Binary Oxide In2O3: MoO3 Thin Films : Study of, Structral, Electrical and Gas Sensing Properties

[1]Dhanwate S. V.,[2]Gosavi R.S., [3]Kothawade N B

[1]Associate Professor and Head Department of Physics, Swami Muktanand College of Science, Yeola(Nashik), India -423401

[2]P.G. Teacher and Associate Professor in Physics, Loknete Ramdas Patil Dhumal ASC College Rahuri Dist. A' Nagar , India 413705

[3]Associate Professor and Head Department of Physics, Arts Commerce and Science College, Kalwan (Manur) Dist. Nashik, India 423501

***Abstract*- It is found that particular gases are not sensed by undopped gas sensors . For the improvement of the sensitivity and selectivity of sensor is most is necessary. The dopants or additives can be used to change the gas sensing characteristics. In the pure material A suitable catalyst or dopant is often added in small percentage to enhance the sensitivity and selectivity. Nanocomposite films of nanocrystalline or amorphous phase of a least two different materials can be developed and used as gas sensor. In_2O_3:MoO_3 binary oxide thin films were prepared using spray pyrolysis technique on glass substrate at 400^0C temperature and taking In_2O_3 as a dopant and MoO_3 as a functional material. The precursor $InCl_3$ and $MoCl_5$ of concentrations 0.1N: 0.1N. The In_2O_3:MoO_3 binary oxide thin films were studied for the parameters like sensitivity, selectivity, response time, grain size, surface area, and stability of the gas sensors which were improved by addition of different dopants, and the results of the analysis are presented in the paper.**

***Keywords* - Gas sensor, spray pyrolysis technique, binary oxide thin films,In_2O_3, MoO_3,Thin film, XRD, SEM and EDS.**

INTRODUCTION

The SMOs used as gas sensor materials, are crystalline in nature and they are connected to their neighboring grains by necks. These interconnected grains form larger aggregates which are connected to their neighbors by grain boundaries.The sensitivity and selectivity of sensor can be improved by dopants or additives which can change the gas sensing characteristics. A suitable catalyst or dopant is often added in small percentage in the pure material to enhance the sensitivity and selectivity.Dopant element into In_2O_3 sensing materials may cause the change of crystalline structure and grain size as well as impurity levels and surface defects, which can significantly improve the gas sensing performances of In_2O_3 gas sensor.MoO_3 exhibits the highest value of work function among the non-soluble transition metal oxides. MoO_3 nanoparticles have attracted a great deal of attention due to their unique physical and chemical properties that differ from those in the bulk, in particular for their high surface-to-volume ratio.

METHODOLOGY

The binary oxide In_2O_3: MoO_3 thin films were deposited by modified spray pyrolysis setup developed, designed and assembled in laboratory to overcome limitations of conventionally designed setup; such as number of optimized parameters, reliability and homogeneity of the deposited films. Binary oxide In_2O_3: MoO_3 thin films were prepared by spray pyrolysis technique. The spray Pyrolysis process was carried out at substrate temperature 400^0C.The precursor $InCl_3$ and $MoCl_5$ of concentrations 0.1N, 0.2N and 0.3N were used. The thin films of In_2O_3: MoO_3 were prepared for concentration in proportion of 0.1N: 0.1N. The characterization of the deposited film such as SEM, EDS, XRD, resistivity, activation energy, TCR and gas sensing property were studied to find out the changes due to dopant.

RESULTS AND DISCUSSION

The material nature and sensor operation study was done with the help of electrical and structural characterization. XRD gives the details of the effect of crystallite size and material phase. Surface morphology/specific surface area determined by using

SEM, and EDS gives chemical composition. The prepared material/films can be used as a gas sensor analyzed by using such types of different characterization techniques.

The structural characteristics of Binary oxide In_2O_3: MoO_3 thin films at 0.1N: 0.1N, was studied with the help of Surface Morphology using Scanning Electron Microscopy (SEM) ,Elemental analysis using Energy Dispersive X-Ray Analysis (EDAX) ,Structural characterization using X Ray Diffraction (XRD).

