

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).

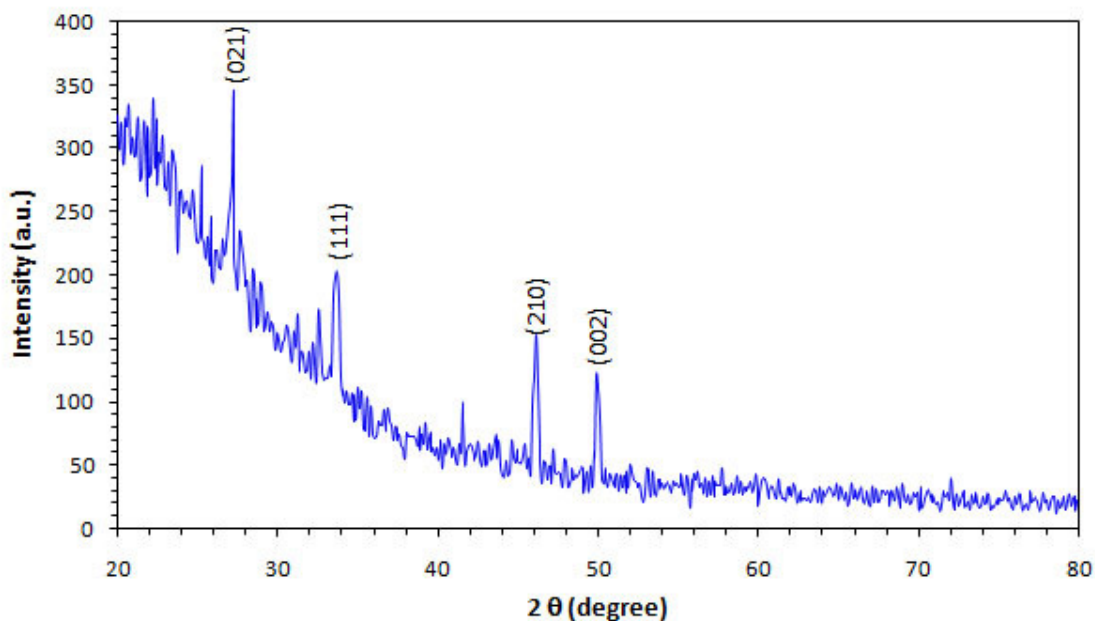


Figure 2. X-ray diffraction spectra of MoO₃ thin film.

b. Surface Morphology

To observe the surface morphology, scanning electron micrographs (SEM) of a thin film sample were taken. Figure 2 shows the SEM of the MoO₃ 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.

