CHAPTER 5

PREPARATION AND CHARACTERIZATION OF MoO₃ THIN FILMS

Molybdenum trioxide thin films were fabricated on glass substrates. The concentration of the precursor solution was varied in the range 0.01, 0.03, 0.05 and 0.07 M to optimize for homogeneous quality film. The structural, Optical, Morphological and Compositional characterizations of the prepared MoO₃ thin films were done. The gas sensing property of the fabricated MoO₃ thin film gas sensor were tested for acetone, ethanol, Toluene and NH₃ vapour at room temperature. The sensitivity, selectivity, response time and recovery time of MoO₃ thin film sensor to the above said gases were obtained.

5.1. Materials Used

Analytical reagent grade molybdenum oxide powder (99.9% pure, Merck, Germany), 99.9% pure liquid ammonia solution (Merck, Germany) and de-ionized water were used for the preparation of molybdenum trioxide thin films.

5.2. Preparation of Precursor Solution

The required amount of molybdenum oxide powder was dissolved in equal mixture of liquid ammonia solution and de-ionized water for the preparation of 0.01, 0.03, 0.05 and 0.07 M molybdenum trioxide precursor solutions. The mixture was continuously stirred at room temperature to get a homogeneous mixture using magnetic stirrer. Finally, 0.01, 0.03, 0.05 and 0.07 M ammonium metamolybdate solutions were prepared and then the solutions were filtered. The filtered ammonium metamolybdate solutions of 0.01, 0.03, 0.05 and 0.07 M were used for the preparation of molybdenum trioxide thin films of 0.01, 0.03, 0.05 and 0.07 M concentrations respectively.
5.3. Preparation of Molybdenum Trioxide (MoO$_3$) Thin Films

The cleaned glass substrates were preheated to 250°C. The spray rate was maintained as 2.5 ml/min. The distance between spray nozzle and the substrate was fixed as 28 cm. The precursor solution of different molarities of molybdenum trioxide (0.01, 0.03, 0.05 and 0.07 M) was sprayed through a specially designed stainless steel nozzle of 0.01mm bore diameter over the preheated glass substrates. Compressed air was used as carrier gas. The substrate temperature and the air pressure were controlled by the microprocessor controlled spray pyrolysis setup. In each trial, the quantity of the spraying solution was taken as 10 ml. The solution was sprayed with the help of microprocessor controlled peristaltic pump. All the spray parameters were kept constant as shown in table 5.1.

Table 5.1. Spray parameters of molybdenum trioxide thin films prepared on glass substrates.

<table>
<thead>
<tr>
<th>Spray parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of solution</td>
<td>0.01, 0.03, 0.05 &amp; 0.07 M</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Distance between spray nozzle and substrate</td>
<td>28 cm</td>
</tr>
<tr>
<td>Spray rate</td>
<td>2.5 ml/min</td>
</tr>
<tr>
<td>Solution Quantity</td>
<td>10 ml</td>
</tr>
<tr>
<td>Air pressure</td>
<td>6 kg/cm$^2$</td>
</tr>
<tr>
<td>Annealing temperature</td>
<td>300 °C</td>
</tr>
<tr>
<td>Duration of annealing</td>
<td>1 hr</td>
</tr>
</tbody>
</table>
After deposition, all the prepared films were allowed to cool down slowly to room temperature. The coated MoO$_3$ thin films were found to be uniform, pin hole free and well adherent to the glass substrates. The colour of the as deposited film was bluish grey and changed to dark grey when annealed at 300˚C in air (Bouzidi et al., 2003).

5.4. X-ray Diffraction Studies on Molybdenum Trioxide Thin Films

The crystalline structure of the prepared molybdenum trioxide thin films were studied using X-ray diffraction data. X-ray diffraction (XRD) patterns of molybdenum trioxide thin films prepared at different concentrations 0.01, 0.03, 0.05 and 0.07 M before and after annealing are shown in figure 5.1 and 5.2 respectively.

