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# PREPARATION OF $MoO_3$ THIN FILMS BY SPRAY PYROLYSIS AND ITS GAS SENSING PERFORMANCE

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***Abstract- $MoO_3$ thin films have been prepared by a simple spray pyrolysis technique at substrate temperature 250°C. The structure and morphology of thin films are characterized by X-ray powder diffraction (XRD), scanning electron microscopy and UV-vis spectroscopy. The gas sensing properties of $MoO_3$ thin film is studied at gas concentration 400 ppm and working temperature of 100–400 °C. It was found that the sensitivity depended on the working temperatures and also $H_2S$ gas concentration. The results show that the $MoO_3$ thin film can be used to fabricate high performance $H_2S$ gas sensors.***

**Index terms*:* $MoO_3$ thin film, spray pyrolysis, sensor.**

# I. INTRODUCTION

Gas sensors based on metal oxide semiconductors may be used in a wide variety of applications including gas monitoring and alarm applications [1–4]. Considerable research has been carried out on the development of chemical sensors based on semiconductor metal oxides such as $SnO_2$, ZnO, and $TiO_2$ [5, 6]. Among the semiconductor metal oxides, $MoO_3$ with band gap energy of 2.39-2.9 eV is an excellent candidate for catalytic, electrochromic and gas sensing applications [7, 8]. $MoO_3$ has been well known for its application as a catalyst for the oxidation of hydrocarbons and reduction of NOx in the chemical and petroleum industry [9-12]. Efforts were also made to examine and improve the gas sensing properties of $MoO_3$ based devices to detect $H_2$ [8, 13], CO [13, 14], $NH_3$ [8, 10, 15], and LPG [8]. Imawanet al. [15] studied the RF sputtered MoO3 thin films for sensing responses to various gases, including CO, $CH_4$, $SO_2$, $NO_2$ and $NH_3$ in the temperature range of 250 $^oC$ and 475 $^oC$. They revealed that $MoO_3$ was highly sensitive to $NH_3$ at 425$^oC$ and that the gas sensitivity dropped with decreasing film thickness (<300 nm). Multilayered sputter deposited $MoO_3$ by the same research group resulted in improved $H_2$ sensing properties and low cross sensitivity towards $NH_3$ [13]. It is also shown that the sensitivity and selectivity to target gases can be altered by adding other metal oxides to $MoO_3$ [16, 17]. A number of techniques was reported for the deposition of $MoO_3$ including pulse laser deposition [10], thermal evaporation [18], sputtering [19], sol–gel [20], spray pyrolysis [21], chemical vapour deposition [22, 23] and electrodeposition [24]. The deposition of $MoO_3$ using spray pyrolysis techniques is advantageous as it can produce highly crystalline and stratified structures. This is an important feature since high crystallinity and having layered formation can allow for greater sensitivity.

In this paper, the authors report about the response of $MoO_3$ thin films to various gases such as CO, $Cl_2$, $NH_3$ ethanol and $H_2S$. It emerges that the film exhibit good response to these gases at the temperature range of 100–400 $^oC$. In this work, spray pyrolysis technique has been used for the deposition of $MoO_3$. Samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-vis spectroscopy.

## 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)

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

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.

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

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).

