MgO INCORPORATED ZnO NANOSTRUCTURED BINARY OXIDE THIN FILM ETHANOL GAS SENSOR

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***Abstract*: In the present research work, MgO incorporated ZnO nanostructured binary oxides thin films have been prepared on alumina substrate by using thermal evaporation technique. The structural analysis, surface morphology and elemental compositions were studied by XRD, SEM and EDAX techniques respectively. Crystal structure, composition and crystalline grain size were studied using XRD tool. The crystalline grain size of pure ZnO and MgO incorporated ZnO thin films were found 45 nm and 23 nm respectively using Debye Scherer's formula. The developed thin films were exposed to various concentrations of ethanol to determine sensitivity. Maximum sensitivity has been found to the ethanol gas 86.71% at room temperature and concentrations of ethanol gas 150 ppm. Films also quick response time (~ 13 sec) and recovery time (~ 21 sec).**

***Keywords*: Binary oxide, Grain size, ethanol gas, PPM, Thermal Evaporation system.**

I. INTRODUCTION:

The first decade of 21st century has been named as sensor decade. The sensor is an electronic device that detects various form of input signal. Particularly, metal oxide semiconductor (MOS) and composite gas sensors present incredible preferences due to their quick detecting, straightforward execution, low costs. They have stable chemical & thermal properties over expanded time of utilization. The sensors are required essentially for estimation of actual amounts and for utilization of controlling a few frameworks. The particular requirement for gas detection and observing has arisen as a challenge. The exposure of harmful and unsafe gases can cause heart problems, respiratory track sicknesses, cellular breakdown in the lungs, decrease in hemoglobin, mental hindrance, visual deficiency, absent mindedness, migraines, hypertension and so forth Gases from auto and modern depletes are polluting the climate [1, 2].

Ethanol is colorless and combustible oxygenated hydrocarbon gas. It is generally called alcohol. High centralization of ethanol in human body can meddle with the mind capacities and can cause harming. The people groups dealing with ethanol union have extraordinary changes of being casualties of respiratory and stomach related track malignancy. So there is an incredible interest and arising difficulties for monitoring ethanol gas at appropriate track level. The sensors based on SMO and composites materials play a vital role to detect and monitor ethanol gas [2, 4].

Zinc oxide (ZnO) is an inexpensive nontoxic n type semiconducting material with wide direct band gap (Eg = 3.37 eV) at room temperature and with high exciton binding energy (60 meV) [1]. Due to the intrinsic defects of oxygen vacancies and zinc interstitials, undoped ZnO usually exhibits n-type conductivity with typical carrier concentration. ZnO thin films exhibit different micro morphologies and perform different characteristics, which means improving electrical and gas sensing properties of ZnO thin films by means of intentional doping and appropriate synthesis techniques is feasible. At present, many researches on ZnO have focused on doping elements to lower the resistivity of the film. Thus, more researches have focused on n-type doping. Recent progress in exploring n-type doping of ZnO thin films has shown extensive application perspectives of ZnO-coated devices and has attracted considerable interest [5-7].

Magnesium oxide (MgO) is an n type semiconductor with wide-band gap (~7 eV). It has a low electron affinity. MgO is mostly suited for electron emission applications, especially in a plasma environment. Recently, magnesium oxide has been studied extensively due to its stable secondary electron emission and protective layer for plasma related devices [8-10]. MgO has the ability to tune the band gap of zinc oxide without changing the parameter like lattice constant [15]. Hence, current MgO has selected for dopant in this work.

Based on the thickness layer of deposited material on the substrate, films are divided into two different ways- one is thick film and another is thin film. The thickness range of thick and thin films is 15 µm to 80 µm and 50 nm to 300 nm respectively. Physical vapour deposition method is commonly preferred to develop thin films. PVD technique is used in the various fields. In the physical vapour deposition method, phase of material changes from solid to a vapour and the phase again converted into solid at the time of preparation of thin film that is vapour condensation on the substrate shown in Figure 1 [11-13].