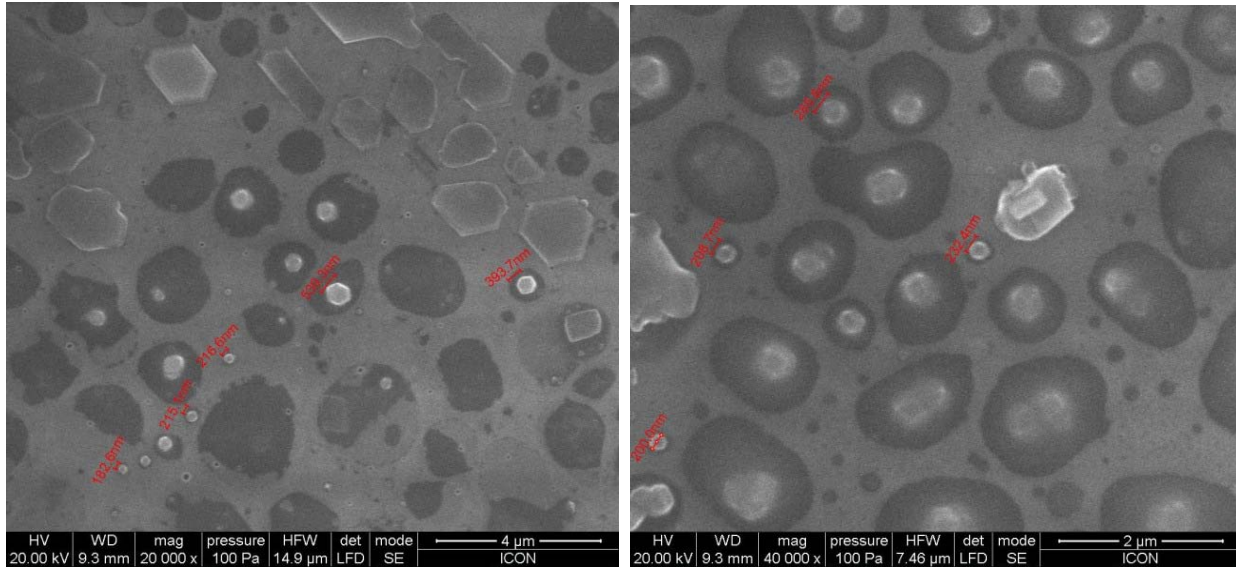


Figure 2. Scanning electron micrographs of MoO₃ thin film.

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 MoO₃ thin a film is widely reported [27].

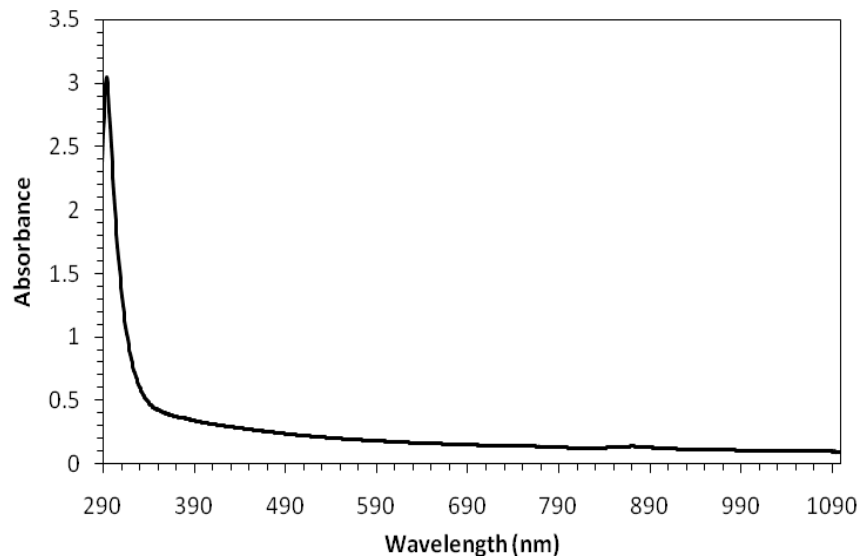


Figure 3. UV-vis spectra of MoO₃ thin film.

d. Electrical Properties of MoO₃ Thin Film

i. I-V Characteristics

Figure 4 depicts the I-V characteristics of MoO₃ thin film at room temperature in air ambient. I-V characteristics observed to be symmetrical in nature, indicating the ohmic nature of contact.

