Chapter - IV

APPLICATIONS OF MoO$_3$ FILMS
With the advent of silicon technology, most of the measurements and control systems are electronic in nature and every measuring system needs a sensor to detect and convert into a suitable form of the signal. The detected signal is further processed for the automation of the systems. A basic electronic measuring system consists of an input transducer, signal conditioner and output transducer with unit of appropriate power supply. The transducer constitutes the key portion of the system. It is classified as sensor and actuator. The sensor is at the output of the measuring instrument which senses the input signal and gives output to a signal conditioner while the actuator gives its output to the control systems. During the last two decades it was realized that, in general, the progress in signal processing was not going to improve signal to noise ratio. It is essential to improve it at the sensor component itself. Therefore the fundamental research in sensor was given a priority.

The gas sensors, which are an element of the chemical domain, detect the gases present in the environment. The gases that are present in different ambient include hydrogen (H$_2$), carbon monoxide (CO), methane (CH$_4$), nitrous oxide (NO$_x$), liquid petroleum gas (LPG), carbon dioxide (CO$_2$), oxygen (O$_2$), ammonia (NH$_3$) etc. For the detection of these gases different types of sensors [1, 2] are used and being developed with advanced technology for the daily life requirements viz., cost, high sensitivity to a particular gas, low operating temperatures, ease of operation, small size with possible alarm system etc.

Of late, the interest has been focused to identify new promising metal oxide materials with more suitable structure and good electrical properties. Molybdenum oxide is well known from investigations in the field of catalysis for oxidation of hydrocarbons and alcohols. The chemical and structural similarities of molybdenum to tungsten whose oxides prove sensing capability have led to the scientific community to consider the properties of MoO$_3$. In the present investigations it is aimed to study the NH$_3$, CO and CH$_4$ gas sensing properties of MoO$_3$ thin films deposited on Al$_2$O$_3$ substrates by sputtering of dc reactive magnetron sputtering. This chapter deals with the applications of MoO$_3$ thin films in gas sensors of NH$_3$, CO and CH$_4$. The photochromic performance of MoO$_3$ films deposited with the configuration of glass/CdS/MoO$_3$. 
4.1 Preparation of MoO$_3$ films

Thin films of molybdenum oxide were deposited on single Al$_2$O$_3$ substrates maintained at the optimized conditions such as the oxygen partial pressure of $2 \times 10^{-4}$ mbar, substrate temperature of 523 K and sputtering power of 5.7 W/cm$^2$ are used to study the gas sensing of NH$_3$, CO and CH$_4$.

The gas sensors are being characterized by two methods (i) using dynamic system and (ii) static system [3]. In the present work static system was employed. The static system consisted of a vacuum chamber (vacuum bell jar, vacuum $\sim 10^{-5}$ mbar) in which the sample, heater and temperature sensors are arranged with electrical connections. The gas inlet and the air admittance valves are arranged at the base plate in order to inject the gas and air. A heater made of kanthol wire, a chromel - alumel thermocouple and the gas sensor are arranged inside the chamber. In a static system, the sensor is tested for gas sensing as follows. The temperature of the sensor is controlled by varying the current flow through the heater measured with an accuracy of $\pm 5^\circ$C using a temperature indicator. The electrical characteristics of the sensor are observed by changing its temperature from 523 to 773 K in air ambient and this response is considered as a reference response for the calculation of sensitivity. In order to easily inject the gas the chamber is evacuated slightly ($10^{-2}$ mbar) using rotary pump. After injecting the test gas, all the valves are closed to avoid the test gas leakage during the experiment. Then the resistance of the sensors is measured by changing the sensor temperature in air plus injected gas ambient. The output of the sensor was measured using the voltage divider circuit as shown in fig. 4.1. After completing the temperature scan, the gas is leaked out; the other cycles were carried out by injecting fresh gas into the chamber.

The sensitivity factor of the sensor was measured by using the above circuit. The gas sensor sensitivity $S$, is defined as the ratio of the change in electrical resistance in air ($R_a$) and the test gas ($R_g$) to its resistance in air ($R_a$) i.e

$$S = [(R_a - R_g) / R_a] / C_g$$

---(1)

where $C_g$ is the concentration of the test gas.
4.1.1 Gas sensing properties of MoO₃ films

Measurements of the electrical conductivity were carried out in dry synthetic air. The gas sensitivity of the molybdenum oxide films was tested regarding the gases NH₃, CO and CH₄ with a concentration of 300 ppm. The sensitivity was investigated for a temperature range between 523 and 773 K. Fig. 4.2 shows the variation of sensitivity with the temperature of ammonia, carbon monoxide and methane gases for higher concentration of 300 ppm. The sensitivity was found to be increase with operating temperature. The maximum sensitivity was observed for NH₃ is at around 723 K. The sensitivity for CO and CH₄ was low at these operating temperatures and showed maximum sensitivity at 773 K. Mutschell et al [2] observed the MoO₃ films showed high sensitivity was at around 698 K for NH₃. Sensing mechanism of semiconducting oxides generally involved chemisorbed ions which modulate the carrier concentration in the surface [4].

