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SYNTHESIS AND CHARACTERIZATIONOF OF BINARY OXIDE In_2O_3 : MoO_3 THIN FILMS

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ABSTRACT

The sensitivity and selectivity of undoped gas sensor can be improved by dopants or additives which can change the gas sensing characteristics The gas sensors are not able to sense for a particular gas in this condition to improve the sensitivity and selectivity of sensor is most important task.. A suitable catalyst or dopant is often added in small percentage in the pure material to enhance the sensitivity and selectivity. Nanocomposite term contain mixture of two or more nano oxide materials like binary oxide, ternary oxide. Nanocomposite films consists of nanocrystalline or amorphous phase of a least two different materials In_2O_3:MoO_3 binary oxide thin films were prepared by using spray pyrolysis technique on glass substrate at 400^0C temperature. In_2O_3 as dopant and MoO_3 as a functional material in film. The precursor $InCl_3$ and $MoCl_5$ of concentrations 0.1N:0.3N. 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 :- Gas sensor, spray pyrolysis technique , binary oxide thin films,In_2O_3 , MoO_3,Thin film, XRD , SEM and EDS.

INTRODUCTION

A suitable catalyst or dopant is often added in small percentage in the pure material to enhance the sensitivity and selectivity. The semiconductor metal oxide is 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. 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 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 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. Binary oxide In_2O_3: MoO_3 thin films were prepared by spray pyrolysis technique.. The thin films of In_2O_3: MoO_3 were prepared for concentration in proportion of 0.1N:0.3N . 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

The study of structural characteristics of Binary oxide In_2O_3: MoO_3 thin films at 0.1N:0.3N was studied by techniques such as Surface Morphology using Scanning Electron Microscopy (SEM) , Elemental analysis using Energy Dispersive X-Ray Analysis (EDAX) ,Structural characterization using X Ray Diffraction (XRD) .Electrical and structural 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/specific surface area determine using SEM, and chemical composition determine using EDS. The prepared material/films can be used as a gas sensor analyzed by using such types of different characterization techniques.

1. X-RAY DIFFRACTION ANALYSIS (XRD)

To understand 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.

