A STUDY OF PHYSICAL AND GAS SENSING PROPERTIES OF BINARY OXIDE In_2O_3: MoO_3 THIN FILMS.

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

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

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

ABSTRACT

thin films of In_2O_3:MoO_3: was prepared by spray pyrolysis technique by using $InCl_3$ and $MoCl_5$ of concentrations 0.1N, 0.2N. A suitable dopant is often added in small percentage in the pure material to enhance the sensitivity and selectivity.The X-ray diffraction and particle size was evaluated the surface morphology was studied by using SEM The changes in 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 :- XRD , SEM and EDS.Gas sensor,binary oxide thin films,In_2O_3, MoO_3,Thin film,

INTRODUCTION

Recent studies have shown that the physical properties of nanoparticles are enhanced significantly by various processing techniques and with composition. This method is used to obtain improved properties , more homogeneity and particle distribution , thereby influencing structural, electrical and morphological properties of SMOs. 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 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.

EXPERIMENTAL METHODS

The high purity AR grade material were used for the deposition of binary oxide In_2O_3: MoO_3 thin films modified spray pyrolysis setup has been 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. 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 were used. The thin films of In_2O_3: MoO_3 were prepared for concentration in proportion of 0.1N:0.2N. The study of characteristics such as SEM, EDS,XRD, resistivity, activation energy, TCR and gas sensing property were done to study the changes due to dopant.

RESULTS AND DISCUSSION

In the present synthesis Structural, Electrical and Morphological characterization is one of the most important aids to study the material nature and sensor operation. The effect of crystallite size and material phases can be determine using XRD, surface morphology can be determine using SEM, and chemical composition determine using EDS. The prepared films can be used as a gas sensor analyzed by using such types of different characterization techniques.

X-RAY DIFFRACTION ANALYSIS (XRD)

Structural characterization was carried out with the help of XRD. The structure and phases of binary oxide In_2O_3: MoO_3 thin films on glass substrate fired at 400^0C XRD study had been considered. X-ray diffraction analysis of In_2O_3: MoO_3 thin films were carried out in $20\text{-}80^0$ range using X powder 12(CuKα) Radiation.