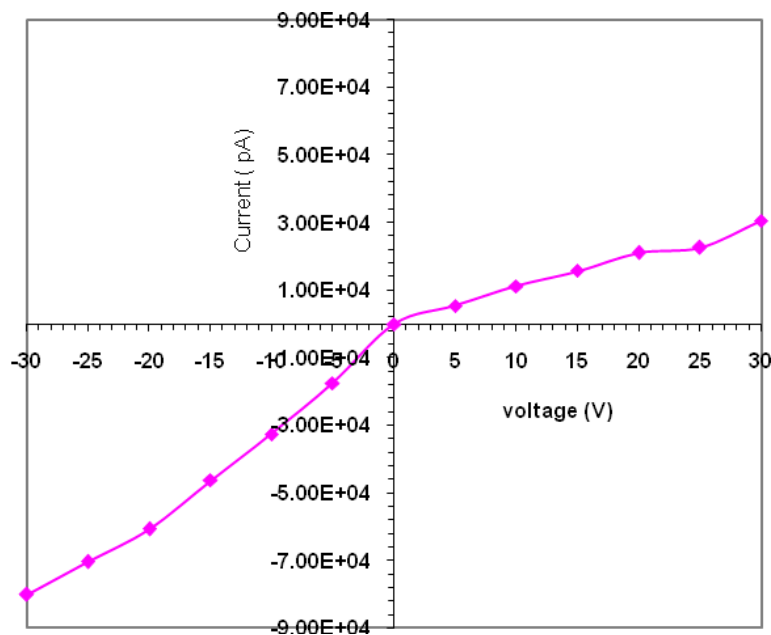


Figure 4. I-V characteristics of MoO₃ thin film.

ii. Electrical Conductivity

Fig. 5 shows the dependence of conductivity of MoO₃ 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.

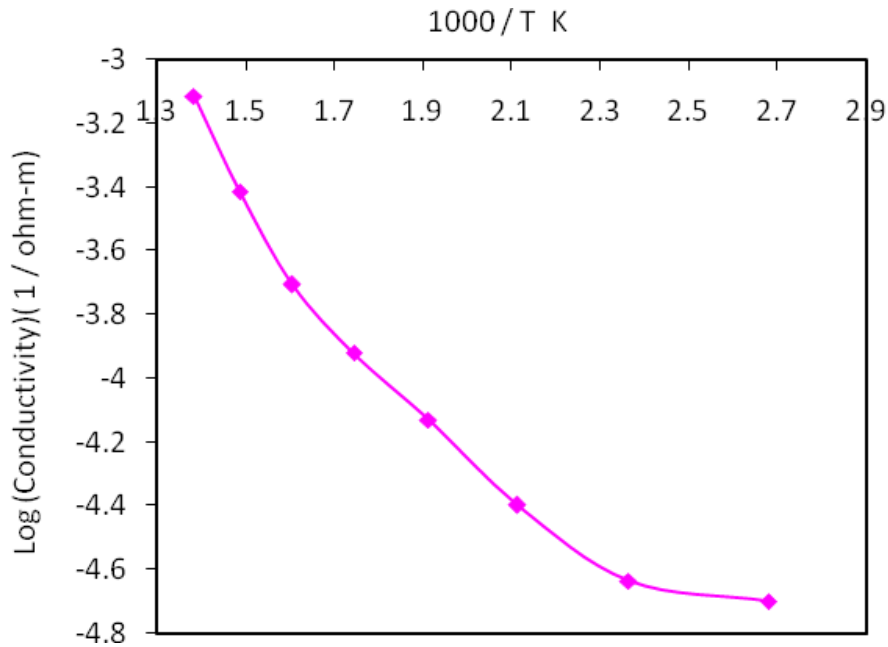


Figure 5. Variation of conductivity with temperature.

e. Gas Sensing Performance

The conductance of the sensor in dry air was measured by means of conventional circuitry 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

$$S = (G_g - G_a) / G_a \quad (4)$$

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 MoO₃ Thin Film

Figure 6 presents the variation in the gas response to various gases (1000 ppm) with operating temperatures ranging from 100° to 400°C. It is noted from the graph that response increases with increasing temperature, and attains a maximum at 300°C for H₂S and at 200°C for ethanol and decreases with further increase in operating temperature.