From the XRD pattern, it was observed that all the as-deposited films were amorphous. The annealed MoO$_3$ thin films of 0.01, 0.03, 0.05 and 0.07 M annealed at 300˚C predicted the polycrystalline nature. The obtained peaks were indexed with respect to JCPDS 05-0508 and revealed orthorhombic MoO$_3$ phase. The peaks at (0 k 0) with k=2, 4 and 6 exhibited the existence of the layered structure with orthorhombic phase in annealed MoO$_3$ thin films of 0.01, 0.03, 0.05 and 0.07 M concentrations. The films coated at 0.03M and 0.05 M were well formed and have orientations in (0 4 0) plane. However, the films coated with 0.05 M are more crystalline.

As the concentration of the precursor solution increased, a slight shift in 2θ value was observed for the preferential peaks. However, crystallite orientation is not altered. This revealed that the growth of crystallite orientation is independent of the concentration of the precursor solution.
Figure 5.1. XRD Pattern of as-deposited molybdenum trioxide thin films
Figure 5.2. XRD Pattern of annealed molybdenum trioxide thin films
The crystallite size of molybdenum trioxide thin films before and after annealing were calculated from peak broadening using Debye-Scherrer’s formula which is defined as,

\[ d = \frac{(0.9 \lambda)}{\beta \cos \theta} \quad \text{(5.1)} \]

where, \( \lambda \) = wavelength of X-rays = 1.5404 x 10\(^{-10} \) m, \( \beta \) = FWHM of diffraction peak and \( \theta \) = Diffraction angle corresponding to the peak.

The average crystallite size of before and after annealed at 300°C MoO\(_3\) thin films were estimated individually from the FWHM of each peak and the average of all peaks were taken to obtain the average crystallite size. The calculated crystallite size of prepared molybdenum trioxide thin film is tabulated in table 5.2.

The lattice parameters of the prepared orthorhombic MoO\(_3\) thin films were calculated and compared with the standard values of lattice parameters \( a= 4.0129 \) Å, \( b=13.8954 \) Å and \( c=3.7196 \) Å of the orthorhombic MoO\(_3\) thin film with JCPDS 05-0508 and were found to be in good agreement with the literature (Bouzidi et al., 2003a). The calculated lattice parameters are tabulated.

The micro strain (\( \varepsilon \)) is calculated using the relation

\[ \varepsilon = \frac{(\beta \cos \theta)/4}{\delta} \quad \text{(5.2)} \]

The value of dislocation density (\( \delta \)) is calculated using the relation

\[ \delta = \frac{1}{D^2} \quad \text{(5.3)} \]

The effect of concentration on the micro structural parameters of MoO\(_3\) thin films were summarized in table 5.2.
Table 5.2. Micro structural properties of the annealed MoO$_3$ thin films obtained at different concentrations

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Crystallite Size (nm)</th>
<th>Strain $\varepsilon \times 10^{-4}$</th>
<th>Dislocation Density $\delta \times 10^{14}$ (lines / m$^2$)</th>
<th>Lattice constants (Å$^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Experimental values</td>
<td>Standard values</td>
</tr>
<tr>
<td>0.01</td>
<td>19.366</td>
<td>18.85372</td>
<td>17.4005</td>
<td>a= 4.0454 b=13.8954 c=3.6991</td>
</tr>
<tr>
<td>0.03</td>
<td>24.80333</td>
<td>14.03538</td>
<td>15.1146</td>
<td>a=3.9643 b=13.9118 c=3.7113 a= 4.0129 b=13.8554 c=3.6976</td>
</tr>
<tr>
<td>0.05</td>
<td>49.478</td>
<td>7.33812</td>
<td>13.2476</td>
<td>a=3.9439 b=13.8589 c=3.6908</td>
</tr>
<tr>
<td>0.07</td>
<td>56.426</td>
<td>6.9923</td>
<td>7.7523</td>
<td>a=3.9749 b=13.8733 c=3.6909</td>
</tr>
</tbody>
</table>