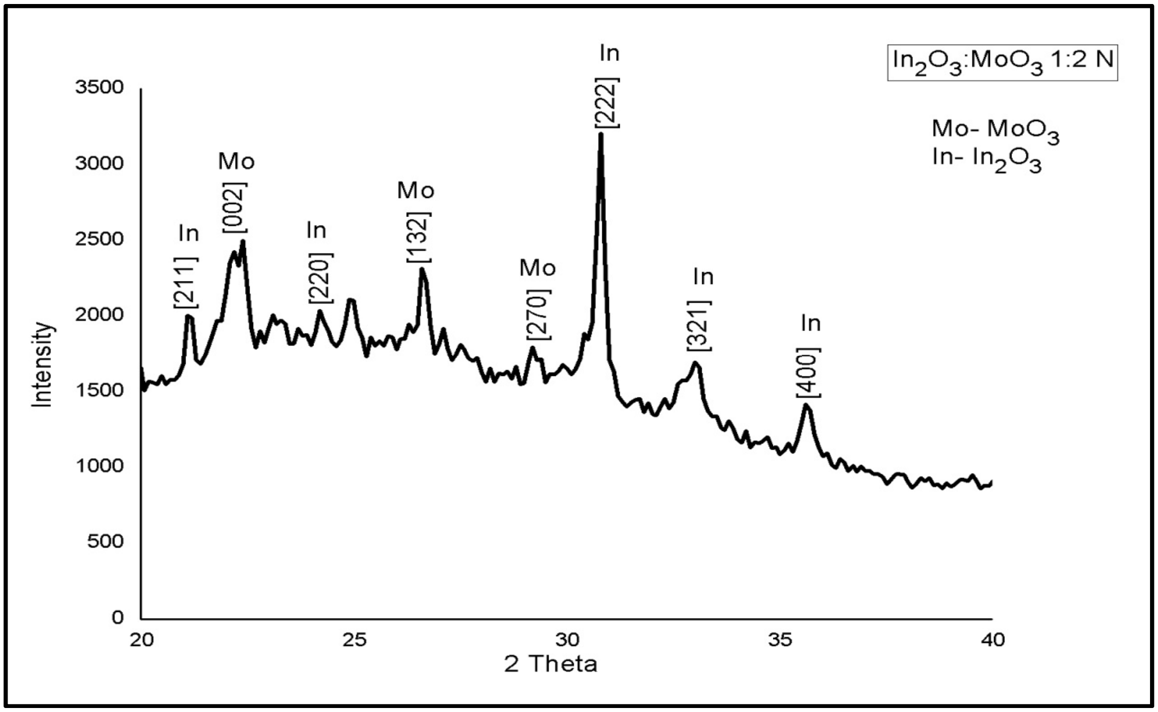

Figure: XRD of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.2N

XRD of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.2N is shown in table

Plane (hkl)	2θ	d-spacing	Intensity	I/Io	FWHM
In- 211	21.15	4.19576	1989.0	620	1.4897
Mo-002	22.35	3.97415	2334.0	72.8	2.488
In- 220	24.96	3.56417	2105.0	65.7	4.061
Mo-132	26.64	3.34296	2317.0	72.3	4.226
Mo-270	29.16	3.05938	1708.0	53.3	8.048
In- 222	30.80	2.90042	3206.0	100.0	1.902
In- 321	33.01	2.71096	1634.0	52.8	1.902
In- 400	35.67	2.51505	1416.0	44.2	1.902

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.

As per structural analysis the grain size were calculated by using Scherrer formula. The grain size of film at concentrations 0.1N:0.2N, were found 5 nm.

SCANNING ELECTRON MICROSCOPY (SEM)

Scanning Electron Microscopy (SEM) technique is used to study Surface Morphology. Scanning Electron Microscopy (SEM) (Model JOEL 6300 LA Germany) was utilized to characterize the surface morphology.

Figure shows the SEM of binary oxide In_2O_3:MoO_3 thin films of 0.1N: 0.2N was deposited on glass substrate using a Spray Pyrolysis Technique and fired at 400^0C.The magnifications of all SEM images are taken at 10000X.

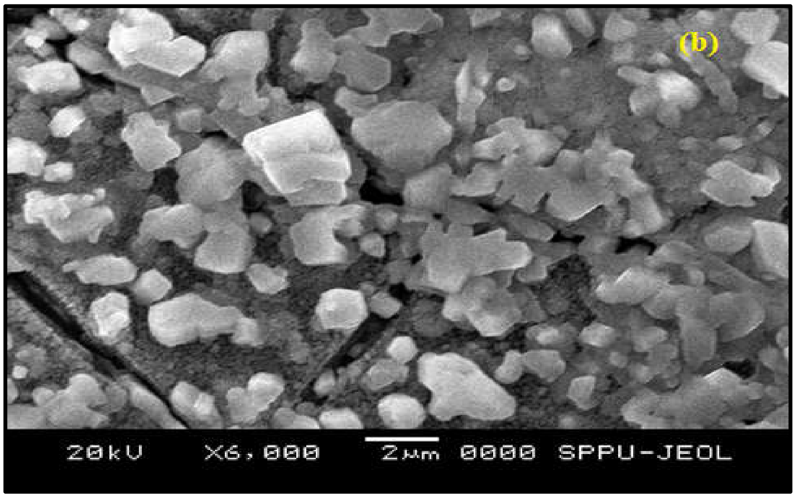

Figure : SEM of Binary oxide In_2O_3: MoO_3 thin with concentration 0.1N:0.2N

Binary oxide In_2O_3: MoO_3Films prepared by Spray Pyrolysis were observed to be non porous as per SEM analysis. As per SEM analysis, the average particle size of film was calculated by using image j software.

The average particle size of film at concentrations 0.1N:0.2N was foundas 525nm.

The specific surface area of Binary oxide In_2O_3: MoO_3thin film was calculated using BET method for spherical particles using the equation ,

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

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

The specific Surface area with 0.1N:0.2N concentrations of binary oxide In_2O_3: MoO_3 was found as 39.42009m^2/g.