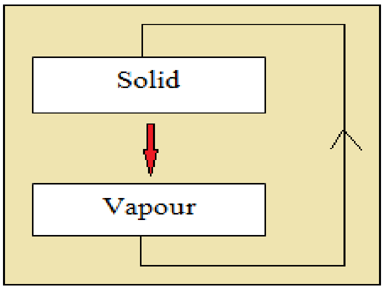

Figure 1: Conversion of phase of material in PVD

High operating temperature, minimum response time, low sensitivity and selectivity such types of some problems still occurs in the developing of ZnO based gas sensor. The researchers have been work to solve these problems by using different top down and bottom approaches of synthesis. Addition of some metals or metal oxides in base material also enhanced the electrical, structural properties of material i.e. doping with various metals or metal oxides in the functional material [14]. Hence, the current research work focus on the developed of MgO incorporated ZnO nanostructured binary oxide thin film by thermal evaporation technique and study of its properties like structural and ethanol gas sensing.

II. EXPERIMENTAL WORK:

Preparation thin films by thermal evaporated technique:
In this research work, commercial available AR grade (99% purity) ZnO and MgO nano powders were used. ZnO is base material and MgO as a dopant used for preparing binary oxide thin film gas sensor. Thin films were prepared by using thermal evaporated system. The system consist vacuum pump system, which was evacuated to 10^{-5}-10^{-6} mbar pressure by rotary and diffusion pump appropriate arrangement shown in Figure 2. The chamber was filled with vacuum and for deposition purpose clean alumina substrates were used, the alumina substrates were cleaned using acetone and IR lamp. Nano powders place in molybdenum boat by some standard arrangement and using maximum voltage power supply, which was used as the target for evaporation. Then, prepared thin film were annealed using muffle furnace at temperatures 550 ^{o}C and then used further study.

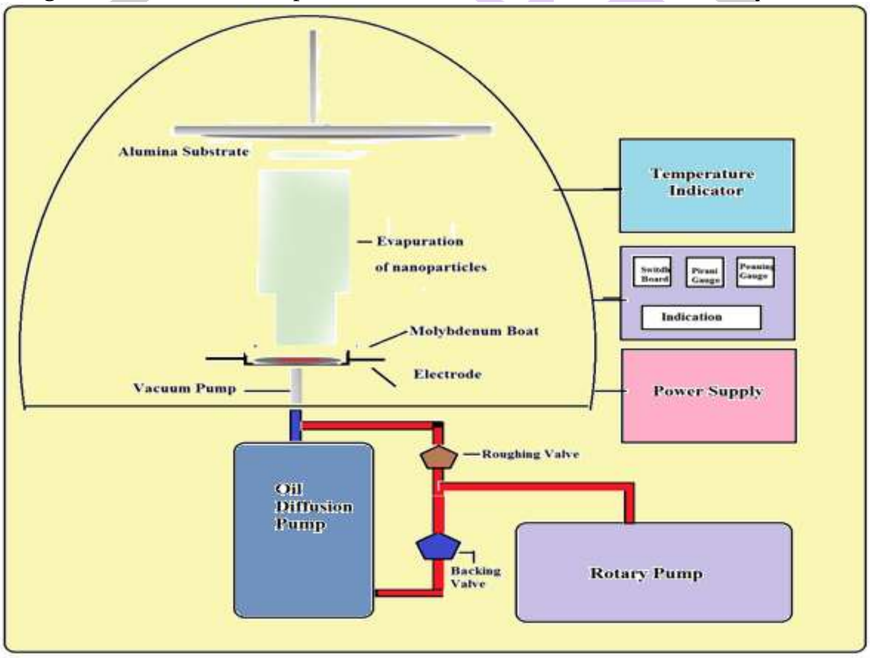

Figure 2: Thermal Evaporation system

III. RESULT AND DISCUSSION:

Structural characterizations: The developed pure ZnO and MgO incorporated ZnO thin were characterized by FESEM, EDS and XRD to study the surface morphology, elemental composition analysis and structural properties respectively. The thickness of the thin films was measured by using Taylor-Hobson (Taly-step UK) system. The thickness of the films was observed in the nm range.

X-Ray Diffraction (XRD):
X-ray diffraction is a powerful tool for analysis and determined of materials properties such as the crystal structure, orientation and also grain size. Interplaner distance for different plane can be measure using Bragg's law equation 1[16].

$$n\,\lambda = 2\,d\,sin\theta \qquad \text{------ (1)}$$

Where, n: is an number (1, 2, 3, 4,….) that represents the order of the interface, λ: is the X-ray wave length, d: is the interplaner distance and θ: represent the include angle.

