II. EXPERIMENTAL

For the deposition of MoO_3 thin films by spray pyrolysis technique, the precursor solution was prepared by dissolving MoO_3 powders (LR grade, Loba Chimie, 99.5% pure) in ammonia solution separately thereby forming ammonium molybdate. The homogenous solution of ammonium molybdate was formed at room temperature. The undergoing chemical reactions are given in Eqs. (1)

$$MoO_3 + 2NH_3 + H_2O \rightarrow (NH_4)_2MoO_4 \quad (1)$$

The solution was sprayed onto the glass substrates. The substrate temperature was maintained at 350^{o}C, and continuously monitored by a chromel-alumel thermocouple fixed to the hot plate. The pyrolytic decomposition of $(NH_4)_2MoO_4$ on the surface of the substrates results in the formation of MoO_3 thin films according to the following equation:

$$(NH_4)_2MoO_4 \rightarrow MoO_3 + H_2O \uparrow + 2NH_3 \uparrow \quad (2)$$

The MoO_3 films were then annealed at 550^{o}C for 30 min in air. After 30 min, the films were slowly cooled to room temperature and later on used for the characterization. Surface morphology was observed using a scanning electron microscope (SEM). For structural determination an X-ray diffraction (XRD) technique with CuKa (l=1.5405 Å) line was used. Optical absorption measurements in the range of 350-850 nm were carried out using model Hitachi 330 spectrophotometer.

III. RESULTS AND DISCUSSION

a. Structural Analysis

The structure of MoO_3 thin film was analyzed with X-ray diffractogram (D8 ADVANCE Bruker AXS) using CuKα radiation with a wavelength of 1.5406 Å. The observed peaks from XRD spectrum is well matches with the standard data [25]. The average crystallite size was calculated from major peaks using Scherer formula [26] which was found to be 124 nm, indicating their nanocrystalline nature.

$$T = 0.9 \lambda / \beta \cos\theta \quad (3)$$

Eq. (3) is Scherer formula, t is crystallite size, β is the full width at half maximum and λ is the wavelength of X-ray used (1.5406 Å).

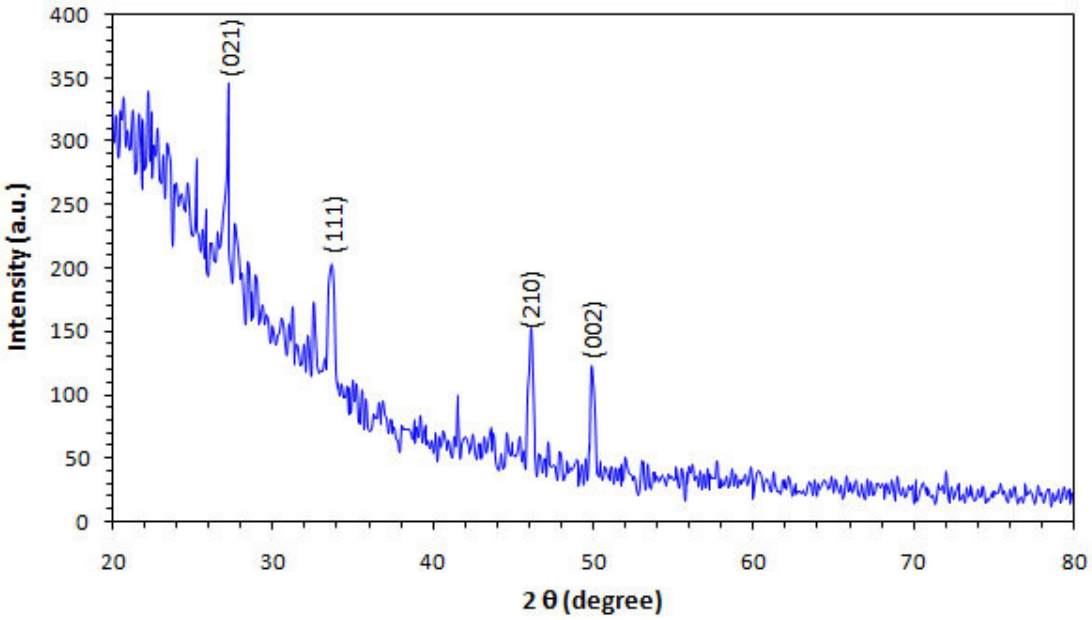


Figure 2. X-ray diffraction spectra of MoO_3 thin film.

b. Surface Morphology

To observe the surface morphology, scanning electron micrographs (SEM) of a thin film sample were taken. Fiure 2 shows the SEM of the MoO_3 thin film sample. It is observed that the substrate is well covered by a non-uniform film with spherical and hexagonal shaped particles. Excess solute precipitate gets deposited on some parts of the substrates. This may be due to non-optimized spray rate.