1.SCANNING ELECTRON MICROSCOPY (SEM)

The Surface Morphology study was done by Scanning Electron Microscopy (SEM) (Model JOEL 6300 LA Germany)

The SEM of binary oxide In_2O_3:MoO_3 thin films of 0.1N: 0.1N deposited on glass substrate using a Spray Pyrolysis Technique and fired at 400^0C was obtained as shown infigure. with magnifications of image at 10000X.

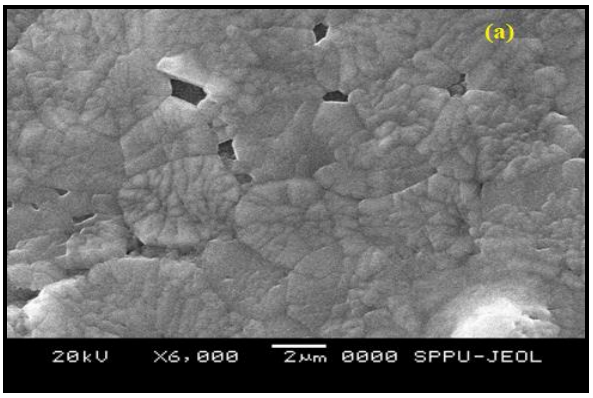

Figure : SEM of Binary oxide In_2O_3: MoO_3 thin with concentration 0.1N:0.1N

SEM analysis shows non porous nature of Binary oxide In_2O_3: MoO_3 Films prepared by Spray Pyrolysis. The average particle size of film was calculated by using image j software using SEM analysis. The average particle size of film was found as 255nm at concentrations 0.1N:0.1N.

BET method was used to determine the specific surface area of Binary oxide In_2O_3: MoO_3thin film.

The following equation was used,

$$S_w = \frac{6}{\rho d}$$

Where, d is the diameter of the particles, ρ is the density of the particles.

The specific Surface area with different concentrations of binary oxide In_2O_3: MoO_3 was found as 37.40401 m^2/g.

2.ENERGY DISPERSIVE X-RAY ANALYSIS (EDS)

The elemental analysis of Binary oxide In_2O_3: MoO_3 thin films was done using EDAX (JOEL, JED Germany). The EDAX analysis was used to found the presence of In, Mo and O as expected, no other impurity elements were present in the all samples.

Figure shows count (along Y- axis) Verses KeV (along X-axis) EDS of 0.1N:0.1N concentration of binary oxide In_2O_3: MoO_3 thin films.

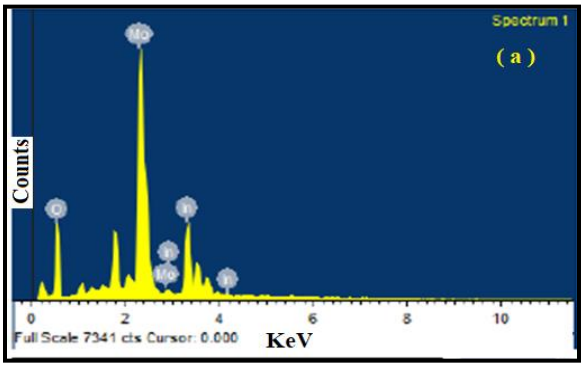

Figure : EDS of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.1N

The EDAX spectra, shows that the mass% and at. wt.% of In, Mo and O is nearly matched.

The table gives details of EDS of Binary oxide In_2O_3: MoO_3 thin film with Concentration 0.1N:0.1N

Element	Atomic %
O	85.84
Mo	10.24
In	3.93

3.X-RAY DIFFRACTION ANALYSIS (XRD)

The structure and phases of binary oxide In_2O_3: MoO_3thin films on glass substrate fired at 400^0C was determined by XRD study. X-ray diffraction analysis of In_2O_3: MoO_3thin films were carried out in 20-80^0 range using X powder 12(CuKα) Radiation.

