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Studies on Ethanol Gas Sensing Properties of Al_2O_3-doped ZnO Thick Films

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Abstract

The thick films of undoped and Al_2O_3 - doped ZnO were prepared by screen printing technique. AR grade Zinc Oxide powder (99.9% pure) was mixed mechnochemically with different wt. %(0.5, 1 and 3) of Aluminium Chloride (Hexahydrate) ($AlCl_3.6H_2O$) in Acetone medium to obtain Al_2O_3 - ZnO composite material. The prepared materials were sintered at 1000°C for 12h in air ambience and reground to ensure sufficiently fine particle size. The electrical, structural and morphological properties of the films were investigated. The X-ray diffraction analysis of undoped and Al_2O_3 - doped ZnO material showed the polycrystalline nature. The surface morphology of the films was studied by SEM indicating that the films are granular and porous. The final composition of each film was determined by EDAX analysis. The gas response of undoped and doped ZnO films was studied for different gases such as CO, H_2, NH_3, and Ethanol at operating temperature ranging from 50°C to 450°C. The undoped ZnO film showed the poor response to Ethanol gas, while the film doped with 1 wt. % Al_2O_3 gave the good response to ethanol gas (500ppm) at 400°C. The selectivity, response and recovery time of the sensor were measured and presented.

Keywords

Thick films; ZnO; Al_2O_3; Ethanol Gas; Gas Response; Selectivity; Response and Recovery Time

Introduction

In recent years, the concern over environmental protection and increasing demands for monitoring hazardous and inflammable gases in industry and home have attracted extensive interests in developing gas sensors for these gases. Due to the advantages of small size, low cost, simple operation and good reversibility, the semiconductor sensors have become the most promising devices among the solid-state chemical sensors. Many semiconductor oxides such as ZnO, SnO_2, TiO_2, Cr_2O_3, Fe_2O_3, In_2O_3, CeO_2, WO_3, and CuO, have been explored to detect the toxic and inflammable gases, such as CO, CO_2, NO_x, H_2S, LPG and ethanol.

In order to enhance the catalytic activity (oxidation), the oxides were doped with it using mechanical mixing of some impurities. The aim of the present research work is to enhance the catalytic activity (oxidation) of Zinc Oxide (ZnO) using mechanical mixing of Al_2O_3 which is weak n-type semiconductor material with wide band gap (8.8 ev) for bulk material in different crystalline form and good thermal stabilit, and works as good catalyst with semiconductor when the gases such as H_2S and Ethanol come in contact with. The conventional oxide-mixing techniques; powders are produced more homogeneous after the sintering process.

Zinc Oxide is a wide band gap semiconductor with a bandgap of 3.37 eV and a large binding energy of 60 meV. It is an important semiconductor material, having a wide range of applications such as, luminescent devices, solar cells, chemical sensors etc, whose conductivity can be tailored by controlling the deviation from stoichiometry and by doping. Appropriate doping can provide electronic defects that increase the influence of oxygen partial pressure on the conductivity. In this work, Al^{3+} substitution on Zn^{2+}(was chosen due to the small ion size of Al^{3+} compared to that of Zn^{2+}(Al^{3+} (0.53Å) and Zn^{2+} (0.74 Å).

Ethanol is a hypnotic (sleep producer) gas having toxic nature. Heavy exposure and-/or consumption of alcoholic beverages, particularly by smokers, increase the risk of cancer of the upper respiratory and digestive tracks. Among women, the chances of breast

cancer increase with alcoholic consumption or exposure. Those working on ethanol synthesis have great chances of being victims of respiratory and digestive track cancer. So there is a great demand and emerging challenges for monitoring ethanol gas at trace level.

Experimental procedure

Preparation of Functional Material

AR grade Zinc Oxide powder (99.9% pure) was sintered at 1000°C for 12 h. The sintered Zinc Oxide powder (99.9% purity) was mixed mechnochemically with different wt. %(0.5, 1 and 3) of Aluminium Chloride (Hexahydrate) ($AlCl_3.6H_2O$) in Acetone medium to obtain Al_2O_3 - ZnO composite materials. The prepared composite materials were sintered at 1000°C for 12h in air ambience and reground to ensure sufficiently fine particle size.

