into the mixed phase of α- and β- phase of MoO₃ when the
Figure 3.42 Fourier transform spectra of MoO$_3$ films
bias voltage increased to -90 V. At substrate bias voltage of -120 V, the presence of only (0k0) reflections clearly showed that the films formed were orthorhombic with layered structure of α-phase MoO₃. The substrate bias voltage further increased to -150 V, the diffraction pattern exhibited the (110), (200) and (022) along with (0k0) reflections indicated the coexistence of α- and β-phase of MoO₃. The lattice parameter of the films formed at the substrate bias voltage of -120 V was \( a = 0.398 \) nm, \( b = 13.860 \) nm and \( c = 0.369 \) nm. In the present study polycrystalline films were obtained at substrate bias voltages \( \geq -90 \) V. The enhancement of crystallinity with the bias voltage may be attributed to the accelerated interaction of positive ions in the plasma with the growing surface. The substrate bias induced the positive ions with high energy which enhanced the diffusion of deposited particles and/or the relaxation of the growing surface was probably increased by the collision of the accelerated positive ions in the sheath of the plasma [63]. Therefore, application of negative bias voltage increased the energy of positively charged particles bombarding the substrate and initiated the process of sputtering from the surface of growing films. It can be understood that the ion bombardment on the substrates has a
similar effect of substrate heating. To the best of our knowledge there were no reports on the substrate bias voltage influenced properties of MoO$_3$ films formed by magnetron sputtering. The amorphous to crystalline transformation with the substrate bias voltage was also observed in the indium tin oxide films formed at the bias voltage of -50 V [64], cadmium oxide films formed at -30 V [65] in dc reactive magnetron sputtered where as the tantalum oxide [66] films at -100 V by dc magnetron sputtered MoO$_3$ films.

AFM images of MoO$_3$ films deposited at different substrates bias voltages are shown in figure 3.45. The surface morphology of the films significantly varied with the substrate bias voltage. The AFM micrograph of MoO$_3$ films formed under unbiased condition showed spherical particles of small grains of various sizes because of the amorphous nature of the films. When the substrate bias voltage increased to -120 V the size of the grain increased due to the polycrystalline nature and improved in the crystallinity of the films. These films showed a pyramid like morphology which may exist by the accumulation of needle like crystallites [39] indicative of the layered nature of MoO$_3$. At higher substrate bias voltage of -150 V the grain size again decreased to a lower value. Many of the researchers reported the relation ship between the grain size and the energy of ions during sputtering. Yang et al. [58] reported that the grain size was larger in moderate range of negative bias voltage. At low bias voltages the adatoms mobility was low on the surface of the substrates. The low adatom mobility leads to smaller islands at the initial stage and therefore smaller size grains. At moderate substrate bias voltages i.e -90 V to -120 V where adatom obtained more energy by ion bombardment which increased the adatom mobility and form large sized grains. At higher substrate bias voltages (≥ -150 V) the ion bombardment on the film with high energy and consequently the high energy ions damage the films hence the decrease in the size of the grains [67].

The electrical conductivity of the films was influenced by the substrate bias voltage applied during the deposition. The dependence of electrical conductivity of the films on the substrate bias voltage is shown in figure 3.46. The films formed on unbiased substrates showed higher electrical conductivity of $3.6 \times 10^{-4} \, \Omega^{-1} \, \text{cm}^{-1}$
Figure 3.46 Electrical conductivity of MoO$_3$ films formed at different substrate bias voltages

due to the presence of oxygen ion vacancies. The electrical conductivity of the films decreased to $4.5 \times 10^{-5}$ $\Omega^{-1}$cm$^{-1}$ with the increase of substrate bias voltage to -120 V. The decrease of electrical conductivity with the increase of substrate bias voltage was due to the partial filling of oxygen ion vacancies. The films formed at higher substrate bias voltage of -150 V showed a slight increase in the electrical conductivity to $6.5 \times 10^{-5}$ $\Omega^{-1}$cm$^{-1}$ was due to improvement in the crystallinity and generation of oxygen ion vacancies by the partial dissociation of the constituent elements [30].

Figure 3.47 shows the optical transmittance spectra of the films formed under various substrate bias voltages. It is seen from the figure that the optical transmittance of the films formed on unbiased substrate was low. The optical transmittance of the films increased with the increase of substrate bias voltage. The low optical transmittance at low
Fig. 3.45 AFM micrographs of MoO$_3$ films formed at different substrate bias voltages: (a) 0 V (b) -120 V and (c) -150 V
substrate bias voltage was due to the oxygen ion vacancies. As the substrate bias voltage increased to -120 V the density of scattering centers of molybdenum decreased thereby increase in the optical transmittance. Further increase of substrate bias voltage to -150 V a slight decrease in the transmittance was due to the oxygen ion vacancies. The increase of substrate bias voltage up to -120 V leads to the shift in the optical absorption edge towards lower wavelength region thereafter it slightly shifted towards higher wavelength side. The optical band gap of the films formed on unbiased substrates was 3.03 eV. The optical band gap of the films increased to 3.22 eV with the increase of substrate bias voltage to -120 V. The increase of optical band gap with the increase of substrate bias voltage was due to the decrease of oxygen vacancies in the films. Further increase of substrate bias voltage to -150 V the optical band gap decreased to 3.18 eV due to the creation of oxygen ion vacancies in the films. Julien et al. [68] reported the optical band gap of 3.37 eV in the films formed at room temperature by vacuum evaporation where those deposited at high substrate temperature of 573 K the band gap decreased to 2.80 eV due to the formation oxygen ion vacancies. Figure 3.48 shows the wavelength dependence of
refractive index of the films formed at different substrate bias voltages. The refractive index of the films was high at higher photon energies. It decreased with the increase of the photon energy in all the films. The refractive index of the films increased from 2.03 to 2.13 with the increase of substrate bias voltage from 0 to -120 V due to improvement in the crystallinity and packing density of the films. Further increase of substrate bias voltage to -150 V the refractive index decreased to 2.09 due to the formation of oxygen ion vacancies.

![Refractive index of MoO₃ films](image)

*Figure 3.48 Refractive index of MoO₃ films formed at different substrate bias voltages*
REFERENCES


Results and Discussions


Chapter - III

Results and Discussions