From the table, it is obvious that the annealed molybdenum trioxide thin films are polycrystalline as compared with the as deposited amorphous molybdenum trioxide thin films and the crystallinity increases with concentration till 0.05 M thin films. The crystallite size of MoO$_3$ thin films of different concentrations were increased by increasing the concentration. It is observed that the micro strain and dislocation density decreased as there was an increase in the crystallite size. However, the films prepared at 0.07 M precursors showed less crystalline formation resulting 0.05M as optimum concentration in this method at other optimum parameters.
5.5. Surface Morphology by Scanning Electron Microscope

The horizontal cross sectional study of thin films provides the information about surface morphology of thin film. The surface morphological study of molybdenum trioxide thin film was carried out by Scanning Electron Microscope (SEM). Figures 5.3 and 5.4 showed the surface morphology of molybdenum trioxide thin film prepared with 0.03 and 0.05 M concentrations.

SEM micrographs exhibited that the surface morphology of as deposited films coated with 0.03 M and 0.05 M appear to be uniform with moderately smooth and covered by small grains.

![SEM image of as-deposited molybdenum trioxide thin film of 0.03 M](image)

**Figure 5.3a.** SEM image of as-deposited molybdenum trioxide thin film of 0.03 M
Figure 5.3b. SEM image of as-deposited molybdenum trioxide thin film of 0.05 M

Figure 5.4a. SEM image of annealed molybdenum trioxide thin film of 0.03 M
Figure 5.4b. SEM image of annealed molybdenum trioxide thin film of 0.05 M

After annealing at 300 °C, MoO₃ thin films prepared at 0.03 M observed to be smooth and uniform in surface with random cracks. The morphology of MoO₃ thin films prepared at 0.05 M exhibited elongated rod-like crystallites of dimensions 882.04 nm x 286.36 nm x 233.24 nm and the crystallites are randomly oriented. The randomly oriented rod-like crystallites on the surface of MoO₃ thin films were reported in Mo oxides thin films prepared by many researchers (Patil et al., 2008).

Also, the porosity of the annealed MoO₃ thin film prepared at 0.05 M was increased. Porous morphology predicted by the annealed MoO₃ thin films revealed that they can be a good sensor device.
5.6. Energy Dispersive X-ray Analysis (EDAX) of Molybdenum Trioxide Thin Films

The compositional analysis was performed using Energy Dispersive X-ray Analysis. The EDAX spectrum of as-deposited and annealed molybdenum trioxide thin films prepared at 0.05 M are shown in figure 5.5 and 5.6 respectively. The spectrum reveals that the presence of molybdenum (Mo) and oxygen (O) by their respective characteristic peaks at 2.293 KeV and 0.525 KeV. The composition of elements presented in as-deposited and annealed MoO$_3$ thin films are given in table 5.3 and 5.4 respectively. The spectrum provided a clear evidence of the presence of the expected elements (Mo and O) in the as-deposited and annealed molybdenum trioxide thin films. Also the presence of the other elements are due to glass substrate.

![Figure 5.5. EDAX spectrum of as-deposited molybdenum tri-oxide thin film of 0.05 M](image)
Figure 5.6. EDAX spectrum of annealed molybdenum tri-oxide thin film of 0.05 M

Table 5.3. Composition of elements presented in as-deposited molybdenum tri-oxide thin films of 0.05 M

<table>
<thead>
<tr>
<th>Element</th>
<th>(keV)</th>
<th>Mass%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O  K</td>
<td>0.525</td>
<td>6.32</td>
<td>18.41</td>
</tr>
<tr>
<td>Na K</td>
<td>1.041</td>
<td>2.16</td>
<td>4.39</td>
</tr>
<tr>
<td>Mg K</td>
<td>1.253</td>
<td>1.18</td>
<td>2.26</td>
</tr>
<tr>
<td>Si K</td>
<td>1.739</td>
<td>24</td>
<td>39.81</td>
</tr>
<tr>
<td>Ca K</td>
<td>3.69</td>
<td>4.33</td>
<td>5.04</td>
</tr>
<tr>
<td>Mo L</td>
<td>2.293</td>
<td>61.99</td>
<td>30.1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 5.4. Composition of elements presented in annealed molybdenum tri-oxide thin films of 0.05 M