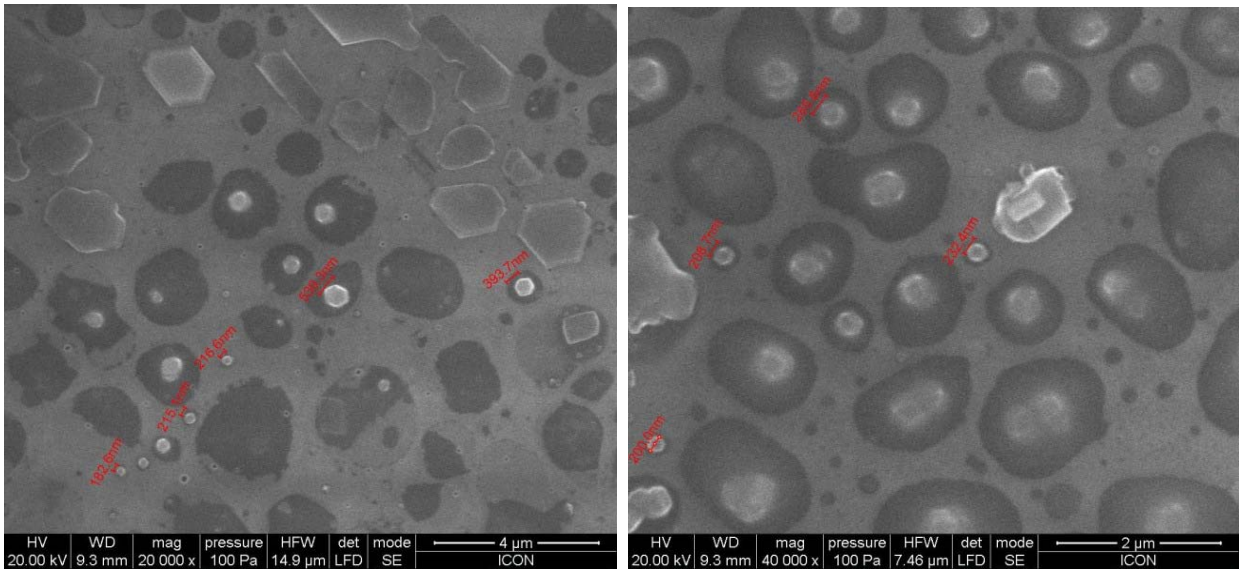


Figure 2. Scanning electron micrographs of MoO_3 thin film.

c. Optical Properties

The absorption spectra of thin films were recorded in the wavelength range 290–1100 nm run at room temperature. The sharp of the absorption edge suggests a single phase. The band gap energy calculated from the absorption spectra is 3.59 eV, for polycrystalline MoO_3 thin a film is widely reported [27].

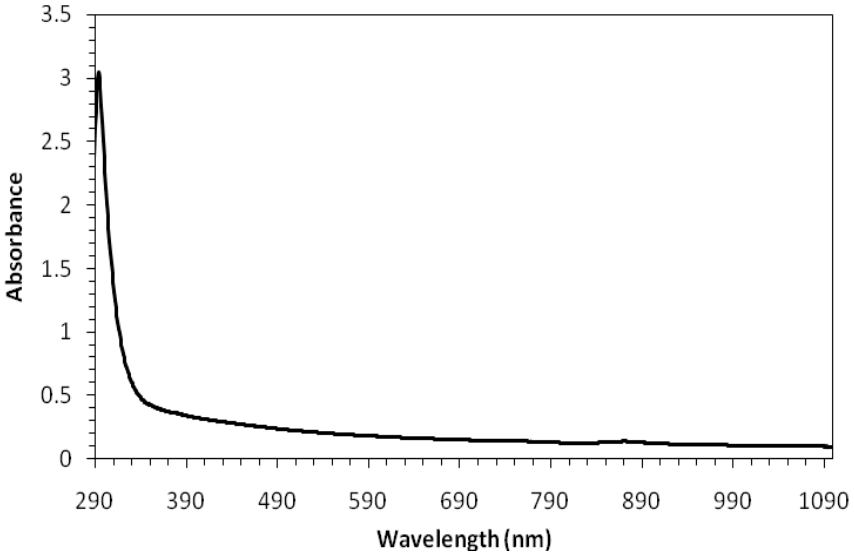


Figure 3. UV-vis spectra of MoO_3 thin film.

d. Electrical Properties of MoO_3 Thin Film

i. I-V Characteristics

Figure 4 depicts the I-V characteristics of MoO_3 thin film at room temperature in air ambient. I-V characteristics observed to be symmetrical in nature, indicating the ohmic nature of contact.