ENERGY DISPERSIVE X-RAY ANALYSIS (EDS)

The EDAX analysis of Binary oxide In_2O_3: MoO_3 thin films with normality 0.1N:0.2N on glass substrate and fired at 400^{0}C was studied using (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:0.2N concentration of binary oxide In_2O_3: MoO_3 thin films.

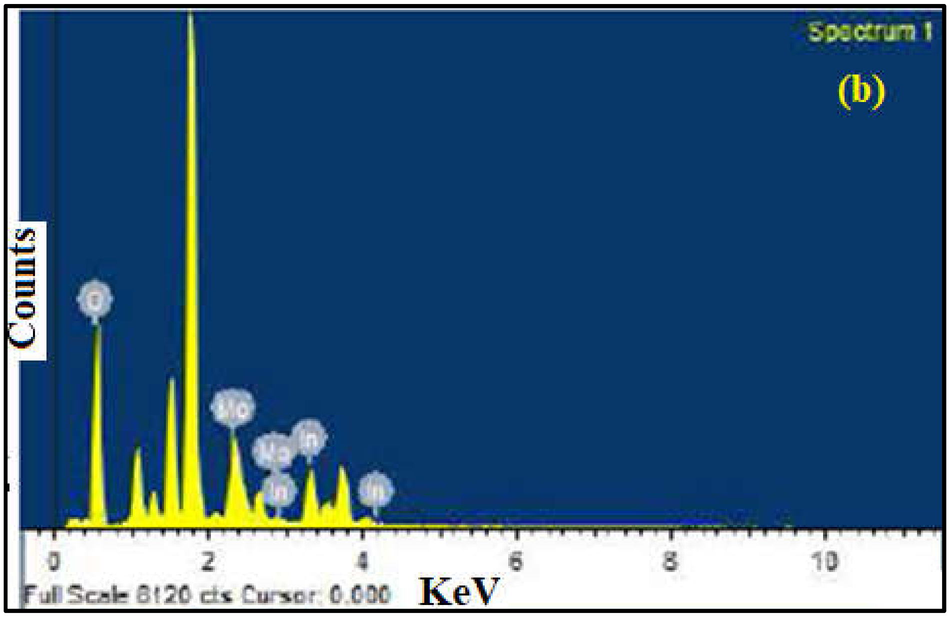

Figure : EDS of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.2N

From the EDAX spectra, it is found that mass% and at. wt.% of In, Mo and O is nearly matched.

EDS of Binary oxide In_2O_3: MoO_3 thin film with Concentration 0.1N:0.2N is shown in table

Element	Atomic %
O	95.29
Mo	2.82
In	1.89

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.

RESISTIVITY

Electrical characterization was carried out with the help of DC resistance of In_2O_3:MoO_3 thin films with normality 0.1N:0.2Non glass substrate and fired at 400^0C was measured by using half bridge method as a function of temperature. Figure shows resistance variation of In_2O_3:MoO_3thin films with normality 0.1N:0.2N temperature variation in an atmosphere. There is decrease in resistance 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:0.2Nfalls 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,