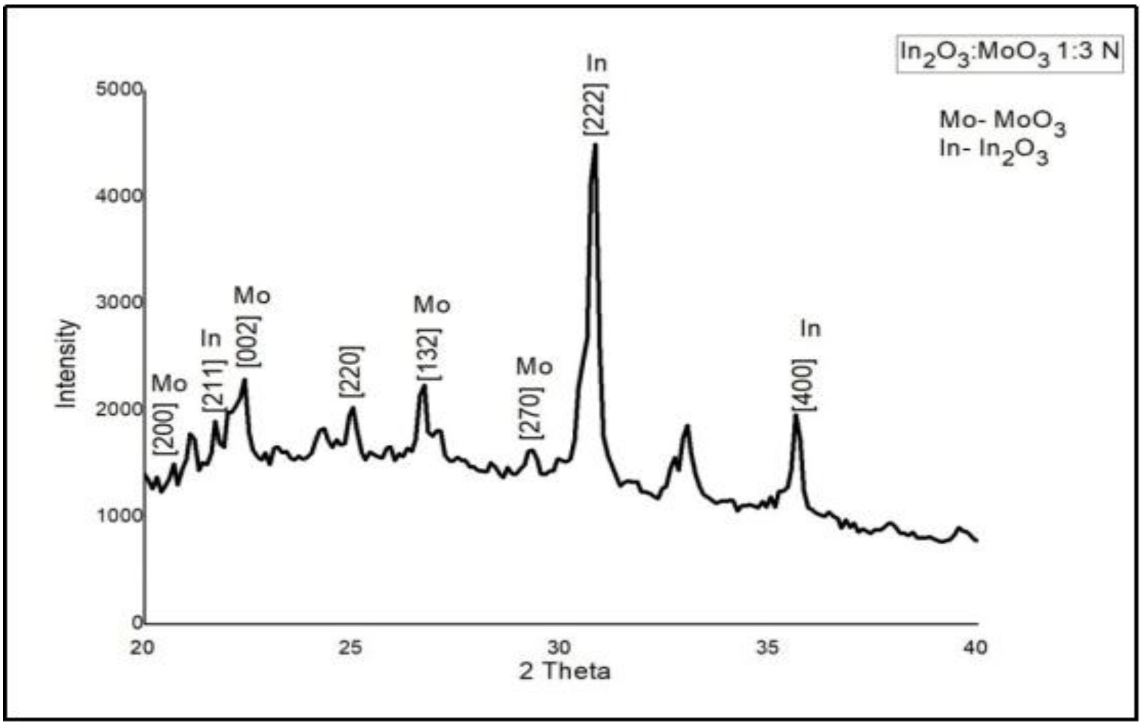

Figure: XRD of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.3N

XRD of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.3N is shown in table

Plane (hkl)	2θ	d-spacing	Intensity	I/Io	FWHM
Mo- 200	20.67	4.29343	1500	33.4	1.668
In- 211	21.11	4.20445	1784	39.7	1.668
Mo- 002	22.39	3.96640	2295	51.1	2.424
Mo- 220	24.96	3.56417	2028	45.1	4.139
Mo- 132	26.68	3.33752	2238	49.8	3.710
Mo- 270	29.29	3.04583	1632	36.3	8.195
In- 222	30.80	2.90042	4494	100	0.525
In - 400	35.58	2.52110	1445	32.2	0.522

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:0.3N, were found 18 nm.

2. 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: 0.1N 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.

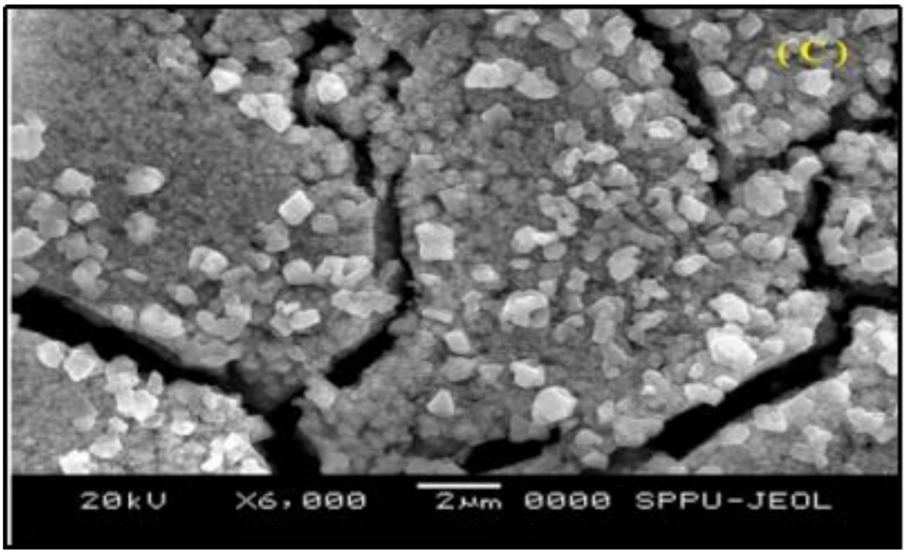

Figure : SEM of Binary oxide In_2O_3: MoO_3 thin with concentration 0.1N:0.3N

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:0.3N was found as 315 nm.
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 different concentrations of binary oxide In_2O_3: MoO_3 was found as 40.06662 m^2/g.

3. ENERGY DISPERSIVE X-RAY ANALYSIS (EDS)

The elemental analysis of Binary oxide In_2O_3: MoO_3 thin films with normality 0.1N:0.3N on glass substrate and fired at 400^0C was studied 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:0.3N concentration of binary oxide In_2O_3: MoO_3 thin films.