Preparation of Thick Films

The thixotropic paste was formulated by mixing the fine powder of functional material with ethyl cellulose (a temporary binder) in an organic solvent such as butyl cellulose, butyl carbitol acetate and terpineol etc. The ratio of the inorganic to organic part was kept at 75:25 (Volume) in formulating the paste. This paste was screen-printed on a glass substrate in a desired pattern (1.5 cm X 0.5 cm). The films were dried under infrared radiation for 45 minutes. To remove the organic vehicle, the films were fired at a temperature of 550°C for 30 min then attained at room temperature in a muffle furnace.

Thickness Measurements

The range of thicknesses of the films was observed from 65 to 75 μm. The reproducibility in thickness of the films was possible by maintaining the proper rheology and thixotropy of the paste.

Physical Characterization

Structural Analysis

In order to understand the structural properties of Al_2O_3 - doped ZnO composite powder materials at different dopant concentration, X-ray diffraction analysis of these sintered powders was carried out in the 20-80° range using Cuk_α radiation.

Fig.1 shows XRD patterns of undoped- ZnO and Al_2O_3 (0.5, 1 and 3 wt. %) – doped ZnO.

Fig.1 (a) shows XRD patterns of undoped ZnO material. The observed diffraction peaks are corresponding to the hexagonal wurtzite structure of ZnO and well matched with the JCPDS (76-0704) reported data of ZnO. The sharp peaks of XRD were attributed to ZnO material observed to be polycrystalline in nature. The higher peak intensities of an XRD pattern is due to the better crystallinity with preferred orientation along the (101) direction.

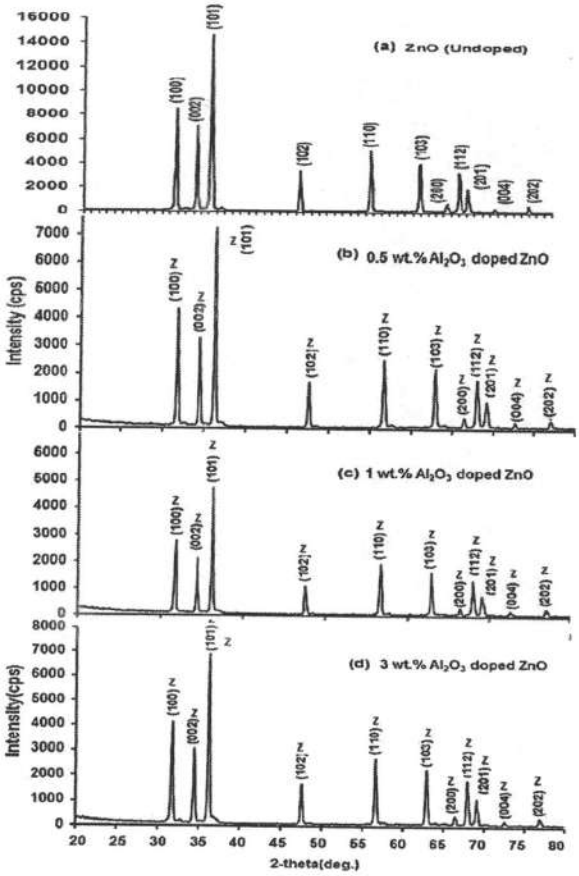


FIG. 1 XRD PATTERN FOR Al_2O_3 –DOPED ZnO COMPOSITE MATERIAL

Figs. 1(b - d) shows the XRD patterns of Al_2O_3 (0.5, 1 and 3wt. %) – ZnO composite material. For all compositions, formation of only ZnO wurtzite phase is observed in accordance with the reported d-values (JCPDS 76-0704). The possible formation of Al_2O_3 or $ZnAl_2O_4$ phases was not detected. This might be due to relatively low sintering temperature (~1000°C) at which Al into Zn sites might not have occurred to a complete extent.

From the XRD results, it is concluded that the material properties are strongly dependent on Al_2O_3 concentration. The 1 wt. % of Al_2O_3 doping is critical to have high quality ZnO material. Moreover, the (002)

diffraction peak intensity of ZnO: Al_2O_3 decreases. This indicates that the doping concentration deteriorates the crystallinity of the material, which may be due to the formation of the stresses by the difference in ion sizes between Zinc and the dopant and the segregation of dopants around grain boundaries at high doping concentrations.

The average crystallite size was calculated from XRD pattern using Debye Scherer's formula.

$$D = 0.9\lambda/\beta Cos\theta \quad (1)$$

Where D- Average crystallite size, β - Broadening of the diffraction line measured at half maximum intensity (FWHM), λ -Wavelength of the x- ray radiation and θ -Bragg's angle.