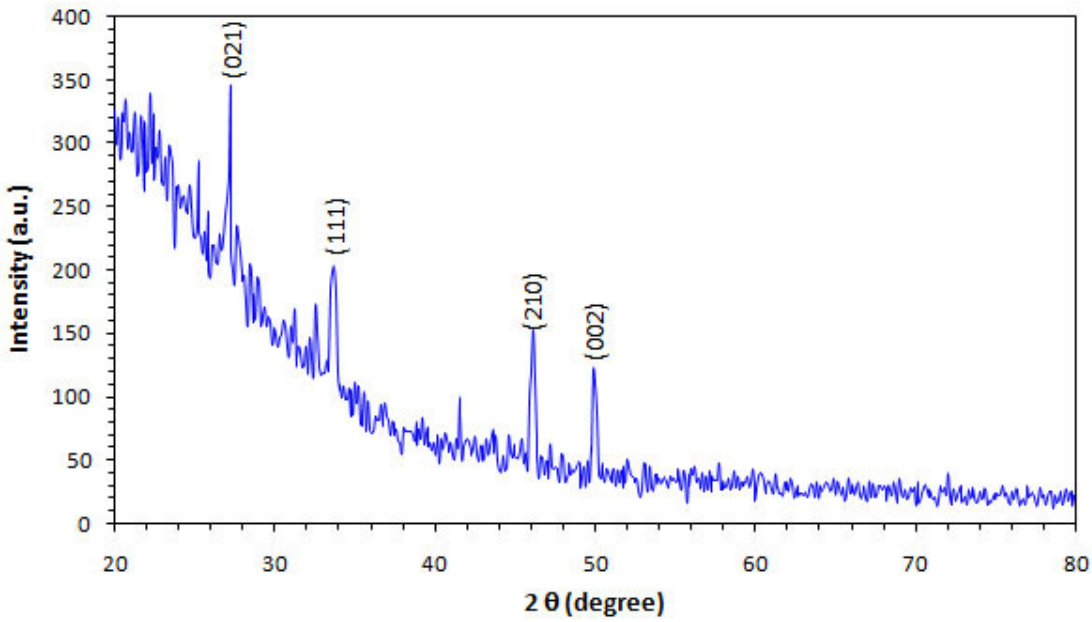


Figure 2. X-ray diffraction spectra of $MoO_3$ thin film.

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.

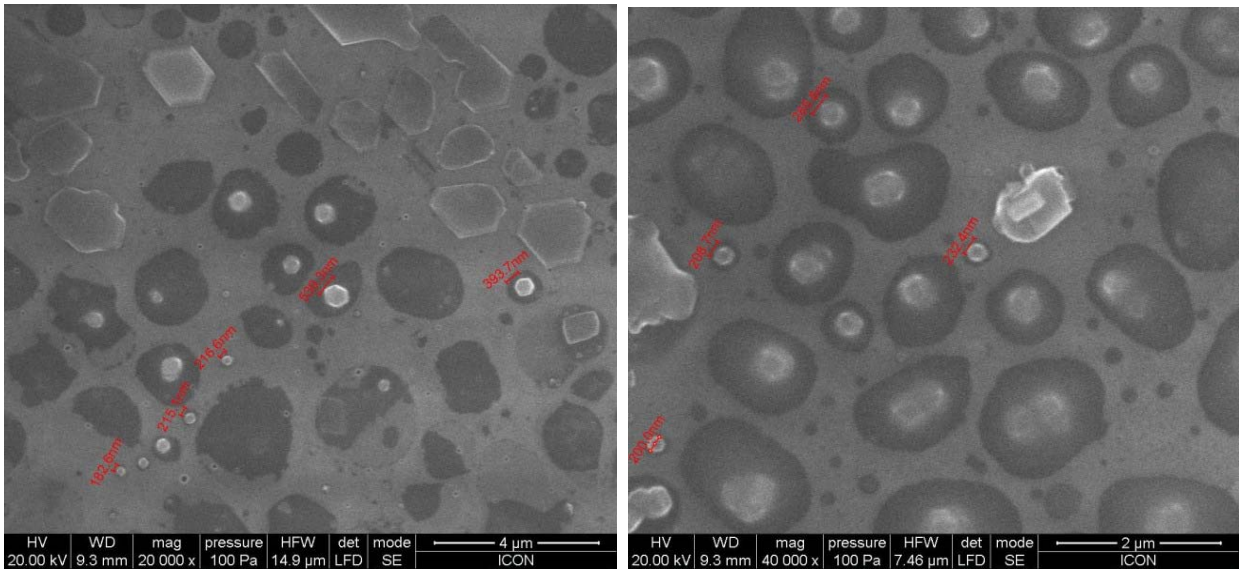


Figure 2. Scanning electron micrographs of $MoO_3$ thin film.