XRD patterns of developed thin films were recorded on Rigaku diffractometer (DMAX-500), X-ray diffractometer with CuKα radiation and wavelength (λ) = 0.5418740, in order to study the effect on structure if any. The thin films were scanned for 2 ϴ ranges from 20◦ to 80◦. The obtained values of 2 ϴ are compared with Joint Committee on Powder Diffraction Standards (JCPDS) data files.

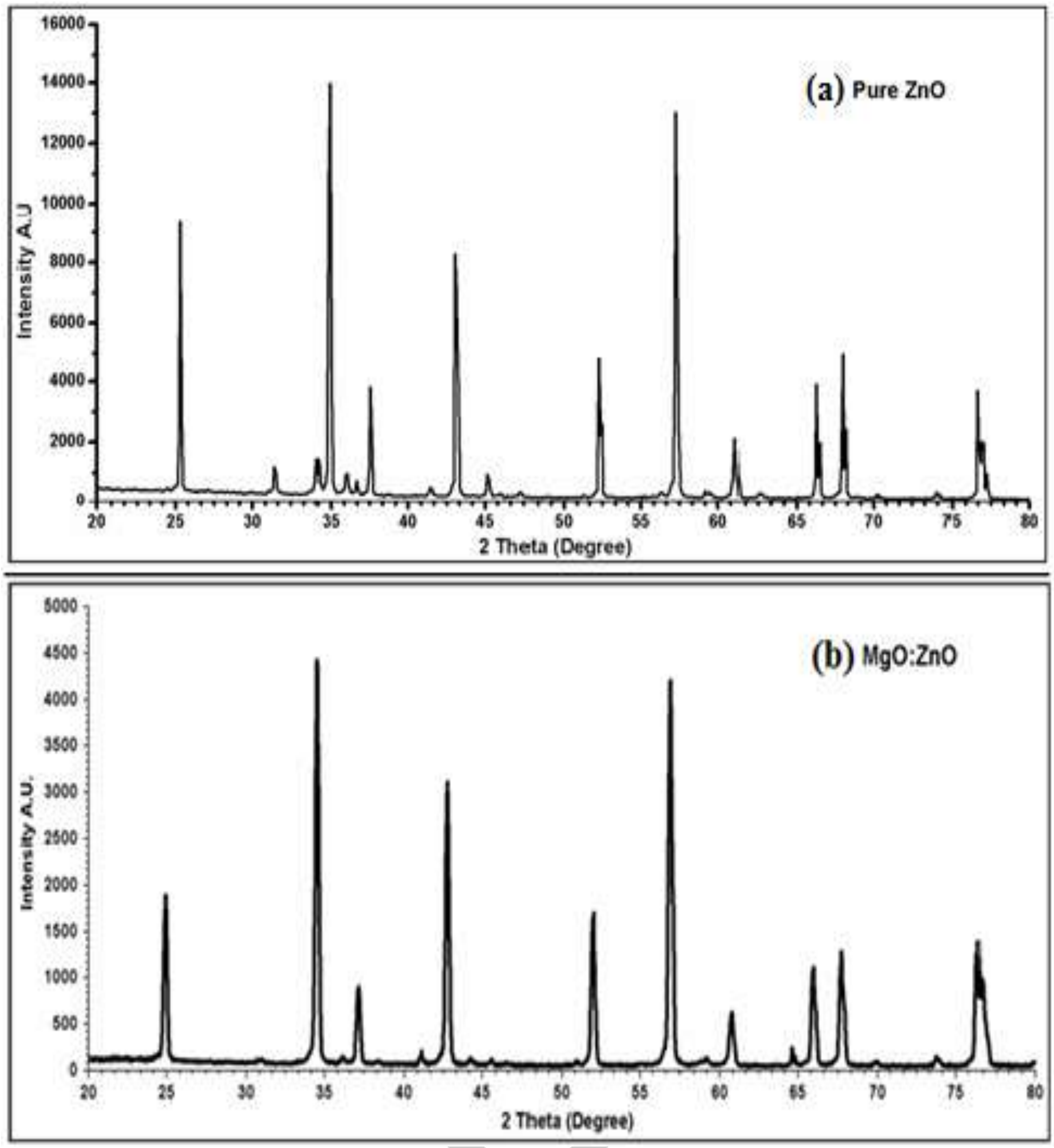

Figure 3: (a) XRD pattern of pure ZnO thin film (b) XRD pattern of MgO incorporated ZnO thin film

Fig. 3 (a) and (b) shows that the XRD patterns of pure ZnO and MgO incorporated ZnO thin films respectively. The preferentially orientated [002] peak at 34.25 for ZnO and [200] peak at 42.98 for MgO is obtained [15]. Equation 2, Debye Scherer's formula is gives the reversal relation between grain size (D) and FWHM.

$$D = \frac{K\lambda}{\beta \cos \theta} \qquad \text{------ (2)}$$

Where, K : shape factor of the average crystallite (0.91), λ : X-ray wavelength, β: Full Width at Half-Maximum (FWHM) in radians and θ: Bragg angle.
From Table 1 and 2 films exhibits the increase in the (*FWHM*) which indicates a decreasing in the grain size (D) [17].