The crystallite size for undoped ZnO lies in between 27-36 nm while Al_2O_3 - doped ZnO lies in between 10-36 nm. Thus the crystallite size varies with doping concentration of Al_2O_3 in ZnO samples. Slightly broadening of diffraction lines may be attributed to small crystalline effects.

Micro Structural Analysis of the Films

The surface morphology and chemical composition of the films were analyzed using a scanning electron microscope [SEM model JEOL 6300 (LA) Germany] coupled with an energy dispersive X-ray analysis. (EDAX, JEOL, JED-2300, Germany).

SEM images in Fig. 2 show the surface morphology of undoped ZnO and Al_2O_3 (0.5, 1 and 3 wt. %) – doped ZnO thick films. Fig. 2 (a) shows the micrograph of pure ZnO thick film. It consists of randomly distributed particles with smaller size and shape and with limited porosity. The particle size of films varies in between 186 nm to 190 nm. Plane-view SEM investigation of Fig.2 (b-d) reveals a porous structure of Al_2O_3 doped - ZnO thick films. Petal-shaped particles of various sizes (156-225 nm) were observed in all samples. The majority of these particles appear several times larger than the average crystallite sizes calculated from X-ray diffraction data (10-36 nm) thus, indicating that most of the particles comprise multiple crystallites. No systematic variation in the microstructure of the ZnO films as a function of the doping concentration was observed.

In Fig.2 (b), the Al_2O_3 additives distributed on ZnO grains would be very less, so they are not sufficient to accelerate the sensing reaction with the target gas, hence it shows the poor response to the target gas.

In Fig. 2(c), the Al_2O_3 additives present on the ZnO grains are at an optimum level leading to high porosity and large effective surface area available for the adsorption of oxygen species. The ZnO film doped with 1 wt. % Al_2O_3 was observed to be the most sensitive to ethanol than the other films.

In Fig.2 (d), Al_2O_3 particles present over ZnO surface would be greater than optimum level, Which reduces the porosity and resists reaching the target gas to the inter-grain boundary of Al_2O_3 –ZnO, hence the film shows poor response to ethanol gas.

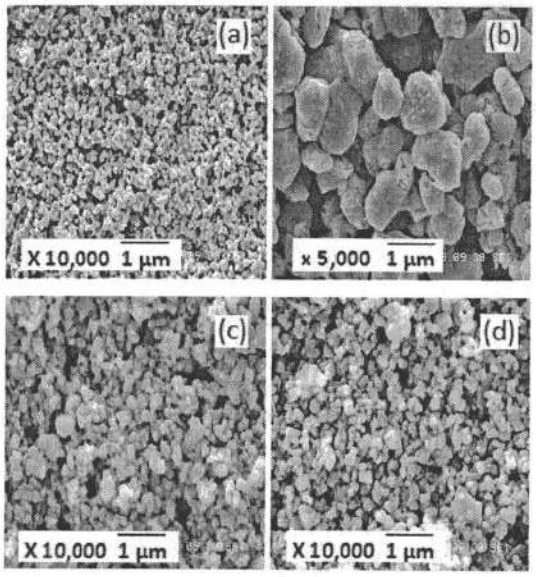


FIG. 2 SEM IMAGES OF (a) UNDOPED ZnO, (b) 0.5 wt.% (c)1 wt.% AND (d) 3 wt.% Al_2O_3 – ZnO FILMS

The specific surface area was determined by the equation (2).

$$S = \frac{6}{\rho * D} \quad (2)$$

Where S is specific surface area, ρ is density of material and D is diameter of particle. The specific surface area of the films is shown in Table 1.

TABLE 1 PARTICLE SIZE AND SPECIFIC SURFACE AREA OF Al_2O_3 -DOPED ZNO FILMS.

Sr. No.	Wt. % of Al_2O_3	Particle size (nm)	Specific Surface Area(m^2/gm)
1	Pure ZnO	186	5.75
2	0.5	156	34.60
3	1	195	27.91
4	3	225	25.00

Elemental Analysis of the Films

The composition of undoped and Al_2O_3 -doped ZnO thick films was analyzed by energy dispersive X-ray analysis.

TABLE 2 QUANTATIVE ELEMENTAL ANALYSIS OF UNDOPED AND AL_2O_3 -DOPED ZNO FILMS.