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].

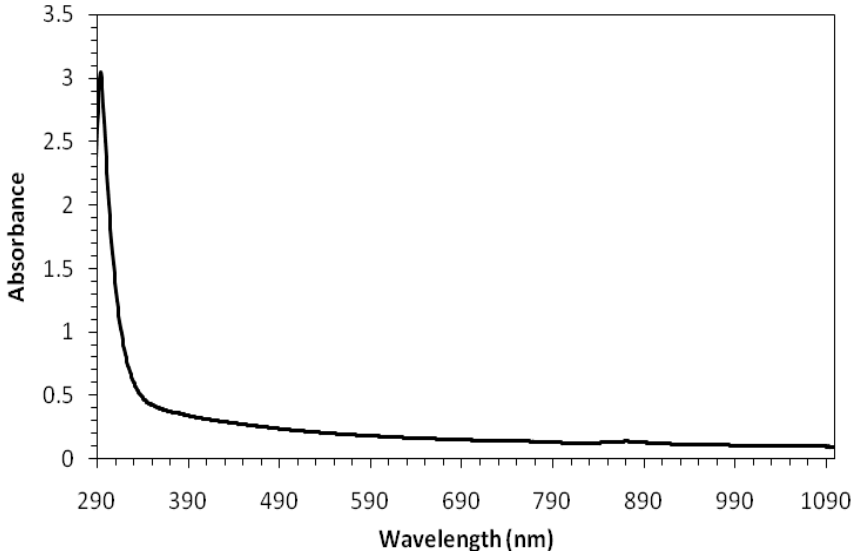


Figure 3. UV-vis spectra of $MoO_3$ thin film.

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.

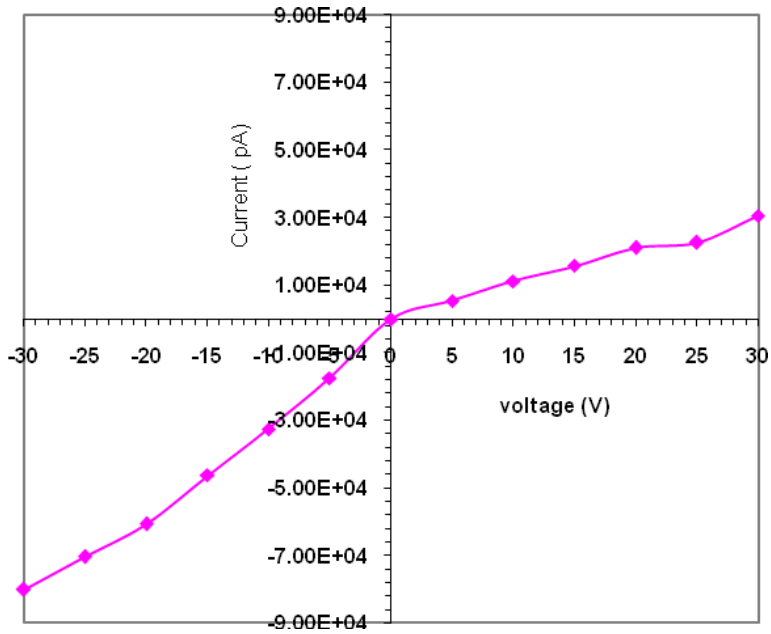


Figure 4. I-V characteristics of $MoO_3$ thin film.

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.