$$\rho = (R \text{ x } A) / l$$

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

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

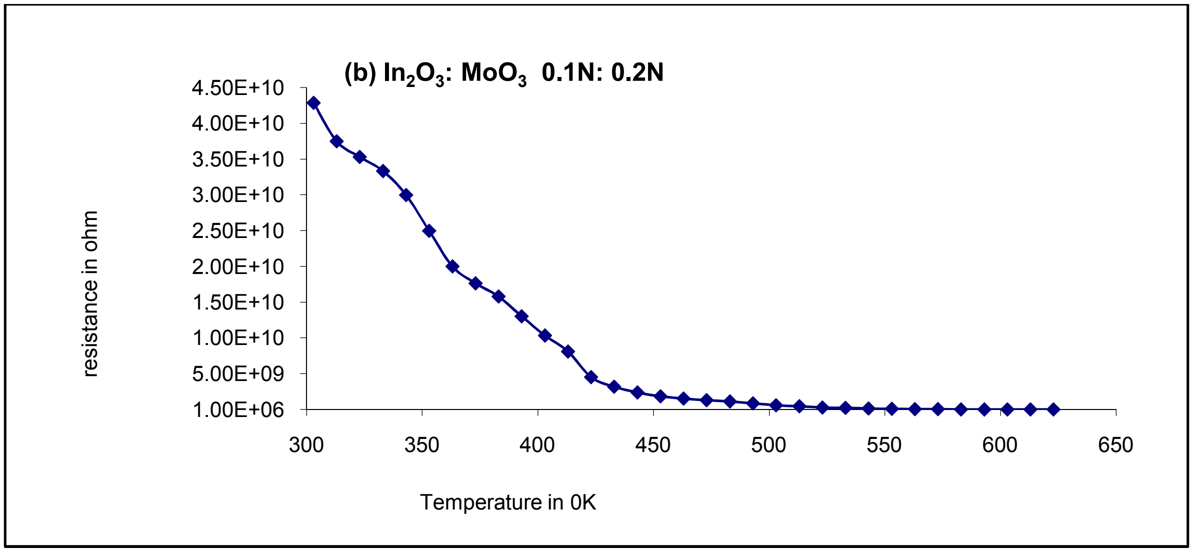

Figure: Resistance of Binary oxide In_2O_3: MoO_3 thin with concentration 0.1N:0.2N

The resistivity of binary oxide In_2O_3:MoO_3sample with concentrations 0.1N:0.2N, of MoO_3 as additives in TiO_2 film was calculated 10.500 x10^3 Ω-m.

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:0.2N.

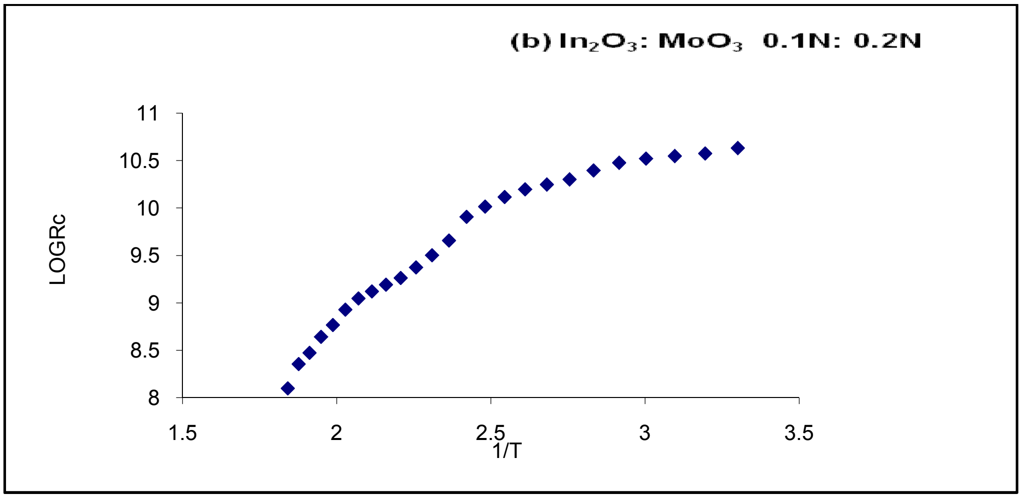

Figure: Activation energy of Binary oxide In_2O_3:MoO_3 thin film with concentration 0.1N:0.2N

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 0.2998 eV and 0.7420 eV respectively at 0.1N:0.2N .

TEMPERATURE COEFFICIENT OF RESISTANCE (TCR)