Elements	ZnO (undoped)	Doping level(Al_2O_3- ZnO)		
		0.5 wt. %	1wt. %	3 wt.%
O (mass %)	19.66	19.78	20.07	20.16
Zn (mass %)	80.34	79.99	79.14	78.87
Al (mass %)	--	0.23	0.79	0.97
Total	100	100	100	100

Table.2 gives quantitative elemental analysis of undoped and Al_2O_3 -doped ZnO thick films at different doping concentration. The EDAX analysis shows presence of only Zn, Al and O as expected, no other impurity elements were present in the thick films. The EDAX result shows variation in Zn/O ratio and Al/Zn ratio with variation in doping concentration. The mass percentage(%) of Zn and O in each sample was not as per stoichiometric proportion. The entire samples were observed to be oxygen deficient that would promote the adsorption of relatively large amount of oxygen species favorable for higher gas response. It suggests the role of Al as one of the either providing additional adsorption sites for the reaction or stabilizing the sites already existing on the ZnO surface. The stabilizing action of Al ions can be visualized as the localization of the free electron of Zinc into ZnO by overlapping them with their own electron clouds.

Electrical Conductivity of the Films

Fig.3 shows the variation of log (conductivity) with reciprocal of temperature of undoped and Al_2O_3-doped ZnO films. It is clear from graph that the conductivity of these films goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows that the materials are semiconducting nature.

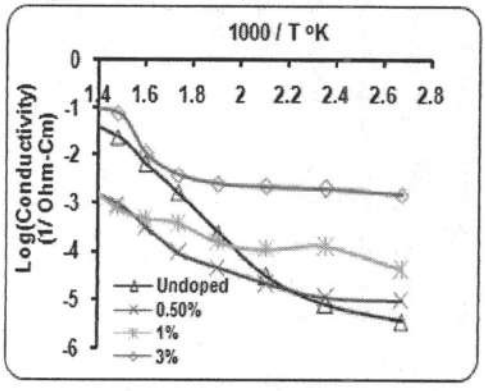


FIG.3 CONDUCTIVITY- TEMPERATURE PROFILE OF UNDOPED AND Al_2O_3 - DOPED ZnO FILMS

Fig.3 shows that the conductivity of films increases with increase in dopant concentration of Al_2O_3.. Thus, it was found that the conductivity of Al_2O_3- ZnO films is strongly dependent on the Al_2O_3 dopant concentration.

Gas Sensing Performance

The gas sensing performance of undoped and Al_2O_3-doped ZnO thick films was studied by using static gas sensing system. The conductance of thick films was measured as a function of temperature in air as well as in CO, H_2, NH_3, and Ethanol gases atmosphere. The operating temperature was varied from 50°C to 450°C. From the measured conductance in air as well as in gases atmosphere, the gas response was determined at particular operating temperature using the equation (3).

$$S = \frac{(G_{gas} - G_{air})}{G_{air}} \quad (3)$$

Where G_{air} = conductance of thick film in air.

G_{gas} = Conductance of thick film in gas.

Fig. 4 shows the variation in the gases response of 1wt. % Al_2O_3 -doped ZnO film for the gases viz: CO, H_2, NH_3 and ethanol as the function of operating temperatures. The doped film shows the highest response to Ethanol gas (500 ppm) at 400°C. The response goes on increasing with increase in operating temperature, attains its maximum (at 400°C) and then decreases with a further increase in operating temperature. It is clear from the graph that the optimum operating temperature is 400°C for ethanol gas.

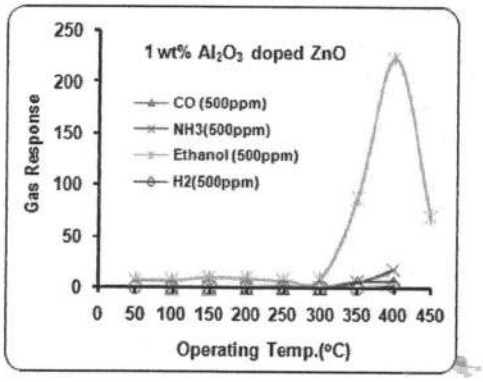


FIG. 4 VARIATION IN GAS RESPONSE WITH OPERATING TEMPERATURE OF 1 wt. % Al_2O_3 –DOPED ZnO FILM

Fig.5 shows the variation in Ethanol gas sensing performances of undoped- ZnO and Al_2O_3 doped-ZnO thick films at different doping concentration (0.5, 1 and 3 wt. %) as the function of operating

temperatures ranging from 50°C to 450°C.