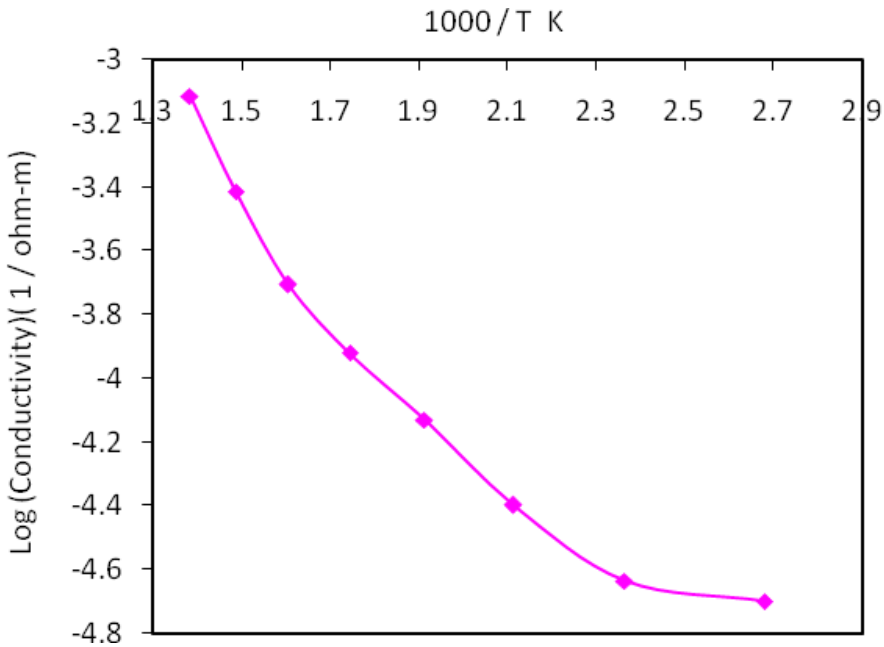


Figure 5. Variation of conductivity with temperature.

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.

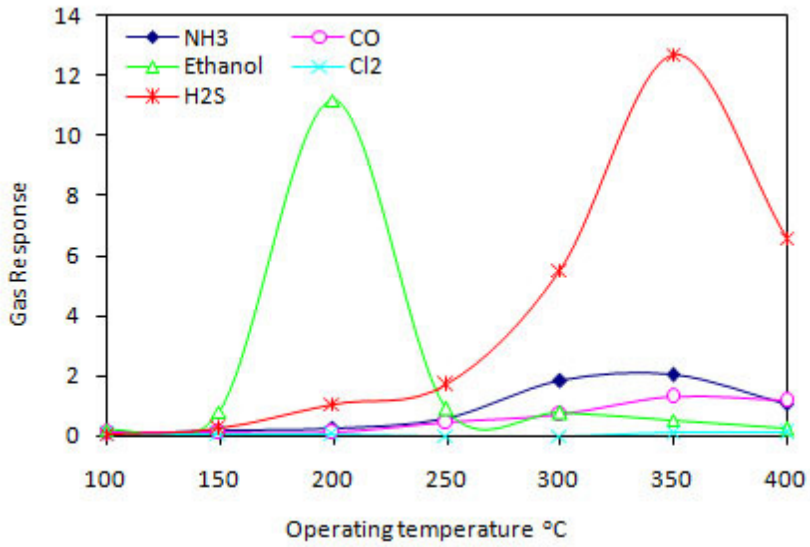


Figure 6. Variation of gas response with temperature.