Table 1: Structure Parameters of pure ZnO thin films

2theta [deg]	d [A]	I/I0	Counts	FWHM
25.521	3.4904	374.8	844	0.2004
31.633	2.8285	72.4	163	0.2004
33.837	2.6491	8.6	19	0.2004
34.288	2.6153	119.4	269	0.2004
35.090	2.5574	1000.0	2251	0.2004
36.192	2.4820	55.6	125	0.2004
36.843	2.4396	24.3	55	0.2004
37.745	2.3834	200.4	451	0.2004
41.653	2.1684	19.2	43	0.2004
43.206	2.0939	878.6	1978	0.2004
45.360	1.9994	59.6	134	0.2004
47.465	1.9155	11.5	26	0.2004
52.475	1.7438	319.6	719	0.2004
56.483	1.6292	14.4	65	0.4008
57.485	1.6032	860.7	1938	0.2004
59.388	1.5563	13.6	31	0.2004
61.292	1.5124	110.0	248	0.2004
62.795	1.4798	12.5	28	0.2004
66.402	1.4079	296.2	667	0.2004
68.106	1.3768	389.5	877	0.2004
70.310	1.3389	10.5	24	0.2004
74.268	1.2771	14.7	33	0.2004
76.823	1.2408	242.1	545	0.2004
77.074	1.2374	209.5	943	0.4008

Table 2: Structure Parameters of MgO incorporated ZnO thin film

2theta [deg]	d [A]	I/I0	Counts	FWHM
24.810	3.5887	412.3	619	0.2800
34.450	2.6034	1000.0	1502	0.2800
36.090	2.4888	12.8	17	0.2400
37.090	2.4240	189.8	285	0.2800
41.010	2.2009	19.8	17	0.1600
42.190	2.1420	20.8	49	0.4400
42.690	2.1181	676.4	1016	0.2800
44.150	2.0513	13.2	9	0.1200
45.490	1.9940	9.2	8	0.1600
51.910	1.7615	360.6	464	0.2400
56.390	1.6317	33.0	64	0.3600
56.830	1.6201	979.5	1681	0.3200
57.330	1.6072	8.3	7	0.1600
59.090	1.5634	13.2	14	0.2000
60.670	1.5264	124.3	213	0.3200
64.570	1.4433	23.1	10	0.0800
65.910	1.4172	240.5	413	0.3200
67.590	1.3860	271.8	408	0.2800
73.690	1.2856	18.6	20	0.2000
75.870	1.2540	12.3	26	0.4000
76.270	1.2484	287.3	493	0.3200
76.550	1.2446	201.8	346	0.3200
76.850	1.2405	65.6	98	0.2800

As per structural analysis the grain size were calculated by using Debye Scherer's formula. The grain size of pure ZnO and MgO incorporated ZnO thin films were found 45 nm and 23 nm respectively. X-ray diffraction patterns revealed that the crystallinity of ZnO films can be improved by addition of MgO.

Field Emission Scanning Electron Microscope (FESEM):
To observe small structures on the surface of cells, film and material FESEM is used. It is a versatile tool for study of morphology of the film. Instead of light, FESEM is works with electrons. Particle has a negative charge. These electrons are liberated by a field emission source with accelerated in a high electrical field gradient. According to a zig-zag pattern object is scanned by electrons. FESEM provides information of the samples, which allow us to inspect the shape, size and diameter of the film. In order to study the morphological effect of MgO incorporated ZnO the film, FESEM analysis was carried out. FESEM {Model JOEL 6300 LA GERMANY} was utilized to characterize the surface morphology. The average particle size and diameter of nanoparticles (spherical particles) were determined using Image-J software.