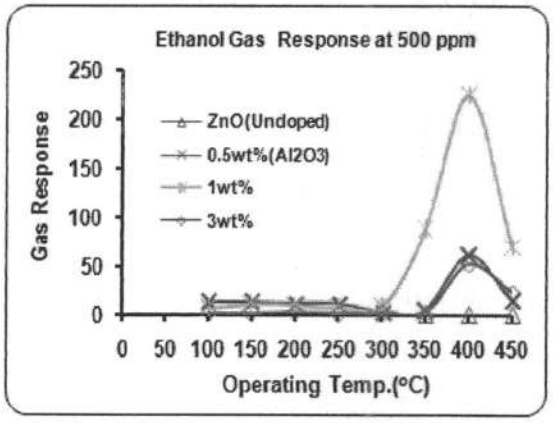
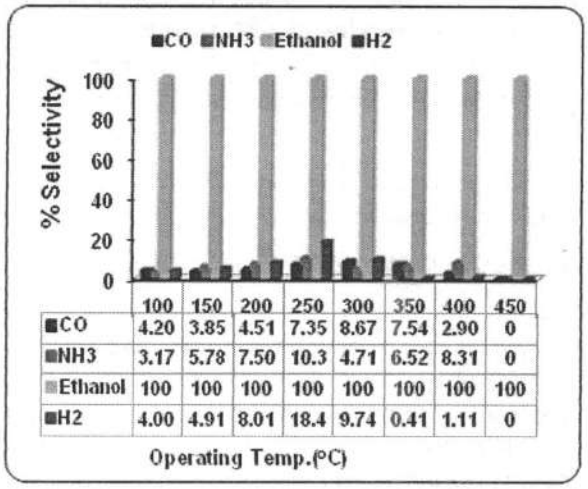


FIG. 5 VARIATION IN ETHANOL GAS RESPONSE WITH OPERATING TEPMERATUE OF UNDOPED AND Al_2O_3-DOPED ZnO FILMS

It was noted from the graph that the undoped ZnO thick film was observed to be poor response for Ethanol gas while all doped films showed the good response to Ethanol gas at 400 °C. The gas response increases with increase in temperature and then decreases with further increase in operating temperature. It has been observed that the increased gas response of thick film sensor is due to the dopants or additives which enhance the chemisorptions of the film to specific gases.

Selectivity of doped ZnO Film

The selectivity is the ability of a sensor to respond to certain gas in the presence of other gases. Percentage selectivity of one gas over the other is defined as the ratio of maximum response of other gas to the maximum response to the target gas at the optimum temperature.



	100	150	200	250	300	350	400	450
CO	4.20	3.85	4.51	7.35	8.67	7.54	2.90	0
NH3	3.17	5.78	7.50	10.3	4.71	6.52	8.31	0
Ethanol	100	100	100	100	100	100	100	100
H2	4.00	4.91	8.01	18.4	9.74	0.41	1.11	0

FIG. 6 % SELECTIVITY OF 1wt. % Al_2O_3 -DOPED ZnO FILM

The bar diagram in Fig. 6 indicates percentage selectivity of 1wt. % Al_2O_3 - doped ZnO thick film as a function of operating temperature for different gases. It is clear from the bar diagram that the doped thick film (1 wt. % Al_2O_3) is more selective to ethanol against the other gases viz: CO, NH_3, and H_2. This is the main feature of Al_2O_3 - ZnO thick film.

Response and Recovery Time of 1 wt. % Al2O3 -ZnO Film

Response time is the time taken for the sensor to attain 90% of the maximum increase in conductance on exposure to the target gas and recovery time is the time taken by the sensor to get back 90% of the original conductance.

The doped ZnO thick film was quick (~ 10 s) to Ethanol gas while the recovery was (~ 40 s). The quick response may be due to faster oxidation of gas. The aluminium species catalyses the reaction promoting the rapid electron transfers between the adsorbate and substrate.