ii.) Selectivity of MoO3 Thin Film

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

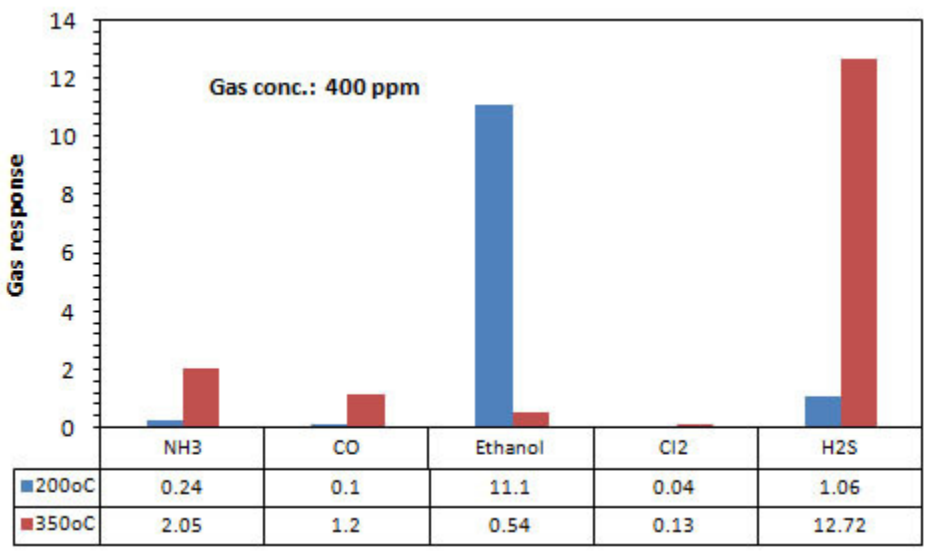


Figure 7. Selectivity of $MoO_3$ thin film.

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$^o$C 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.

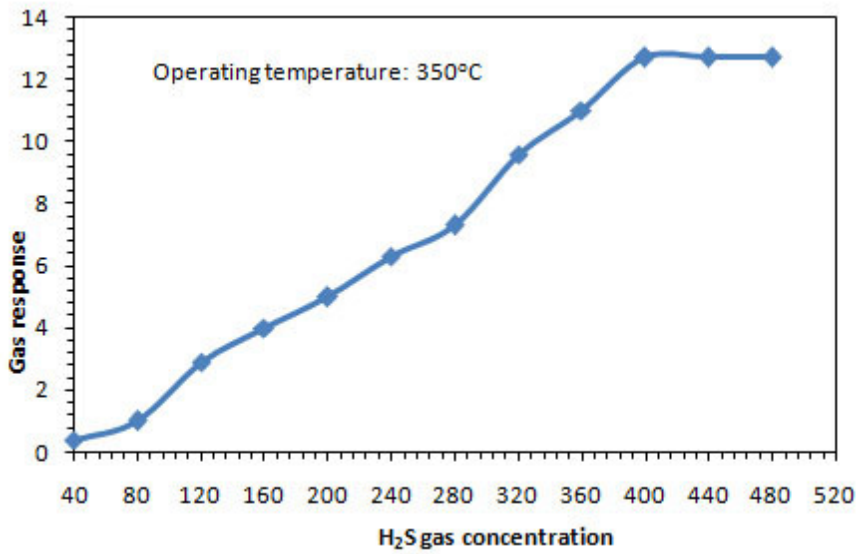


Figure 8. Variataion in sensitivity with $H_2S$ gas concentration.

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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## REFERENCES

[1] W. Gopel, K.D. Schierbaum, "$SnO_2$ sensors: current status and future prospects", Sensors and Actuators B: Chemical, Vol. 26, 1995, pp. 1–12.

[2] H. Baltruschat, I. Kamphausen, R. Oelgeklaus, J. Rose, M. Wahlkamp, "Detection of volatile organic solvents using potentiodynamic gas sensors", Analytical Chemistry, Vol. 69, No. 4, 1997, pp. 743–748.

[3] D.E. Williams, "Semiconducting oxides as gas-sensitive resistors", Sensors and Actuators B: Chemical, Vol. 57, No.1, 1999, pp.1–16.

[4] K. Potje-Kamloth, "Semiconductor junction gas sensors", Chemical Reviews, Vol. 108, No. 2, 2008, pp. 367–399.

[5] L. Liu, T. Zhang, L.Y.Wang, S.C. Li, "Improved ethanol sensing properties of Cu-doped $SnO_2$ nanofibers", Materials Letter, Vol. 63, No. 23, 2009, pp. 2041–2043.