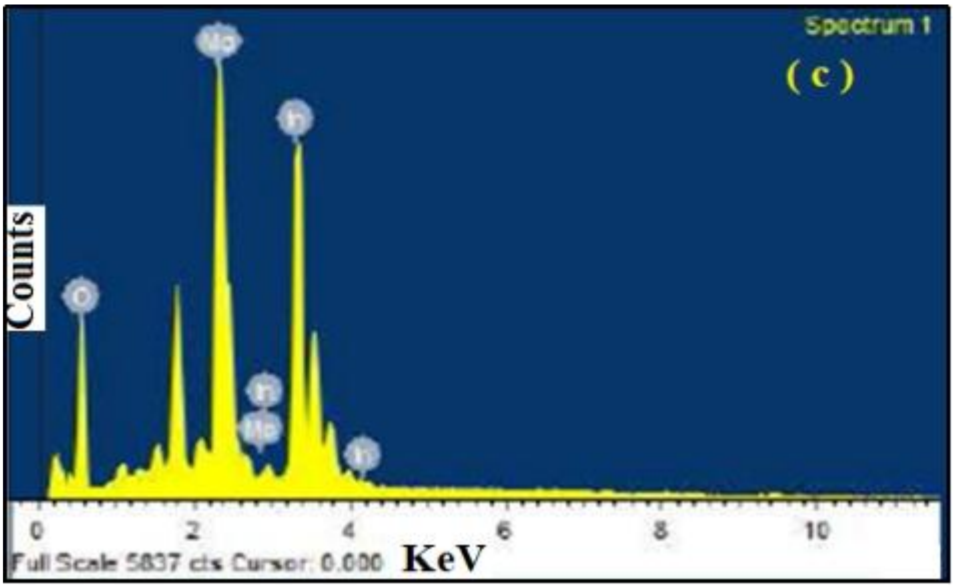

Figure : EDS of Binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.3N

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:0.3N is shown in table

Element	Atomic %
O	85.96
Mo	7.06
In	6.97

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.

4.RESISTIVITY

The DC resistance of In_2O_3:MoO_3 thin films with normality 0.1N:0.3N on 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:0.3N 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:0.3N 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

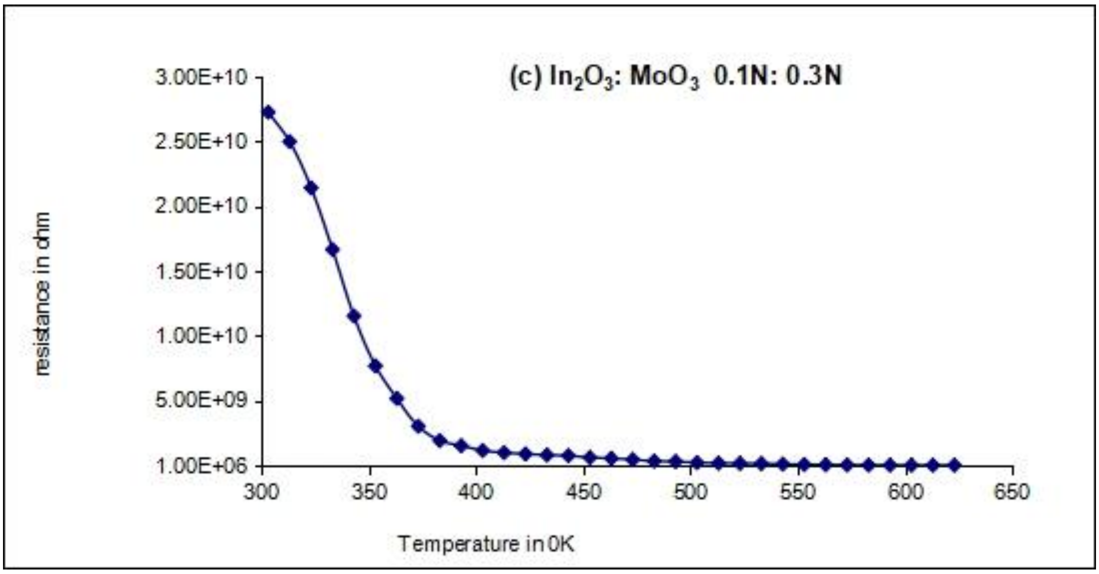

Figure: Resistance of Binary oxide In_2O_3: MoO_3 thin with concentration 0.1N:0.3N