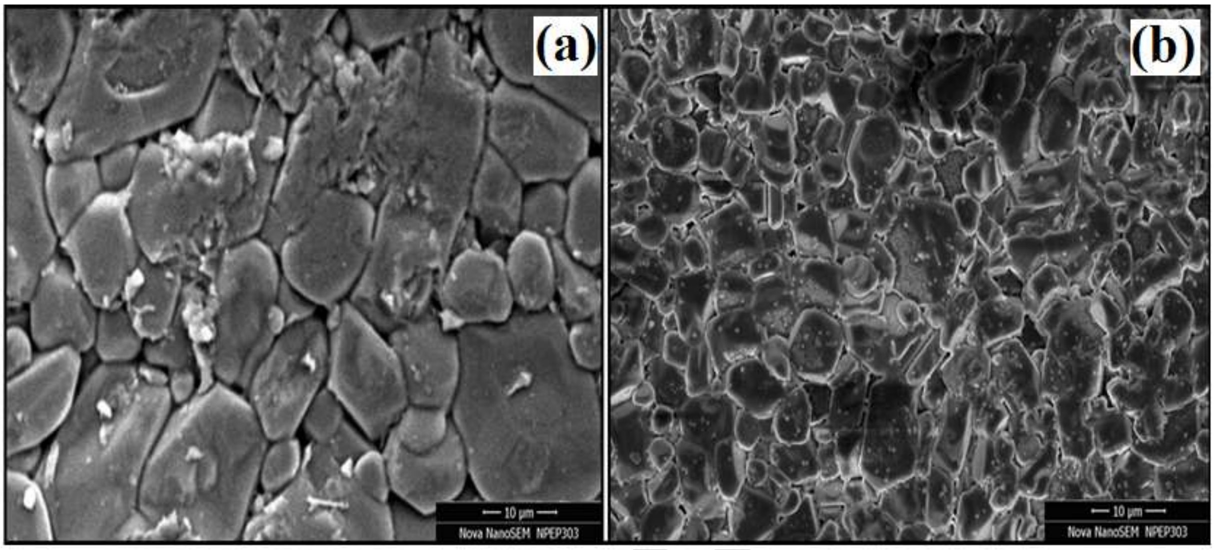

Figure 4: (a) FESEM image of pure ZnO thin film (b) FESEM image of MgO incorporated ZnO thin film

The average particle size of films was calculated by using image J software for spherical particles. The average particle size of pure ZnO and MgO incorporated ZnO thin films were found 118 nm and 103 nm respectively. The size of the grains decreases with the MgO dopant which confirms that more Mg ions diffuse into ZnO during the preparation of film in the vacuum.
From FESEM images figure 4(a) random distribution of smaller size particles due sluggish growth of grains observed. At high magnification image Few ZnO nanowires are observed. MgO incorporated ZnO film shows dense porous surface with well grown nanowires in figure 4(b). Figure 4(b) shows that more voids and micro pores. For sensing application presence of more number of micro pores in the film plays a vital role to enhanced sensitivity of the film [15]. Images show that there is no visible defect over the surface of the film.
The net-like nanostructures are made up of many different nanosheets and showing clearly the porous shapes shown in figure 4 (a) and (b). A large area of the porous two-dimensional structure has been found in figure 4(b) as compare to figure 4(a), such types of results reported [15- 18].

Energy Dispersive Spectroscopy (EDS):

EDS technique is mostly used for identifying the elemental composition of the specimen. The EDS analysis system works as an integrated feature of a Scanning Electron Microscope. The elemental analysis was carried out carried out using energy dispersive X-ray spectrometer EDAX (JOEL-2300, Germany).