[6] Y. Wang, W.Z. Jia, T. Strout, A. Schempf, H. Zhang, B.K. Li, J.H. Cui, Y. Lei, "Ammonia gas sensor using polypyrrole-coated $TiO_2$/ZnO nanofibers", Electroanalysis, Vol. 21, No. 12, 2009, pp. 1432–1438.

[7] A. K. Prasad, P.I. Gouma, "$MoO_3$ and $WO_3$ based thin film conductimetric sensors for automotive applications", J. Mater. Sci., Vol. 38, No. 21, 2003, pp. 4347–4352.

[8] S.S. Sunu, E. Prabhu, V. Jayaraman, K.I. Gnanasekar, T.K. Seshagiri, T. Gnanasekaran, "Electrical conductivity and gas sensing properties of $MoO_3$", Sens. Actuators B, Vol. 101, No. 1, 2004, pp. 161–174.

[9] M. Ferroni, V. Guidi, G. Martinelli, M. Sacerdoti, P. Nelli, G. Sberveglieri, "$MoO_3$- based sputtered thin films for fast $NO_2$ detection", Sens. Actuators B, Vol. 48, 1, 1998, pp. 285–288.

[10] S.S. Sunu, E. Prabhu, V. Jayaraman, K.I. Gnanasekar, T. Gnanasekaran, "Gas sensing properties of PLD made $MoO_3$ films", Sens. Actuators B, Vol. 94, 2, 2003, pp. 189–196.

[11] D.B. Dadyburjor, S.S. Jewur, E. Ruckenstein, "Selective oxidation of hydrocarbons on composite oxides", Catal. Rev. Sci. Eng., Vol. 19, No. 2, 1979, pp. 293–350.

[12] M.A. Larrubia, G. Ramis, G. Busca, "An FT-IR study of the adsorption of urea and ammonia over $V_2O_5$-$MoO_3$-$TiO_2$ SCR catalysts", Appl. Catal. B, Vol. 27, No. 3, 2000, pp. L145–L151.

[13] C. Imawan, H. Steffes, F. Solzbacher, E. Obermeier, "A new preparation method for sputtered $MoO_3$ multilayers for the application in gas sensors", Sens. Actuators B: Chem., Vol. 78, 1, 2001, pp. 119–125.

[14] M. Ferroni, V. Guidi, G. Martinelli, P. Nelli, M. Sacerdoti, G. Sberveglieri, "Characterization of a molybdenum oxide sputtered thin film as a gas sensor", Thin Solid Films, Vol. 307, No. 1, 1997, pp. 148–151.

[15] C. Imawan, F. Solzbacher, H. Steffes, E. Obermeier, "Gas-sensing characteristics of modified-$MoO_3$ thin films using Ti-overlayers for $NH_3$ gas sensors", Sens. Actuators B: Chem., Vol. 64, No. 1, 2000, pp. 193–197.

[16] C. Imawan, H. Steffes, F. Solzbacher, E. Obermeier, "Structural and gas-sensing properties of $V_2O_5$–$MoO_3$ thin films for $H_2$ detection", Sens. Actuators B: Chem., Vol. 77, No. 1, 2001 pp. 346–351.

[17] K. Galatsis, Y. Li, W. Wlodarski, C. Cantalini, M. Passacantando, S. Santucci, "$MoO_3$,$WO_3$ single and binary oxide prepared by sol–gel method for gas sensing applications", J. Sol–Gel Sci. Technol., Vol. 26, No. 1, 2003, pp. 1097–1101.

[18] J. Zhou, S.Z. Deng, N.S. Xu, J. Chen, J.C. She, "Synthesis and fieldemission properties of aligned $MoO_3$ nanowires", Appl. Phys. Lett., Vol. 83, No. 13, 2003, pp. 2653–2655.