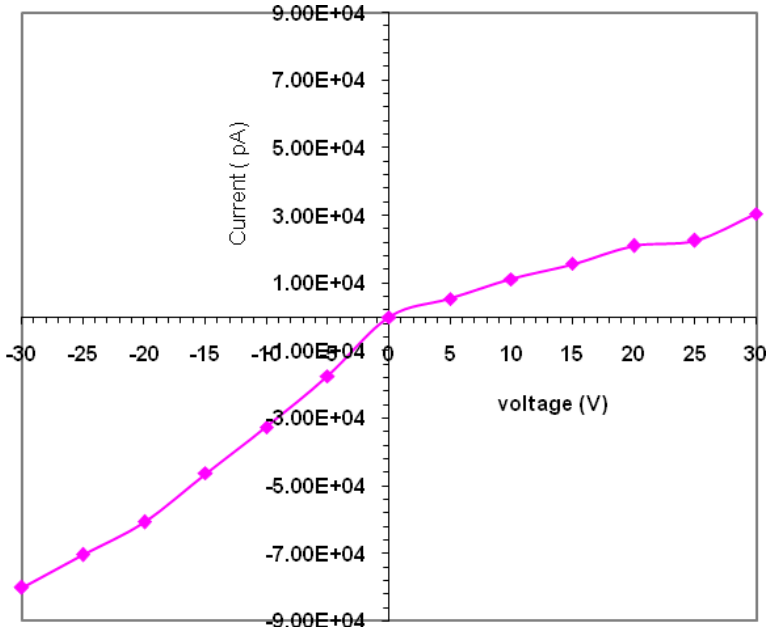


Figure 4. I-V characteristics of MoO_3 thin film.

ii. Electrical Conductivity

Fig. 5 shows the dependence of conductivity of MoO_3 thin film in air ambience. The conductivity of the film goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films.

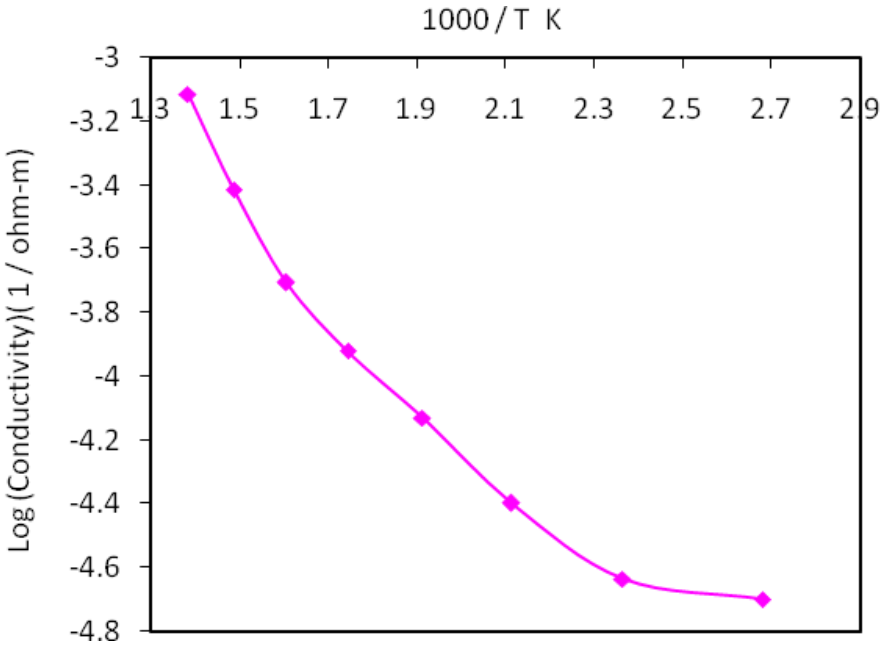


Figure 5. Variation of conductivity with temperature.

e. Gas Sensing Performance

The conductance of the sensor in dry air was measured by means of conventional circuitary by applying constant 10 V voltage and measuring the current by picoammeter. The conductance was measured both in the presence and absence of test gas. The gas response (s) is defined as the ratio of change in conductance in gas to air to the original conductance in air

$$S = (Gg - Ga) / Ga \qquad (4)$$

The selectivity is defined as the ability of a sensor to respond to certain gas in the presence of other gases [28, 29].

i.) Variation of Gas Response with Operating Temperature of MoO_3 Thin Film

Figure 6 presents the variation in the gas response to various gases (1000 ppm) with operating temperatures ranging from 100^o to 400^oC. It is noted from the graph that response increases with increasing temperature, and attains a maximum at 300^oC for H_2S and at 200^oC for ethanol and decreases with further increase in operating temperature.