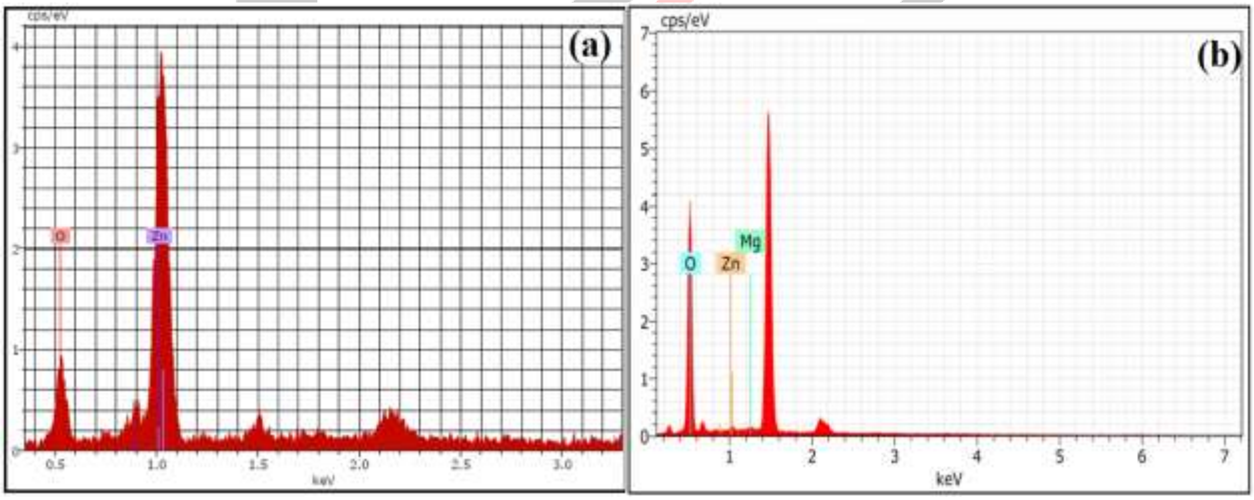

Figure 5: (a) EDS of pure ZnO thin film (b) EDS of MgO incorporated ZnO thin film

The specimen image can be obtained along with the elemental analysis of the selected area/features and distribution of selected elements. The EDS result shows variation of Zn, Mg and O thin films in figure 5 (a) and (b). From the EDS spectra, it is found that atomic wt. % of Zn, Mg and O is nearly matched. As per Energy dispersive analysis by x-ray spectra, the MgO incorporated ZnO film has more oxygen excess. Table 3 gives quantitative elemental analysis of pure ZnO and MgO incorporated ZnO films. This excess oxygen might have been adsorbed during evaporation of material during development of thin film it can be diffusion of MgO with ZnO.

Table 3: Summary of composition elements of the films

Film	Element	Atomic wt. %
Pure	Zn O	43.71 56.29
Incorporated	Zn Mg O	16.81 9.13 74.06

Gas sensing study:

Gas sensing study of MgO incorporated ZnO nanostructured binary oxide thin films developed by thermal evaporation technique has been carried out in a gas test chamber at different concentration of ethanol gas in PPM and different operating temperatures. The resistance of the films was measured by using equation 3 in presence of gas in the test chamber. It is observed that response of MgO incorporated ZnO is more than pure ZnO thin films. MgO incorporated ZnO thin films operated at lower operating temperatures with high sensitivity. In figure 6, it is observed that the MgO doped ZnO thin film had the largest sensing response (86.71 %) at 40 ^{0}C temperature. Also, it is observed that the resistance of the films decreased upon exposure to ethanol gas vapors.

$$S\% = \frac{(Ra-Rg)}{Rg} \times 100 \qquad \text{----- (3)}$$

Where, R_a is resistance of film in air, R_g is resistance of film in gas atmosphere and S% is the Sensitivity of the film in the percentage.

Sensitivity of MgO incorporated ZnO nanostructured binary oxide thin films:

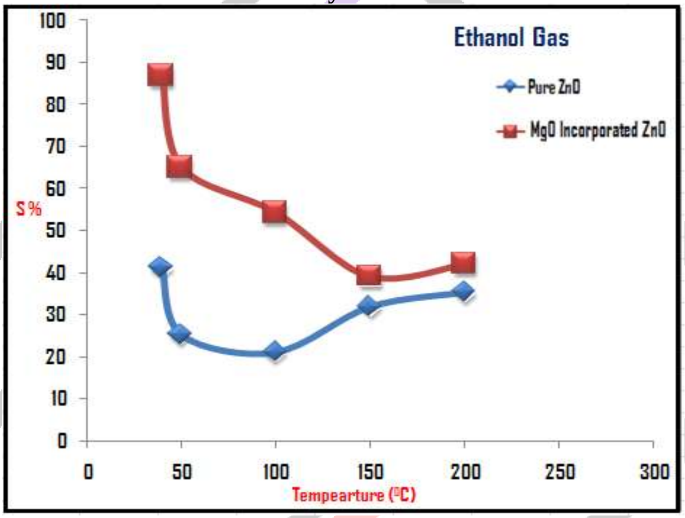

Figure 6: Sensitivity of MgO incorporated ZnO nanostructured binary oxide thin films

The MgO incorporated ZnO nanostructured binary oxide thin films were exposed to gas concentrations of 50, 100, 150 and 200 PPM. The maximum sensitivity 86.71 % at operating temperature 40^{0}C and gas concentration was at 150 ppm.