[19] A.K. Prasad, P.I. Gouma, D.J. Kubinski, J.H. Visser, R.E. Soltis, P.J. Schmitz, "Reactively sputtered $MoO_3$ films for ammonia sensing", Thin Solid Films, Vol. 436, No. 1, 2003 pp. 46–51.

[20] A.K. Prasad, D.J. Kubinski, P.I. Gouma, "Comparison of sol–gel and ion beam deposited $MoO_3$ thin film gas sensors for selective ammonia detection", Sens. Actuators B: Chem., Vol. 93, No. 1, 2003, pp. 25–30.

[21] A. Bouzidi, N. Benramdane, H. Tabet-Derranz, C. Mathieu, B. Khelifa, R. Desfeux, "Effect of substrate temperature on the structural and optical properties of $MoO_3$ thin films prepared by spray pyrolysis technique", Mater. Sci. Eng. B, Vol. 97, No. 1, 2003, pp. 5–8.

[22] K.A. Gesheva, T. Ivanova, "A low-temperature atmospheric pressure CVD process for growing thin films of $MoO_3$ and $MoO_3$–$WO_3$ for electrochromic device applications", Chem. Vap. Deposit., Vol. 12, No. 4, 2006, pp. 231–238.

[23] R.S. Patil, M.D. Uplane, P.S. Patil, "Structural and optical properties of electrodeposited molybdenum oxide thin films", Appl. Surf. Sci., Vol. 252, No. 23, 2006, pp. 8050–8056.

[24] JCPDS data card no. 05- 0506.

[25] S. Ashraf, C.S. Blackman, G. Hyett, I.P. Parkin, "Aerosol assisted chemical vapour deposition of $MoO_3$ and $MoO_2$ thin films on glass from molybdenum polyoxometallate precursors; thermophoresis and gas phase nanoparticle formation", J. Mater. Chem., Vol. 16, No. 35, 2006, pp. 3575– 3582.

[26] B. D. Cullity, Elements of X-ray diffraction, Addison-Wesley Publishing Co., 1956.

[27] R. S. Patil, M.D. Uplane, P. S. Patil, "Electrosynthesis of Electrochromic Molybdenum Oxide Thin Films with Rod-Like Features", Int. J. Electrochem. Sci., Vol. 3, 2008, pp. 259 – 265.

[28] G. E. Patil D. D. Kajale, P. T. Ahire, D. N. Chavan, N. K. Pawar, S. D. Shinde, V. B. Gaikwad, G. H. Jain, "Synthesis, characterization and gas sensing performance of $SnO_2$ thin films prepared by spray pyrolysis", Bulletin of Material Science Vol. 34, No. 1, 2011, pp.1–9.

[29] G. E Patil, D. D. Kajale, V. B. Gaikwad and G. H. Jain, "Nanocrystalline Tin Oxide Thin Film as a Low Level $H_2S$ Gas Sensor" International Journal of Nanoscience, Vol. 10, No. 4, 2011, pp. 1-5.

[30] G. H. Jain and L. A. Patil, "CuO-doped BSST thick film resistors for ppb level $H_2S$ gas sensing at room temperature", Sensors and Actuators B, Vol. 123, 2007, pp. 246-253.

[31] Franke, M.E., Koplin, T.J., Simon, U., "Metal and metal oxide nanoparticles inchemiresistors: does the nanoscale matter?", Small Vol. 2, 2006, p.36–50.

[32] Rothschild A., Komem, Y., "The effect of grain size on the sensitivity of nanocrystalline metal-oxide gas sensors", Journal of Applied Physics, Vol. 95, 2004, pp. 6374–6380.

[33] G. E. Patil, G. H. Jain, "Nanocrystalline $CdSnO_3$ thin film as highly sensitive ethanol sensor", Proceedings of 5th International Conference on Sensing Technology, ICST 2011, (2011), Article Number: 1569476109, pp. 260-263.