The resistivity of binary oxide In_2O_3:MoO_3 sample with concentrations 0.1N:0.3N, of MoO_3 as additives in TiO_2 film was calculated 17.400 x10^3 Ω-m.

5.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:0.3N.

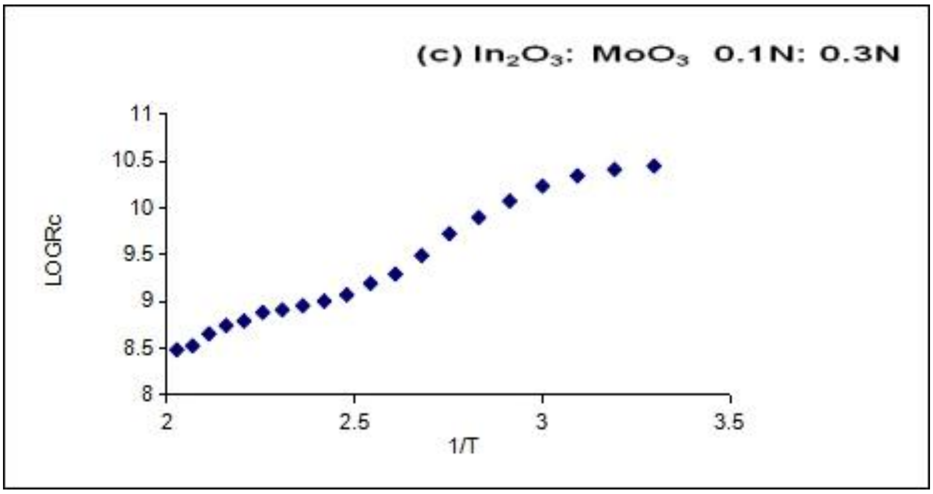

Figure: Activation energy of Binary oxide In_2O_3:MoO_3 thin film with concentration 0.1N:0.3N

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 0.2197eV and 0.6760 eV respectively at 0.1N:0.3N .

6TCR

Temperature coefficient of resistance (TCR) of In_2O_3: MoO_3 thin films prepared at 400^{O}C is calculated by using the following relation,

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

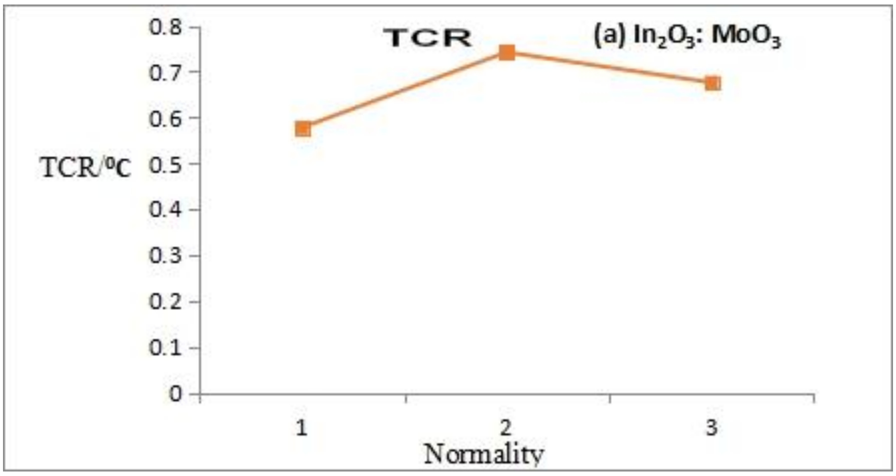

Figure: TCR graph of binary oxide In_2O_3: MoO_3 thin film with concentration 0.1N:0.3N

The temperature coefficient of resistance (TCR) was found as 0.0175 / ^{0} C .