PPM verses Sensitivity:

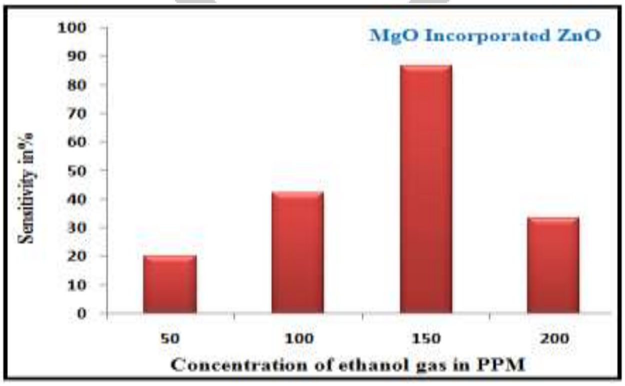

Figure 7: Sensitivity verses ethanol gas concentration in PPM.

Figure 7 shows the variation in sensitivity for MgO incorporated ZnO nanostructured binary oxide thin films to different concentrations of ethanol gas. The maximum sensitivity recorded at 150 PPM.

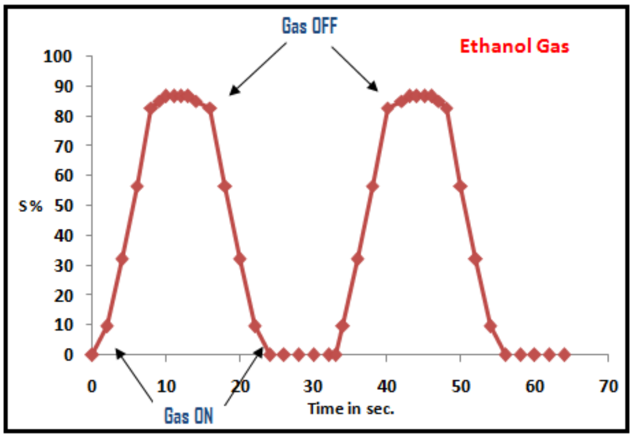

Fig. 8 Response and recovery time of MgO incorporated ZnO nanostructured binary oxide thin films

Figure 8 shows the response time of nanostructured binary oxide thin films (~ 10 sec) while the recovery time was fast (~ 22 sec) for ethanol gas.

Ethanol gas sensing mechanism for MgO incorporated ZnO nanostructured binary oxide thin film:

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Ethanol has reducing gas molecules, with negatively charged oxygen adsorbates, the trapped electrons are given back to conduction band [19]. Metal Oxide Semiconductor gas sensor, operates on the principle of change in resistance value due to the interactions between adsorbed gas and sensing material molecules, when gas interact with film in the surrounding [20]. When ethanol gas exposed on the thin film resistance of the film will decrease due to the exchange of electrons between ionosorbed species and nanostructure particles. The following reaction shows the sensing mechanism-

$$C_2H_5OH_{(gas)} + 6O^{2-}_{(film\ surface)} \rightarrow 2CO_{2\,(gas)} + 3H_2O_{(gas)} + 12\ e^-_{(cond.band)} \quad \text{------------------------}(1)$$

Oxygen ionosorption minimize conduction electrons and thus increases resistance of film. That is oxygen absorption plays a vital role in electrical transport properties of the films. MgO can occupy a regular cation position forming a substitutional solid solution. To maintain electrical neutrality such substitutions will create oxygen vacancies and donate electrons and the overall change in the resistance on exposure of Ethanol gas leading to high sensitivity [19-21].

CONCLUSIONS

MgO incorporated ZnO nanostructured binary oxide thin films could be prepared by thermal evaporation technique on alumina substrate. The structural characteristics confirmed that the developed pure ZnO and MgO incorporated ZnO thin films are nanostructured in nature. The elemental analysis shows nonstoichiometric nature of films. The MgO incorporated ZnO thin film was maximum sensitivity to ethanol gas at operating temperature 40^0C and gas concentration was at 150 ppm because low grain size and excess of oxygen. It has been notice that MgO incorporation ZnO influences the structural and gas sensing properties of thin films. The changes in properties of thin film were useful to enhanced gas response. Response and recovery time is also found very quickly in seconds.

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