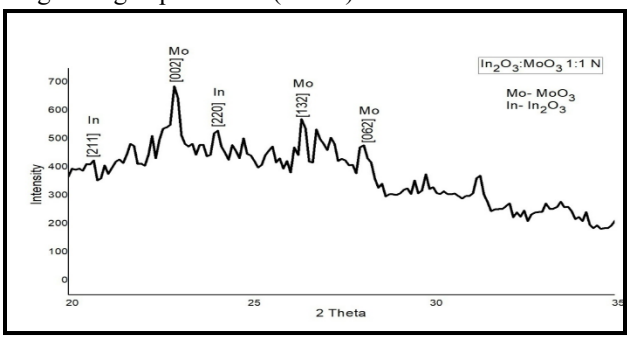

Figure: XRD of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.1N

XRD of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.1N is shown in table

Plane (hkl)	2θ	d-spacing	Intensity	I/Io	FWHM
In- 211	21.68	4.09424	483.0	70.4	1.850
Mo- 002	22.92	3.87575	686.0	100.0	2.884
In- 220	24.16	3.67381	473.0	69	2.847
Mo- 132	26.46	3.36493	537.0	78.3	3.715
Mo- 062	28.14	3.16765	478.0	69.7	4.641

The average grain size was determined by using Debye-Scherer formula,

$$D = 0.9\lambda / \beta \cos\theta$$

β is full angular width of diffraction peak at half maximum peak intensity, λ is wavelength of X-radiation.

The grain sizes of film were found 3 nm.

ELECTRICAL CHARACTERIZATION

The electrical characterization was done to measure the variation in electrical resistance at operating temperatures in air atmosphere, the resistivity, TCR and activation energy.

1. RESISTIVITY

The half bridge method as a function of temperature was used to determine the DC resistance of In_2O_3:MoO_3 thin films with normality 0.1N:0.1Non glass substrate and fired at 400^0C. The resistance variation of In_2O_3:MoO_3thin films with normality 0.1N:0.1N temperature variation in an atmosphere was obtained as shown in figure. The resistance decreases with increase in temperature indicating semiconductor behavior, obeying $R= R_0e^{-\Delta E/KT}$ in the temperature range of 40-350^0C.

The resistance In_2O_3:MoO_3thin films with normality 0.1N:0.1N falls rapidly, decreases linearly up to certain transition temperature and after resistance decreases exponentially with increase in temperature and lastly saturates to steady level.

The resistivity of In_2O_3:MoO_3 thin films at constant temperature is calculated using the relation,

$$\rho = (R \times A) / l$$

$$\rho = (R \times b \times t) / l \quad ohm\text{-}m$$

Where, R = Resistance of In_2O_3 :MoO_3 thin film at constant temperature

t = thickness of the film sample

l = length of the thin film

b = breadth of the thin film

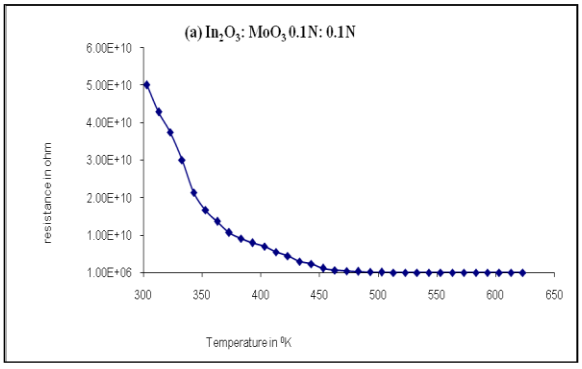

Figure: Resistance of Binary oxide In_2O_3: MoO_3 thin with concentration 0.1N:0.1N

The resistivity of film was calculated 13.125 x10^3 Ω-m.

2. ACTIVATION ENERGY

Figure shows plot of log(R) versus reciprocal of temperature, (1/*T*) for In_2O_3:MoO_3 thin films with normality 0.1N:0.1N.

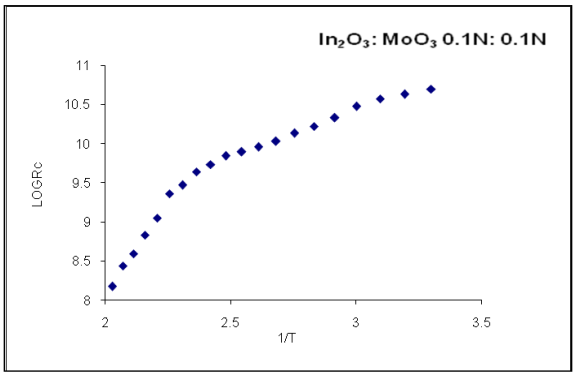

Figure: Activation energy of Binary oxide In_2O_3:MoO_3 thin film with concentration 0.1N:0.1N

This plot is reversible in both heating and cooling cycles obeying the Arrhenius equation

$$R=R_o\, e^{-\Delta E/KT}$$

Where, Ro = the constant = Resistance at room temperature

ΔE = The activation energy of the electron transport in the conduction band,

K = Boltzman constant and

T = Absolute temperature

The Activation energy at high temperature and at low temperature were found 0.1622 eV and 0.5774 eV respectively.