Fig. 4.3 shows the variation of sensitivity with the concentrations for NH₃, CO and CH₄ at operating temperature of 723 K. For ammonia, sensitivity increased linearly with the increase of concentration above 300 ppm. Similarly for CO and CH₄ showed the sensitivity also increased but low when compared to NH₃. Typical response and recovery characteristics of the film sensor operating at 723 K towards 300 ppm of ammonia were about 70 sec and 210 sec respectively which indicate the
Fig. 4.2 Sensitivity of various gases as a function of temperature

Fig. 4.3 Sensitivity as a function of gas concentration

fast response and retracing properties of the sputtered molybdenum oxide sensors towards ammonia. The above results revealed that the MoO$_3$ films were in $\alpha$- phase are capable for detecting NH$_3$, CO and CH$_4$ gases. The maximum sensitivity was observed for NH$_3$ was around at 723 K whereas for CO and CH$_4$ gases exhibits low
sensitivity when compared to NH₃. The response and retracing time of MoO₃ sensor towards NH₃ was about 70 sec and 210 sec.

4.2 Photochromic properties of MoO₃ films

If the energy of the excitation light is greater than the band gap of molybdenum oxide, production of electron hole pairs will take place. As a result, the optical absorption changes markedly, and the colour of the molybdenum oxide films changes. It is known as photochromic effect and has rendered for many technological applications such as optical smart windows, self developing photography etc. Schirner et al. [5] proposed that colouration is similar to that of amorphous WO₃ films. In this case optical absorption of the films is caused by the small polaron transitions between nonequivalent sites of molybdenum (Mo⁵⁺ and Mo⁶⁺)

\[ hν + Mo⁵⁺ (A) + Mo⁶⁺ (B) → Mo⁵⁺ (B) + Mo⁶⁺ (A) \] --- (2)

According to this model, inserted electrons are localized in Mo⁵⁺ sites and polarize their surrounding lattice forming small polarons. Incident photons are absorbed by small polarons which hop between A and B sites. This model is analogous to that presented by Deb [6] who observed that the properties of colour centers in WO₃ are very similar whether generated by photochromism, or electrochromism. The photochromic properties can be enhanced by the use of a double layer system [7], in which a lower band gap semiconductor, i.e. cadmium sulphide, is used as an interlayer between glass substrate and MoO₃. CdS is a wide band gap material \((E_g = 2.44 \text{ eV})\) with a reasonable energy difference of about 0.80 eV when compared to MoO₃ \((E_g = 3.20 \text{ eV})\). The electron affinity of CdS was 4.5 eV which is higher than that of MoO₃ and hence the conduction band of CdS was about 0.5 eV more negative than that of MoO₃. Coupling of two such semiconductor systems has a advantage in electron transfer between CdS and MoO₃.

Hence in the present investigations is aimed to study the photochromism of the MoO₃ films prepared by dc reactive magnetron sputtering technique at the optimized oxygen partial pressure of \(2 \times 10^{-4} \text{ mbar}\), sputtering power of 5.7 W/cm²,
sputtering pressure of $4 \times 10^{-2}$ mbar and at 303 and 373 K where the films were mixed phase of $\alpha$- and $\beta$- MoO$_3$. The glass/CdS/MoO$_3$ films were used to study the photochromic behaviour for different irradiation times.

4.2.1 Preparation of cadmium sulphide films

Thin films of CdS were deposited by thermal evaporation techniques onto glass substrates held at 423 K in a vacuum of $8 \times 10^{-6}$ mbar by evaporating the polycrystalline CdS powder from a resistively heated molybdenum boat. The optical transmittance spectra of CdS film deposited at a substrate temperature of 423 K is shown in fig. 4.4. The thickness of films was 600 nm. The films deposited at 423 K showed the electrical resistivity of $2.5 \times 10^2 \, \Omega \cdot \text{cm}$ and optical band gap of 2.44 eV.

![Optical transmittance spectrum of CdS films deposited at 423 K](image)

**Fig. 4.4** Optical transmittance spectrum of CdS films deposited at 423 K

4.2.2 Photochromic performance of glass/CdS/MoO$_3$ thin film device

To study the photochromic behaviour of MoO$_3$ based system, thin films of CdS with thickness of 0.6 $\mu$m was deposited on glass substrates by vacuum evaporation over which 0.45 $\mu$m thick films of MoO$_3$ was deposited by sputtering of molybdenum target using dc reactive magnetron sputtering in an oxygen partial
pressure of $2 \times 10^{-4}$ mbar, sputtering power of 5.7 W/cm$^2$ and at substrate temperatures of 303 and 373 K since the films formed at these temperatures were mixed phase of $\alpha$- and $\beta$- MoO$_3$. The fabricated device configuration was glass/CdS/MoO$_3$.