<table>
<thead>
<tr>
<th>Element</th>
<th>(keV)</th>
<th>Mass%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>0.525</td>
<td>4.65</td>
<td>21.66</td>
</tr>
<tr>
<td>Si K</td>
<td>1.739</td>
<td>2.24</td>
<td>5.95</td>
</tr>
<tr>
<td>Mo L</td>
<td>2.293</td>
<td>93.11</td>
<td>72.39</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Annealing of thin films lead to recrystallisation and libration of unbound molecules, contaminations and dissociations. The surface roughness in our film is due to such effect (Martin et al., 2004).

5.7. Raman Spectroscopic Studies of Molybdenum Trioxide Thin Films

As we know, Raman spectroscopy is an analytical technique to investigate the quantitative and qualitative composition of materials. We have taken the Raman spectra of molybdenum trioxide thin films using BRUKER: RFS 27 instrument at a spatial resolution of 2mm in back scattering configuration in IIT Chennai. The Raman spectra of ideal MoO$_3$ film annealed at 300 °C was excited with Ar$^+$ laser of 514.5 nm and the spectrum is shown in Fig 5.7 below.

It is obvious that there are three main regions of lattice modes of vibrations 600-900 cm$^{-1}$, 200-400 cm$^{-1}$ and below 200 cm$^{-1}$ in the Raman spectra of molybdenum trioxide thin film. The associated peaks below 200 cm$^{-1}$ corresponds to lattice modes of vibration and intermediate frequencies (200-400 cm$^{-1}$) to the bending mode vibrations of O-Mo-O. The
stretching mode vibrations of Mo-O are related to the peaks at higher frequencies (600-900 cm\(^{-1}\)).

**Figure 5.7. Raman spectrum of molybdenum trioxide thin film of 0.05M annealed at 300° C**

The vibrational modes present in the prepared MoO\(_3\) thin film coated at 0.05 M concentration is given in table 5.5.

From the table, it is observed that the Raman spectrum of annealed MoO\(_3\) thin film confirmed the presence of orthorhombic MoO\(_3\) phase. Also, these Raman spectrum of MoO\(_3\) are in good agreement with the XRD results and provide additional confirmation that the annealed MoO\(_3\) thin films lead to orthorhombic crystallization.
Table 5.5. Vibrational modes of 0.05M Molybdenum trioxide thin film

<table>
<thead>
<tr>
<th>Wave Number (cm(^{-1}))</th>
<th>Modes of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>262</td>
<td>(Mo=O) Vibrational mode</td>
</tr>
<tr>
<td>325</td>
<td>(Mo-O) Bending mode</td>
</tr>
<tr>
<td>365</td>
<td>(Mo-O) Bending mode</td>
</tr>
<tr>
<td>660</td>
<td>(Mo(_3)-O) Stretching mode in orthorhombic MoO(_3) structure</td>
</tr>
<tr>
<td>817</td>
<td>(Mo(_2)-O)Stretching mode in orthorhombic MoO(_3) structure</td>
</tr>
<tr>
<td>995</td>
<td>(Mo=O) Stretching mode in orthorhombicMoO(_3)layered structure</td>
</tr>
</tbody>
</table>

5.8. Atomic Force Microscopy of Molybdenum Trioxide Thin Films

The ideal MoO\(_3\) film deposited under the using ideal parameters and annealed at 300 °C is subjected to Atomic Force Microscopy analysis which is shown in figure 5.8 and 5.9 respectively.

Since MoO\(_3\) crystallizes in the layered form, the layered topography is observed in the AFM images. The surface topography resembles the orthorhombic layered structure with uniform columnar surface of hillocks and valleys.

The rms surface roughness of MoO\(_3\) film is found to increase from 11 nm to 23 nm after annealing. It may be due to the growth of nanocrystallites and formation of large
grains on the surface of the film (Kannan et al., 2014). The maximum height $R_{\text{max}}$ of as-deposited molybdenum trioxide thin film is 104 nm and 34 nm for annealed molybdenum trioxide thin film.