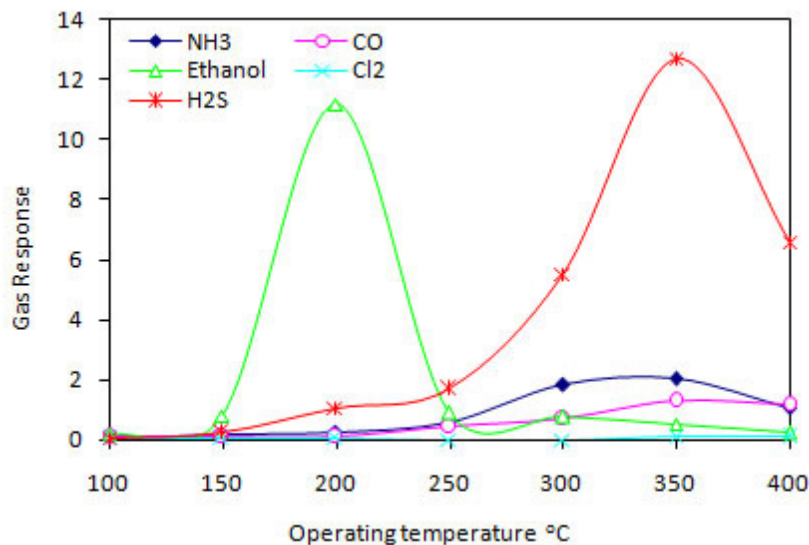


Figure 6. Variation of gas response with temperature.

ii.) Selectivity of MoO₃ Thin Film

Figure 7 presents the bar diagram indicating selectivity of MoO₃ thin film at 350°C to H₂S gas and at 200°C to ethanol against the other gases. The sensor is the most selective to H₂S gas against the other gases.

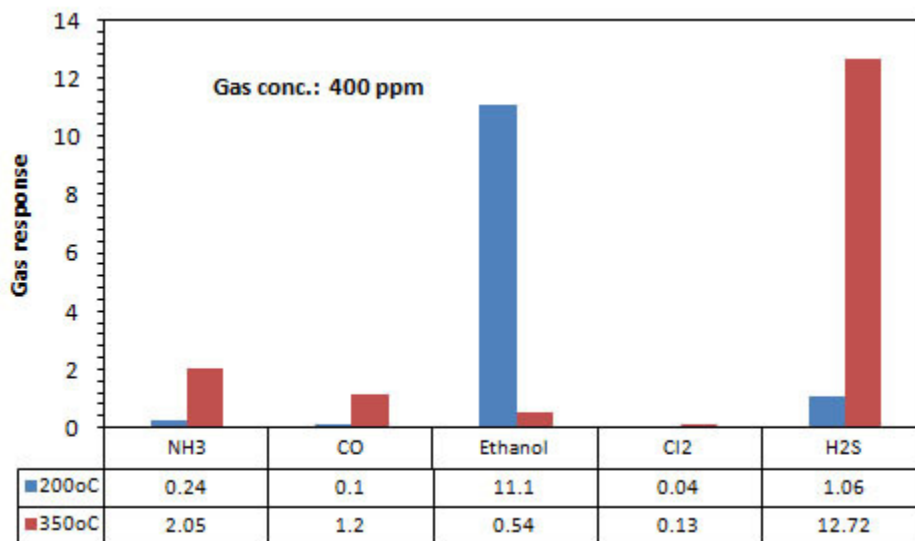


Figure 7. Selectivity of MoO₃ thin film.

iii.) Variation of Sensitivity with Gas Concentration

To test the H₂S gas concentration characteristics, the sensor was exposed to H₂S gas of different concentrations at a constant operating temperature. The sensor responses to H₂S in concentration range (40-480 ppm) are shown in figure 8 at 350°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.

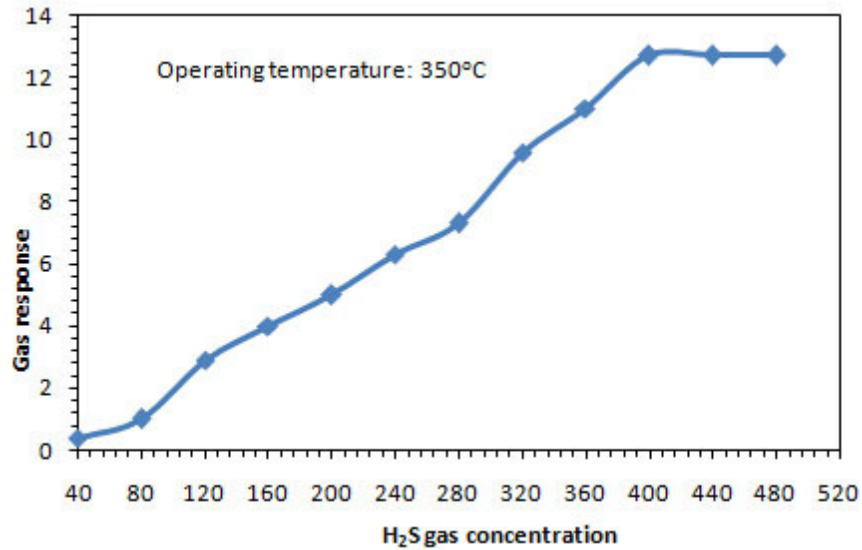


Figure 8. Variataion in sensitivity with H₂S gas concentration.