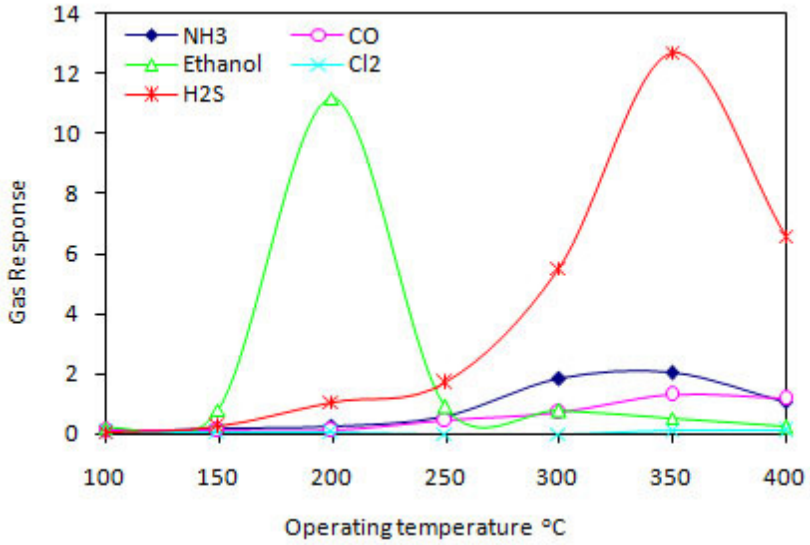
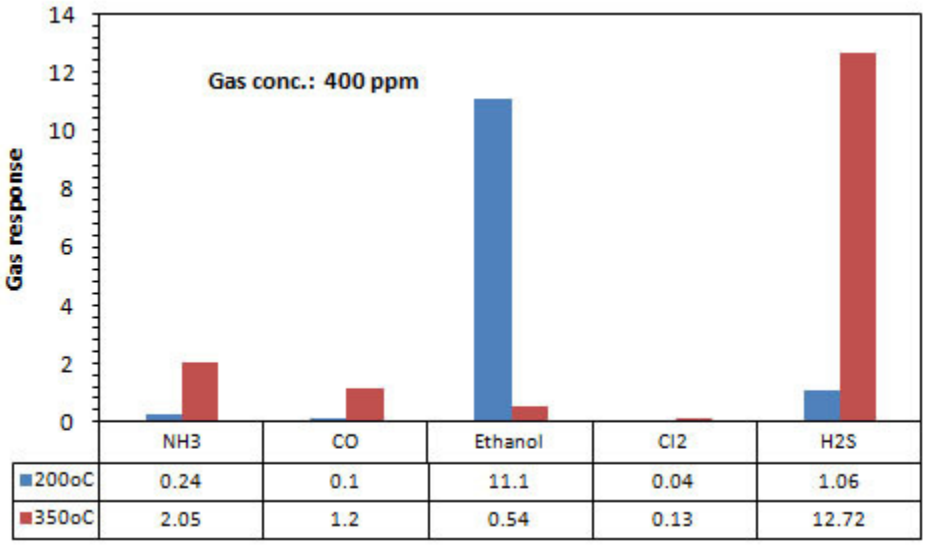


Figure 6. Variation of gas response with temperature.

ii.) Selectivity of MoO3 Thin Film

Figure 7 presents the bar diagram indicating selectivity of MoO_3 thin film at 350^{o}C to H_2S gas and at 200^{o}C to ethanol against the other gases. The sensor is the most selective to H_2S gas against the other gases.



	NH3	CO	Ethanol	Cl2	H2S
200oC	0.24	0.1	11.1	0.04	1.06
350oC	2.05	1.2	0.54	0.13	12.72

Figure 7. Selectivity of MoO_3 thin film.

iii.) Variation of Sensitivity with Gas Concentration

To test the H_2S gas concentration characteristics, the sensor was exposed to H_2S gas of different concentrations at a constant operating temperature. The sensor responses to H_2S in concentration range (40-480 ppm) are shown in figure 8 at 350^oC operating temperature. The response values were observed to increase continuously with increasing the gas concentration up to 400 ppm. The rate increase of response was relatively larger up to 400 ppm and then saturates after 400 ppm. Thus the active region of the sensor would be between 40-400 ppm.