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

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

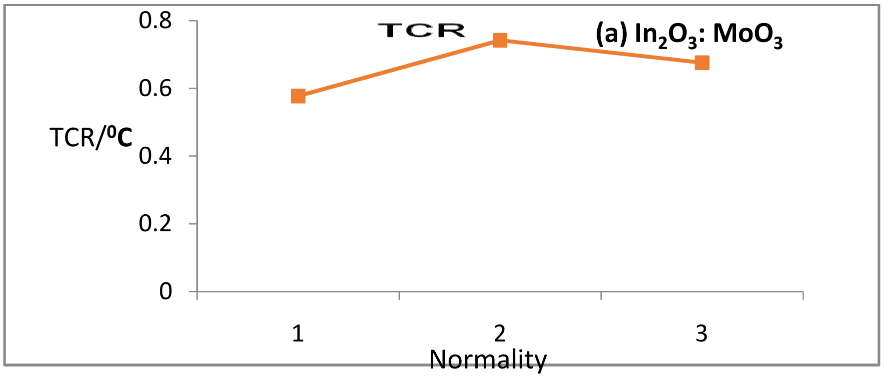

Figure:TCR graph of binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.2N

Figure shows the variation of TCR with operating temperature of the binary oxide In_2O_3: MoO_3thin films. It is found that TCR is negative and its value decreased gradually with increase of operating temperature, The temperature coefficient of resistance(TCR) was found as 0.0300/ ^{0}C .TCR of binary oxide In_2O_3: MoO_3thin film deposits are negative.which suggests an electron emission process which always improves with rise in temperature.

GAS SENSING PROPERTIES

The variation in sensitivity of binary oxide In_2O_3:MoO_3thin films as a function of temperature dependent and for LPG, Ethanol, NH_3, CO and NO_2 gases The operating temperature was varied at the interval of 50°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.

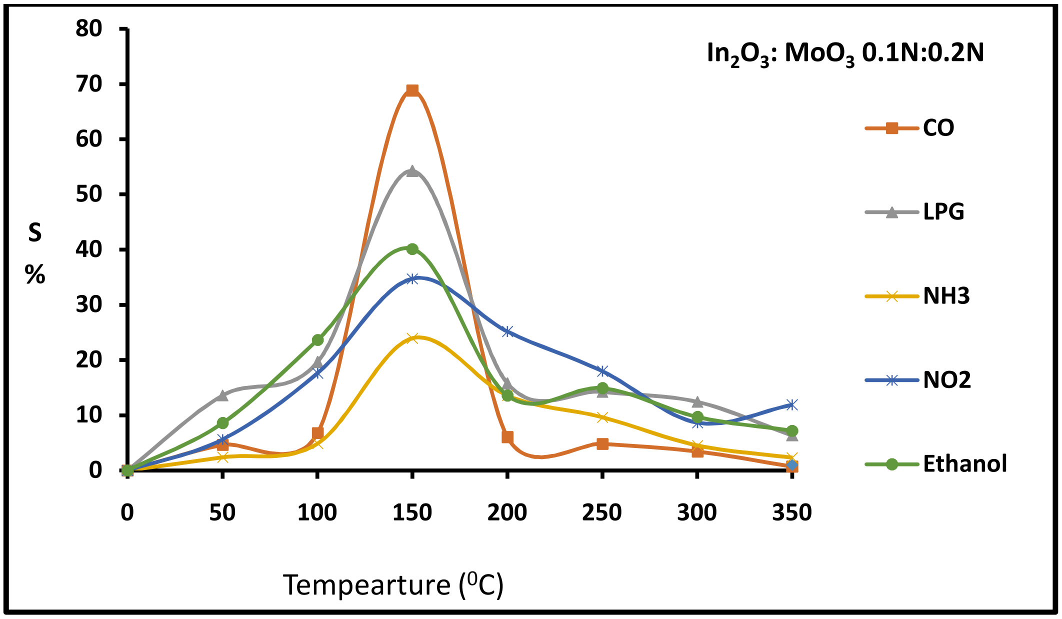

Figure: Gas sensitivity response of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.2N

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:0.2N showed 68.78 % sensitivity for CO gas at operating temperature 150^{0}C and CO gas concentration was at 300 ppm.

CONCLUSION

In binarymetal oxideIn_2O_3:$MoO_3$the average particle size of film at concentrations0.1N:0.2N was found 525 nm. Specific Surface area with different concentrations of binary oxide In_2O_3:MoO_3 was found as 39.42009m^2/g. The atomic % of O, Mo, In were found as 95.29% ,2.82% and 1.89% respectively. XRD gives the grain size of film 5 nm.The resistivity of samplewas calculated 10.500 x10^3 Ω-m.The Activation energy at high temperature and at low temperature were found as 0.2998 eV and 0.7420 eV respectively .The temperature coefficient of resistance were found was 0.0300/ ^{0} C.The film of In_2O_3: MoO_3 at 0.1N:0.2N showed 68.78 % sensitivity for CO gas at operating temperature 150^{0}C and CO gas concentration was at 300 ppm.

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