![3D Atomic Force Micrograph](image)

**Figure 5.8. 3-dimensional Atomic Force Micrograph for as-deposited molybdenum trioxide thin film of 0.05 M concentration**

5.9. Optical Properties of Molybdenum Trioxide Thin Films

The optical transmittance studies of as-deposited and annealed molybdenum trioxide thin films were carried out using PGT90+ spectrophotometer in the wavelength range 300-900 nm. The optical transmittance spectra of as-deposited and annealed MoO$_3$ thin films are shown in Fig 5.10 and 5.11 respectively.
Figure 5.9. 3-dimensional Atomic Force Micrograph for molybdenum trioxide thin film of 0.05 M concentration annealed at 300°C

Figure 5.10. Transmittance curve of as-deposited MoO$_3$ thin film of 0.05 M
All films exhibit good optical transparency. The transmittance of annealed MoO$_3$ thin film samples are found to be slightly lower than the as-deposited MoO$_3$ thin film. This decrease in optical transmittance may be due to polycrystalline nature, high surface roughness and the random orientation of the crystallites of the film which may scatter the incident light. Such variations in transmittance are reported earlier for magnetron sputtered NiO and ZrO$_2$ thin film materials. The transmittance curve of MoO$_3$ thin films revealed that smooth spectra without any interference fringe pattern. This is attributed by the minimum optical reflection from the uniformly coated thin films of small thickness.

Using the optical transmission data, the direct band gap of the as-deposited and annealed MoO$_3$ thin film are estimated from a plot between photon energy $h\nu$ and $(\alpha h\nu)^2$. The Tauc plot of the as-deposited and annealed MoO$_3$ thin films are presented in figure 5.12 and 5.13 respectively. The estimated direct band gap values of as-deposited and
annealed MoO$_3$ thin films are found to decrease from 3.5 eV to 3.4 eV. The obtained band gap values were in good agreement with literature (Bouzide et al., 2003b).

Figure 5.12. Tauc plot for as-deposited MoO$_3$ thin film of 0.05 M

Figure 5.13. Tauc plot for annealed MoO$_3$ thin film of 0.05 M
5.10. Electrical Properties of Molybdenum Trioxide Thin Films

5.10.1. Electrical Resistivity

The usual four probe technique is employed to find the resistivity of the as-deposited and annealed MoO$_3$ thin film. The variation of the resistivity depicts the semiconductor nature of MoO$_3$ thin film. A constant current of 50 nA was setup and the corresponding voltage across the film surface was measured using Keithley digital multimeter. The surface resistance and hence the electrical resistivity were calculated with the help of an interfaced computer software. The variation of surface resistance and the corresponding resistivity of the annealed MoO$_3$ thin film were recorded in the temperature range from 20 to 200°C. Figure 5.14 and 5.15 exhibit the plot of ln($\rho$) versus 1000/T of as-deposited and annealed MoO$_3$ thin film respectively. The temperature versus surface resistance of the as-deposited and annealed film are shown in figure 5.16 and 5.17 respectively.

![Figure 5.14. Plot of ln(\rho) versus 1000/T of as-deposited MoO$_3$ thin film of 0.05 M](image)

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Using a hot probe technique, the prepared MoO$_3$ thin film is found to be a n-type semiconductor. It is observed from the curve, there are three regions of resistance: (i) continuous fall of resistance, (ii) an exponential fall region and (iii) the saturation region. An increase in temperature causes the electrons to acquire enough energy and cross the barrier at grain boundaries (Borse et al., 2008a, Windichmann et al., 1979a). At high temperature, the oxygen adsorbates are desorbed from the surface of the films which can decrease the potential barrier at grain boundaries. The decrease in resistance with increase in temperature indicating the semiconducting behavior obeying Arhenius equation $R = R_o \exp(-\Delta E/KT)$ in the temperature range 20 -200° C. Where, $R_o$, the constant, $\Delta E$, the activation energy, $K$, Boltzmann constant and $T$, Absolute temperature. For the as-deposited MoO$_3$ thin film, the initial resistance value 6.69 G$\Omega$ is constant upto 40° C and that for the annealed MoO$_3$ thin film is 0.872 G$\Omega$ and constant upto 60° C and then falls linearly upto a transition temperature. After the transition temperature, the resistance of