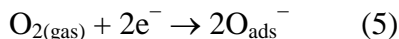
iv.) Response and Recovery Time

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 MoO₃ thin film was 14s and 40s respectively. The large recovery time would be due to lower operating temperature. At lower temperature O₂⁻ species is more prominent adsorbed on the surface, it is less reactive compared to other species of oxygen, O⁻ and O²⁻.

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

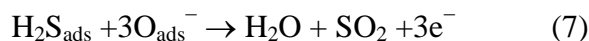
sensitivity [31, 32]. The atmospheric oxygen gets adsorbed on the surface, and depending upon the temperature of operation; different oxygen species are formed on the surface. The gas response by metal oxide semiconductor, in general, can be described as



Initially, (Eq. (5)) the atmospheric oxygen acquires electron from the conduction band of MoO₃ and forms O_{ads}⁻ species on the surface thus decreasing the conductance of the MoO₃.

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 H₂S gas, the reaction (Eq.(7)) takes place thereby forms H₂O and SO₂ gas by releasing electrons back to the conduction band, thus increasing the conductance of the sensor. Again on removal of H₂S the reaction (Eq. (5)) takes place leading to a decrease in the conductance [33]. This can be simply described as in Eq. (7),



IV. CONCLUSION

A simple spray pyrolysis method is used to prepare MoO₃ 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 MoO₃. 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 MoO₃-based sensor was observed to be maximum at 300°C for H₂S and at 200°C for ethanol. The sensor showed good selectivity to H₂S gas against NH₃, Cl₂, CO and ethanol.

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REFERENCES

- [1] W. Gopel, K.D. Schierbaum, "SnO₂ 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 SnO₂ nanofibers", *Materials Letter*, Vol. 63, No. 23, 2009, pp. 2041–2043.
- [6] Y. Wang, W.Z. Jia, T. Strout, A. Schempff, H. Zhang, B.K. Li, J.H. Cui, Y. Lei, "Ammonia gas sensor using polypyrrole-coated TiO₂/ZnO nanofibers", *Electroanalysis*, Vol. 21, No. 12, 2009, pp. 1432–1438.
- [7] A. K. Prasad, P.I. Gouma, "MoO₃ and WO₃ based thin film conductometric 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 MoO₃", *Sens. Actuators B*, Vol. 101, No. 1, 2004, pp. 161–174.

- [9] M. Ferroni, V. Guidi, G. Martinelli, M. Sacerdoti, P. Nelli, G. Sberveglieri, "MoO₃- based sputtered thin films for fast NO₂ 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 MoO₃ 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 V₂O₅-MoO₃-TiO₂ 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 MoO₃ 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-MoO₃ thin films using Ti-overlayers for NH₃ 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 V₂O₅-MoO₃ thin films for H₂ 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, "MoO₃, WO₃ 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 MoO₃ 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 MoO₃ 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 MoO₃ 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 MoO₃ 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 MoO₃ and MoO₃-WO₃ 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 MoO₃ and MoO₂ 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 SnO₂ 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 H₂S 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 H₂S gas sensing at room temperature", *Sensors and Actuators B*, Vol. 123, 2007, pp. 246-253.
- [31] Franke, M.E., Koplín, T.J., Simon, U., "Metal and metal oxide nanoparticles in chemiresistors: 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 CdSnO₃ thin film as highly sensitive ethanol sensor",
Proceedings of 5th International Conference on Sensing Technology, ICST 2011, (2011),
Article Number: 1569476109, pp. 260-263.