The photochromic behaviour of the films was studied by illuminating the device (glass/CdS/MoO$_3$) using 100 W tungsten lamp with a sample separation between film and tungsten lamp of 6.5 cm. The films were illuminated at different times varying from 30 to 120 min. After illumination the samples were kept in dark. The optical absorbance was immediately recorded in the wavelength range 300 – 1500 nm using UV-Vis-NIR double beam spectrophotometer. Fig. 4.5 shows the optical absorption spectra of glass/CdS/MoO$_3$ films deposited at 303 and 373 K temperatures.

![Optical absorption spectra](image)

**Fig. 4.5** Optical absorption spectra for glass/CdS/MoO$_3$ of as-deposited and 373 K

The colour center band for the film deposited at 373 K appears to be stronger than the film deposited at room temperature (303 K). The observed structure in the
optical absorption is an intrinsic property of the MoO$_3$ since the absorption coefficient is of order of $10^5$ cm$^{-1}$ is too high to be attributed to any impurity [8]. Therefore, the origin of optical absorption edge may be due to following one of the five categories. They are (i) interband transitions from filled conduction band to higher excited state bands, (ii) charge transfer absorption from the valence band to a "split – off" Mo$^{5+}$ state, (iii) F or F$^+$ centers in oxygen ion vacancies, (iv) inter valence transfer, which requires largely delocalized electrons with some overlap between metal ions, and (v) small polaron absorption.

Fig. 4.6 shows the optical absorption spectra recorded for glass/CdS/MoO$_3$ samples deposited at 303 K irradiated with a tungsten lamp of 100 W at different times. The photochromic response grew rapidly as the irradiation times increased from 30 to 90 minutes and then decreased with further increase of exposure time. The intensity of the absorption increased with the increase of the irradiation time was due to increased in number of colour centers owing to capture the excited electrons by the positively charged defects.

**Fig. 4.6** Optical absorption spectra for glass/CdS/MoO$_3$ for different irradiation times of the films deposited at room temperature (303 K)
Fig. 4.7 shows the optical absorption spectra for glass/CdS/MoO₃ for different irradiation times of the films deposited at 373 K. As seen from the figure, the optical absorption edge shifted markedly towards higher wavelength side with the increase of irradiation times from 30 to 90 minutes. MoO₃ films deposited at lower substrate temperature were substoichiometric in nature as revealed by X-ray photoelectron spectroscopic measurements (fig. 3.16) resulting in the formation of positively charged defects (oxygen ion vacancies) in the oxide. Thus the substoichiometric molybdenum oxide films contain large number of oxygen ion vacancies, which are positively charged structural defects.

By irradiating with light lamp, F-like centers are formed by the capture of one or two photo generated electrons excited from the valence band to the conduction band. These excited carriers are being injected into MoO₃ and leads to enhancement in the production of colour centers as irradiation time increases. The shift in optical absorption edge towards lower wavelength side may be due to trapped electrons in structural defects. These trapped electrons can be excited into
the empty conduction band, leading to transitions that range from the near infrared to the visible region. The presence of more than one absorption band suggested that there was more than one type of defect responsible for the formation of colour centers. The concentrations of the colour centers in the oxide films were calculated by means of the Smakula equation [9]

\[ N \frac{(E_{\text{eff}}/E)^2}{f_{ij}} = \frac{(mc/2\Pi^2e^2h)}{\int a(\omega) d\omega} \]

where \( N \) is the colour center concentration in \( \text{cm}^{-3} \), \( (E_{\text{eff}}/E) \) is the local effect of polarization, \( f_{ij} \) is the oscillator strength, \( m \) is the electron mass, \( c \) is the light speed, \( e \) is the electron charge, \( h \) is Planck’s constant and \( n \) is the refractive index of the system. The values of refractive index and oscillator strength were taken as 2.0 and 1.8 respectively [10]. The local effect of polarization has a value of 4 [11]. To obtain \( \int a(\omega) d\omega \) we can relate it to the area of the experimental absorption spectra of \( \int a(\lambda) d\lambda \). The last integral was evaluated from 550 to 1100 nm because this is the wavelength where the colour centers generated in the MoO₃ film absorbed by the radiation. Gaussian approximation was used to evaluate the above integral. Fig. 4.8 shows the relative concentration of colour centers as function of different irradiation times. The colour concentration increased with increase of the irradiation times. It was observed from the figure that the higher the exposure times higher the colour concentrations. This may be due to electrons promoted to the conduction band by photoexcitation trapped by oxygen ion vacancies creating colour centers. The presence of \( O^{2-} \) in the \( S^{2-} \) vacancy sites in CdS layers prepared by thermal evaporation. This oxygen can be desorbed by photon irradiation. In this way oxygen migrated into the CdS/MoO₃ interface leaving two electrons bound to the sulphur vacancy. Photochromism is more effective in generating the colour centers when CdS is used as a charge carrier. This is due to the fact that CdS is more sensitive because this semiconductor presents a direct absorption process in creating hole - electron pairs.
Fig. 4.8 Colour center concentrations of the films irradiated with a tungsten lamp for the films deposited at different temperatures.
REFERENCES