Discussion

Gas Sensing Mechanism Al2O3 -Doped ZnO Thick Film

The gas sensing mechanism of the metal oxide semiconductor sensors belong to the surface controlled type, which is based on the change in conductance of the semiconductor. The oxygen adsorbed on the surface directly influence the conductance of metal oxide based sensors. Oxygen is adsorbed on the oxide crystals surface as ions are formed by abstracting free electrons from the metal oxide semiconductors, reducing the electrical conductivity. The amount of oxygen adsorbed on the sensor surface depends on operating temperature, concentration of additives, particle size, and specific surface area of the sensor. In the aerial atmosphere where the partial pressure of oxygen is taken as constant, oxygen is adsorbed on sensor surfaces of - Al_2O_3 –doped- n-type ZnO in the form of O, O_2^- and O^{2-}, depending on the temperature, The state of oxygen on the surface of ZnO sensor undergoes the following reactions:

$$O_{2(gas)} \rightarrow O_{2(ads)} \quad (4)$$

$$O_{2(ads)} + e^- \xrightarrow{\text{up to 200 } ^oC} O^-_{2(ads)} \quad (5)$$

$$O^-_{2(ads)} + e^- \xrightarrow{\text{up to 400 } ^oC} 2O^-(ads) \quad (6)$$

$$O^-_{(ads)} + e^- \xrightarrow{\text{above 400 } ^oC} O^{2-}(ads) \quad (7)$$

The oxygen species capture electrons from the material, which results in the concentration changes of holes or electrons in the Al_2O_3 doped n-type ZnO semiconductor.

In the presences of gases viz: CO, H_2 and NH_3, the sensing mechanism at different temperatures could be expressed through the following reactions.

$$CO + O^-_{(ads)} \xrightarrow{350\,^oC} = CO_2 + e^- \quad (8)$$

$$2NH_3 + 3O^-_{(ads)} \xrightarrow{350\,^oC} N_2 + 3H_2O + 3e^- \quad (9)$$

$$H_2 + O^-_{(ads)} \xrightarrow{400\,^oC} H_2O + e^- \quad (10)$$

In the presences of Ethanol vapours, the reason for a decrease in the resistance may be due to the oxidation of the ethanol vapours upon coming in contact with the Al_2O_3:ZnO film surface, which liberates free electrons and H_2O. Ethanol vapours react with the chemisorbed oxygen and reject the carrier, thereby reducing the resistance of the Al_2O_3: ZnO material.

The possibility of a reaction of ethanol with the Al_2O_3: ZnO sensing layers can be explained as two oxidation states :

$$C_2H_5OH_{(g)} + [O] \rightarrow CH_3CHO + H_2 \quad (11)$$

(The dehydrogenation to acetaldehyde

$$C_2H_5OH_{(g)} + [O] \rightarrow C_2H_4 + H_2O \quad (12)$$

(The dehydration to ethylene)

Where [O] represents the surface oxygen ions.

The first reaction (11) is a process initiating the oxidation by the dehydrogenation to CH_3CHO intermediate, and the second reaction (12) is initiated by the dehydration to C_2H_4. But the selectivity for the two reactions is initiated by the acid–base properties of the oxide surface. The dehydrogenation process is more probable on the oxide surface with basic properties, while the dehydration is favoured on the acid surface.

Finally intermediate products, acetaldehyde and ethylene, are subsequently reduced to CO_2 and H_2O.

$$C_2H_5OH_{(g)} + 6O^{2-}{}_{(\text{film surface})} \rightarrow 2CO_2 + 3H_2O + 12\,e^-{}_{(\text{cond. band})} \quad (13)$$

At higher temperature, the depletion region created by the chemisorptions of oxygen on the surface extends more deeply, providing larger scope for more gaseous elements to be adsorbed, thereby giving a better response. Also, the hydroxyl group desorbs at higher temperatures. Thus for lower temperature operation (<150°C), the surface of the sensor does not get completely desorbed, which causes a smaller change in resistance. Thus Al_2O_3: ZnO composite has found to markedly and effectively promote the sensitivity to ethanol gas.

Summary and Conclusions

From the results obtained, following conclusions can be made for the sensing performance of the sensors.

i. The undoped ZnO thick film showed low response to ethanol gas.

ii. The 1 wt. % Al_2O_3 -doped ZnO thick showed good response to ethanol gas at 400°C.

iii. The 1wt. % Al_2O_3 -ZnO thick film has observed the most porous which showed maximum response to ethanol gas.

iv. The 1 wt. % Al_2O_3 -doped ZnO thick film sensor has good selectivity to ethanol against, CO, NH_3 and H_2 gas at temperatures.

v. The Al_2O_3 –doped ZnO thick film sensors showed very rapid response (~4s) and recovery (~40s) to ethanol gas.

vi. Over long exposure, it was observed that thick film exhibited a good stability and repeatability as gas sensor with consistent pattern and response magnitude. These studies showed that screen printed thick film of Al_2O_3 doped ZnO thick film on glass substrate can be used as ethanol gas sensor.

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