7.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 are 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^oC. 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.

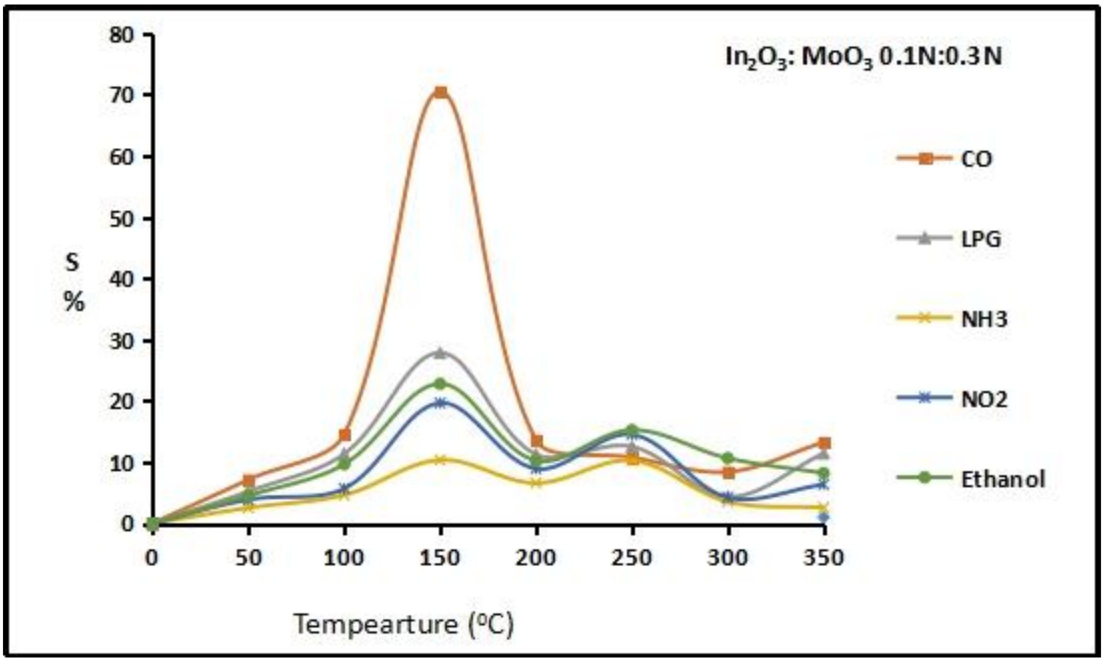

Figure: Gas sensitivity response of Binary oxide In_2O_3 : MoO_3 thin film with concentration 0.1N:0.3N

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:0.3N showed 70.50% sensitivity for CO gas at operating temperature 150^0C and CO gas concentration was at 300 ppm.

CONCLUSION

We have deposited Binary oxide In_2O_3: MoO_3thin films with normality 0.1N:0.3N on glass substrate and fired at 400^0C to change the characteristic properties of thin film . The film was deposited using spray Pyrolysis process at substrate temperature 400^0C. 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:0.3N was found 315 nm. Specific Surface area with different concentrations of binary oxide In_2O_3:MoO_3 was found as 40.06662 m^2/g. The atomic % of O, Mo, In were found as 85.96% ,7.06% and 6.97 % respectively. XRD gives the grain size of film 18 nm. The resistivity of sample was calculated 17.400 $x10^3$ Ω-m. The Activation energy at high temperature and at low temperature were found as 0.2197eV and 0.6760 eV respectively .The temperature coefficient of resistance were found was $0.0175/^0$ C. The film of In_2O_3: MoO_3 at 0.1N:0.3N showed 70.50 % sensitivity for CO gas at operating temperature 150^0C and CO gas concentration was at 300 ppm.

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