3. TCR

Temperature coefficient of resistance (TCR) of In_2O_3: MoO_3thin films prepared at 400^{O}C is calculated by using the following relation,

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right) \ /^O K$$

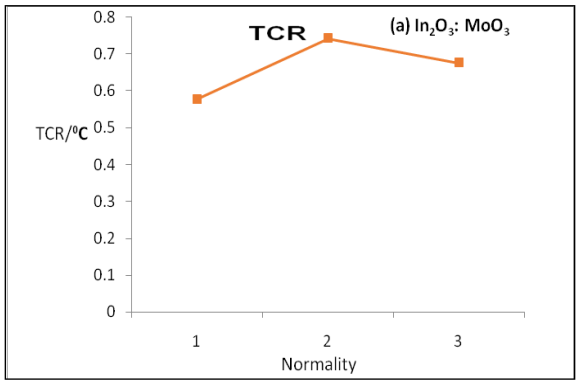

Figure:TCR graph of binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.1N

The temperature coefficient of resistance (TCR) was found as 0.0183/ ^{0}C

4. GAS SENSING PROPERTIES

The main characterization is the optimization of operating temperature of film sample for test gases. On the basis of measured data, the sensitivity and selectivity of thin film sensor for a fixed gas concentration of 1000 ppm in air surrounding condition were estimated.

The variation in sensitivity of binary oxide In_2O_3:MoO_3thin films as a function of temperature and for LPG, Ethanol, NH_3, CO and NO_2 gases [1000 ppm concentration]. The operating temperature was varied at the interval of 50^{o}C. From the measured resistance in air as well as in gas atmosphere, the sensitivity of gas was determined at particular operating temperature using the following equation ,

$$Sensitivity(S) = \left|\frac{R_a - R_g}{R_a}\right| \times 100$$

Where, R_a – resistance of thin film in air atmosphere,

R_g – resistance of thin film in gaseous atmosphere.

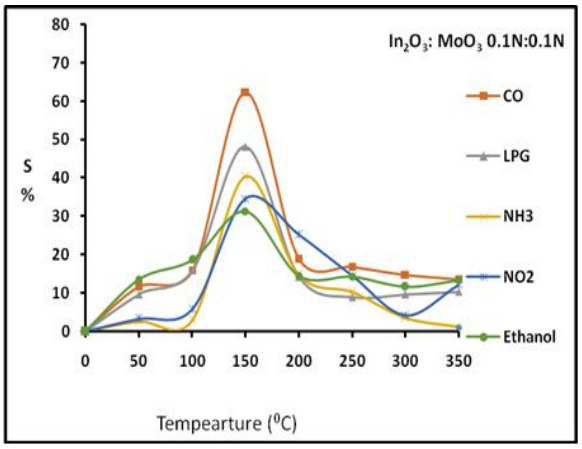

Figure: Gas sensitivity response of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.1N

The film of binary oxide In_2O_3:$MoO_3$was exposed to various gases.The film of binary oxide In_2O_3: $MoO_3$was exposed to various gases. The film of In_2O_3: MoO_3 at 0.1N:0.1N showed 62.35 % sensitivity for CO gas at operating temperature 150^{0}C and CO gas concentration was at 300 ppm.

CONCLUSION

We have deposited Binary oxide In_2O_3: MoO_3thin films with normality 0.1N:0.1N on glass substrate and fired at 400^{0}C to change the characteristic properties of thin film .The film was deposited using spray Pyrolysis process at substrate temperature 400^{0}C.The precursor $InCl_3$ and $MoCl_5$ of concentrations 0.1N, 0.2N and 0.3N were used. The average particle size of film at concentrations0.1N:0.1N was found 255 nm. Specific Surface area with different concentrations of binary oxide In_2O_3:MoO_3 was found as 37.40401m^2/g. The atomic % of O, Mo, In were found as 85.84% ,10.24% and 3.93 % respectively. XRD gives the grain size of film 3 nm.The resistivity of samplewas calculated 13.125 x10^3 Ω-m.The Activation energy at high temperature and at low temperature were found as 0.1622 eV and 0.5774 eV respectively .The temperature coefficient of resistance were found was 0.0183/ ^{0} C.The film of In_2O_3: MoO_3 at 0.1N:0.1N showed 62.35 % sensitivity for CO gas at operating temperature 150^{0}C and CO gas concentration was at 300 ppm.