**Figure 5.15. Plot of ln($\rho$) versus 1000/T of annealed MoO$_3$ thin film of 0.05 M**
annealed MoO$_3$ thin film decreases exponentially and reaches the saturated state. The switching of resistance at temperatures make MoO$_3$ material apt for sensors.

**Figure 5.16.** Plot of resistance versus temperature of as-deposited MoO$_3$ thin film of 0.05 M

**Figure 5.17.** Plot of resistance versus temperature of annealed MoO$_3$ thin film of 0.05 M
5.11. Gas Sensing Properties of Molybdenum Trioxide Thin Films

Usually metal oxide thin films are good gas sensors. However, MoO$_3$ thin films show significant sensing ability of NH$_3$ vapours at very low concentrations of the order from 5 ppm to 200 ppm. Normally gas sensors respond at higher temperatures. We made a novel attempt to detect NH$_3$ vapours at room temperature which is investigated resulting a good response. And also gas sensing the properties are studied for ethanol, acetone and toluene vapours.

5.11.1. Gas Sensing Properties

5.11.1.1. Sensitivity

Similar to WO$_3$, MoO$_3$ is also an n-type semiconductor. The resistance of MoO$_3$ thin films decreases on the exposure of NH$_3$ vapour at room temperature (Aravind et al., 2012a). For reducing gas, the sensitivity of the film was calculated using the relation:

$$ S = \frac{R_a}{R_g} $$

where, $S$ is the Sensitivity, $R_a$ is the resistance of the film in air and $R_g$ is the resistance in test gas NH$_3$. The response of the film at room temperature as a function of NH$_3$ concentration is studied and shown in Figure 5.18. The variation of NH$_3$ sensitivity increases with NH$_3$ concentration in ppm. The maximum sensitivity is observed at 200 ppm concentration of NH$_3$. The sensitivity of the film as a function of NH$_3$ concentration obtained at room temperature is shown in Fig.5.19. It is observed that the response of the film is found to be linear with concentration increased (5 – 200 ppm). Such sensing is observed first time at room temperature. The annealed MoO$_3$ thin film shows remarkable response even at low concentration of NH$_3$ vapour (5 – 25 ppm)
Figure 5.18. The transient response characteristics towards NH$_3$ gas concentration of MoO$_3$ thin film sensor at room temperature

5.11.1.2. Selectivity

The selectivity of MoO$_3$ thin film is tested for 100 ppm concentration of NH$_3$, acetone, ethanol and toluene vapours. The sensitivity in the detection of NH$_3$ vapour is prominent when compared to other vapours at room temperature which is shown in figure 5.20.

5.11.1.3. Response and Recovery Time

The response and recovery time on exposure of NH$_3$ vapour at room temperature on the annealed MoO$_3$ thin film is shown in figure 5.21.
Figure 5.19. Sensitivity of MoO$_3$ thin film sensor towards different concentrations of NH$_3$ at room temperature

Figure 5.20. Response of MoO$_3$ thin film sensor to different vapours for 100 ppm concentration at room temperature
Figure 5.21. Response and recovery time of MoO$_3$ thin film sensor towards 100 ppm NH$_3$ detection at room temperature

The graph reveals that when NH$_3$ is injected into the chamber the resistance decreases and reaches the steady state value. Hence, the sensitivity attained its maximum and the corresponding response time is 40 s. On the other hand, the removal of NH$_3$ from the chamber, the sensitivity decreases rapidly to its initial value hence the recovery time is 50 s. Comparing with WO$_3$ thin film sensor for NH$_3$ at room temperature, the response time is less which may be due to the molecular size. Since the response is high, it is convenient to make an attempt for combination of these two metal oxides for the same gas sensing property.