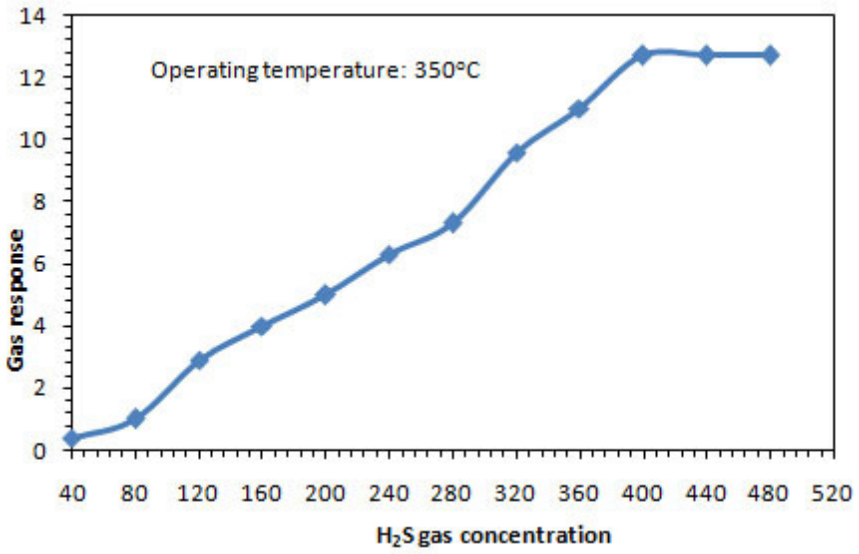


Figure 8. Variataion in sensitivity with H_2S gas concentration.

iv.) Response and Recovery Time

The time taken for the sensor to attain 90% of maximum change in resistance on exposure to gas is the response time. The time taken by the sensor to get back 90% of the original resistance is the recovery time [30]. The response and recovery time of MoO_3 thin film was 14s and 40s respectively. The large recovery time would be due to lower operating temperature. At lower temperature O_2^- species is more prominent adsorbed on the surface, it is less reactive compared to other species of oxygen, O^- and O^{--}.

v.) Gas Sensing Mechanism

It is well known that the gas sensing mechanism in the oxide based materials is surface controlled, wherein; the grain size, surface states and oxygen adsorption play a significant role. The larger surface area usually offers more adsorption– desorption sites and thus the enhanced

sensitivity [31, 32]. The atmospheric oxygen gets adsorbed on the surface, and depending upon the temperature of operation; different oxygen species are formed on the surface. The gas response by metal oxide semiconductor, in general, can be described as

$$O_{2(gas)} + 2e^- \rightarrow 2O_{ads}^- \qquad (5)$$

$$R + O_{ads}^- \rightarrow RO + e^- \qquad (6)$$

Initially, (Eq. (5)) the atmospheric oxygen acquires electron from the conduction band of MoO_3 and forms $Oads^-$ species on the surface thus decreasing the conductance of the MoO_3.

Further, the high surfaces to volume ratio of nanosized particles offer larger number of sites for the adsorption of the oxygen species. It is known that the gas response depends directly on the number of O_{ads}^- species. The reducing gas (R), reacts with $O_{ads}-$ and forms RO (Eq. (6)) with releases of electron back to the conduction band. In the process the conductance again increases. Therefore, sensitivity in general, depends on the reaction (Eq. (5)) that is, availability of R and O_{ads}^- species. The rejuvenation of the conductance takes place on removal of R and the presence of ambient oxygen (Eq. (5)).

More specifically, in the presence of H_2S gas, the reaction (Eq.(7)) takes place thereby forms H_2O and SO_2 gas by releasing electrons back to the conduction band, thus increasing the conductance of the sensor. Again on removal of H_2S the reaction (Eq. (5)) takes place leading to a decrease in the conductance [33]. This can be simply described as in Eq. (7),

$$H_2S_{ads} + 3O_{ads}^- \rightarrow H_2O + SO_2 + 3e^- \qquad (7)$$

IV. CONCLUSION

A simple spray pyrolysis method is used to prepare MoO_3 thin films. The technique is simple and inexpensive and it may be useful for the production of metal–oxide thin film gas sensors. XRD analysis confirmed that the synthesized materials on thin film to be that of the MoO_3. The band-gap energy calculated from an absorption spectrum was 3.59 eV. This value matches exactly with the reported value. The response of the MoO_3-based sensor was observed to be maximum at 300^oC for H_2S and at 200^oC for ethanol. The sensor showed good selectivity to H_2S gas against NH_3, Cl_2, CO and ethanol.

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