REFERENCE

[1] X. Chen, S.S. Mao, Chem. Rev. 107 (2007) 2891–2959.

[2] Y.F. Sun, S.B. Liu, F.L. Meng, J.Y. Liu, L.T. Kong, J.H. Liu, Sensors 12 (2012) 2610–2631.
[3] S. Matsushima, Y. Teraoka, N. Miura, N. Yamazoe, Jpn.J.Appl.Phys.27 (1988) 1798- 1802
[4] J. G. Duh, J. W. Jou, B. S. Chiou, Electrochem.Soc.136 (1989) 2740-2747
[5] S. Basu, A. Dutta, Materials Chemistry and Physics 47(1997) 93-96
[6] G. UozumiM.Miyayama, H.Yanagida, Journal of Materials Science 32 (11) (1997) 2991-2996.
[7] Sian.T.S and Reddy.G.B, Appl.Surf.Sci., 2004,236, 1-5.
[8] Titkov.IE, Delimova.LA, Zubrilov.AS, Seredova.NV, Liniichuk.IA and GrekhovIV: J Mod Opt., 2009, 56, 653–660.
[9] G. Korotcenkov, Sens. Actuators B: chem., 107, 2005, 209–232.
[10] S. Matsushima, Y. Teraoka, N. Miura, N. Yamazoe, Jpn.J.Appl.Phys.27 (1988) 1798- 1802
[11] J. G. Duh, J. W. Jou, B. S. Chiou, Electrochem.Soc.136 (1989) 2740-2747
[12] S. Basu, A. Dutta, Materials Chemistry and Physics 47(1997) 93-96.
[13] X. P. Shen, L. J. Guo, G. X. Zhu, C. Y. Xi, Z. Y. Ji and H. Zhou, RSC Adv., 2015, 5, 64228–64234.
[14] X. Y. Lai, P. Li, T. L. Yang, J. C. Tu and P. Xue, Scr. Mater., 2012, 67, 293–296.
[15] W. W. Chen, Y. K. Liu, Z. J. Qin, Y.
[16] P. Prathap, N. Revathi, K. T. R. Reddy, and R. W. Miles, Thin SolidFilms 518, 1271 (2009).
[17] T. Brezesnski, J. Wang, S. H. Tolbert and B. Dunn, Nat. Mater., 9 (2010) 146.
[18] E. B. Santos, F. A. Sigoli, I. O. Mazali, J. Solid State Chem. 190 (2012) 80-84.
[19] Granqvist.C.G, Handbook of Inorganic Electrochromic Materials, Elsevier, 115.
[20] Sian.T.S and Reddy.G.B, Appl.Surf.Sci., 2004,236, 1-5.
[21] X. Chen, S.S. Mao, Chem. Rev. 107 (2007) 2891–2959.
[22] Y.F. Sun, S.B. Liu, F.L. Meng, J.Y. Liu, L.T. Kong, J.H. Liu, Sensors 12 (2012) 2610–2631.
[23] L.Gao, Li, Q., Song, Z., Wang Sens. Actuators B71 (2000) 179-183
[24] S. Cho, J. Korean Phys. Soc. 60, 2058 (2012).
[25] D.R. Patil, L.A.Patil, Sensors and Actuators B 123 (2007) 546–553.
[26] L. Satyanarayana, K. Madhusudan Reddy, S.V. Manorama, Sensors and Actuators B 89(2003) 62-67.
[27] D.M. Smyth, Solid State 129 (2000) 5–12.
[28] D. V. Ahire, S. D. Shinde, G. E. Patil, K. K. Thakur, V. B. Gaikwad, V. G. Wagh1 and G. H. Jain, International Journal on Smart Sensing And Intelligent Systems, Vol. 5, No. 3, September 2012,Issn 1178-5608