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Influence of Nb_2O_5 doping on ZnO thick film gas sensors

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Thick films of pure and Nb_2O_5 doped ZnO for various concentrations (1 wt. %, 3 wt. %, 5 wt. %, 7 wt. % and 10 wt. %) were prepared on alumina substrates using a screen printing technique. These films were fired at a temperature of 700ºC for two hours in an air atmosphere. Morphological, compositional and structural properties of the samples were obtained using the scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS) and X-ray diffraction techniques respectively. The Ethanol gas sensing studies were carried out in a static gas sensing system under normal laboratory conditions. The surface resistance of thick films decreases when exposed to ethanol gas. The Nb_2O_5 doped films show significant sensitivity to Ethanol gas than pure ZnO film . 3 wt. % Nb_2O_5-doped ZnO film was found to be more sensitive (84%) to ethanol gas exposed at 300°C than other doping concentrations with fast response and recovery time.

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1. Introduction

The recent awareness about environmental pollution has created a need to develop reliable and inexpensive semiconductor gas sensors. Metal oxide semiconductor gas sensors have been used extensively to detect toxic, pollutant hazardous and combustion gases [1, 2]. The semiconducting metal oxides such as SnO_2, ZnO, Fe_2O_3, TiO_2, WO_3 etc. offer the potential for developing portable and inexpensive gas sensing devices, which have advantages of simplicity, high sensitivity and fast response. The working principle of these semiconductor gas sensors is based on change in conductivity when exposed to the target gases [3]. Thick film technology (Screen printing technique) was introduced in the later part of the 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on a thick film technique has been attracted by the sensor field [4]. Screen printing is a viable and economical method to produce thick films of various materials [5-10]. Zinc oxide (ZnO) is a multifunctional material. Because of its high chemical stability, low dielectric constant, large electrochemical coupling coefficient and high luminous transmittance, ZnO based materials have been widely used as dielectric ceramic, pigment, catalyst and sensing material [11,12,13]. As a gas sensing material, it is one of the earliest discovered and most widely used gases sensing material for the detection of hazardous gases [14-18]. It is sensitive to many sorts of gases and has satisfactory stability. The gas sensing performance of the material can be improved by incorporating dopants and additives [19-23] that can modulate the gas sensing characteristics to some extent.

The addition of Niobium ions prevent or modify the particle growth and making feasible the use of sensors fired at high temperatures and offer the most satisfactory response to gases [24].

Ethanol is a hypnotic (sleep producer) gas having toxic nature [25, 26]. Heavy exposure and/or consumption of alcoholic beverages, particularly by smokers, increase the risk of cancer of the upper respiratory and digestive tracks [27, 28]. Alcoholic cirrhosis leads to liver cancer. Amongst women, the chances of breast cancer increase with alcoholic consumption or exposure. Those working on ethanol synthesis are at great risk of becoming victims of respiratory and digestive track cancer. There is hence a great demand with emerging challenges for monitoring ethanol gas at trace level. Considering these aspects, the efforts were made to develop the thick films of ZnO with Nb_2O_5 as dopant on alumina substrates and to investigate their sensing properties for ethanol vapour.

2. Experimental

The ZnO: Nb_2O_5 pastes used in screen printing were prepared by maintaining the inorganic to organic materials ratio of 70:30. Inorganic part consists of a functional material (ZnO), dopant (Nb_2O_5) and glass frit (70 wt. % PbO, 18 wt. % Al_2O_3, 9wt. % SiO_2 and 3wt. % B_2O_3). Organic parts consist of 8% ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA). The Analar (AR) grade ZnO with x wt. % Nb_2O_5 (x = 1, 3, 5, 7 and 10%) and 5 wt. % of glass frit were mixed thoroughly in an acetone medium with mortar and pestle. A solution of EC and BCA in the ratio 8:92 was made, which was added drop by drop until proper thixotropic properties of the paste were achieved. ZnO thick films were prepared on alumina substrates using a standard screen-printing technique. A nylon screen (40s, mesh no.355) was used for screen-printing. The required mask (2 × 1.25 cm) was developed on the screen using a standard photolithography process. The paste was printed on clean alumina substrates (5 x 2 cm) with the help of a mask. The pattern was allowed to settle for 15 to 20 minutes in air. The films were dried under infrared radiation for 45 minutes to remove the organic vehicle and then fired at a temperature of 700^oC for 2 h (which includes the time required to achieve the peak firing temperature , constant firing for 30 minutes at the peak temperature and then to attain the room temperature) in a muffle furnace. During the firing process glass frit melted and the functional material and dopant were sintered. The function of glass frit is to bind the grains of functional and dopant materials together and also to adhere the film firmly to the substrate surface. The structural properties of $ZnO:Nb_2O_5$ films were investigated using X-ray diffraction analysis from $20\text{-}80^0$ [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) with CuKα, λ=0.1542 *nm* radiation] with a 0.1^o/step (2θ) at the rate of 2 s/step. A scanning electron microscopy (SEM- JOEL JED-2300) was employed to characterize the surface morphology. The composition of ZnO thick film samples were analyzed by an energy dispersive X- ray spectrometer (JOEL-JED 6360 LA). The thickness of the films was measured using a Taylor-Hobson (Taly-step UK) system and was observed to be uniform in the range of 20µm to 25µm.

The specific surface area was calculated for spherical particles using the following equation [29].

$$S_w = 6 / \rho d \quad (1)$$

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

The D.C. resistance of the films was measured by using half bridge method in an air atmosphere at different temperatures. The gas sensing studies were carried out on a static gas sensing system under normal laboratory conditions. The electrical resistance of thick films in air (R_a) and in the presence of ethanol vapour (R_g) was measured to evaluate the gas response (S) given by the relation,

$$S = \frac{R_a - R_g}{R_a} \quad (2)$$

where R_a is the resistance of the ZnO: Nb_2O_5 thick films in air and R_g is the resistance of the ZnO: Nb_2O_5 thick films in ethanol vapour atmosphere.

3. Results and discussion

3.1 Elemental Analysis

The elemental compositions of the pure and doped ZnO films were analyzed using an energy dispersive spectrometer and is shown in Table.1. The mass% of Zn and O in each sample was not as per stoichiometric proportion. The ZnO film doped with 3 wt. % was observed to be most oxygen difficient. The deficiency of the constituent material particles or an excess of it leads to the semiconducting behaviour of the material. [25]

Table 1. Composition of Nb_2O_5 doped ZnO films

Element (mass %)	Nb_2O_5				
	1wt. %	3wt. %	5wt. %	7wt. %	10wt. %
O	16.73	16.52	18.70	16.64	18.68
Zn	83.09	81.97	76.91	78.35	73.81
Nb	0.18	1.51	4.39	5.01	7.51

3.2 Structural analysis

The crystalline structure of the films was analyzed with X-ray diffractogram in the $20\text{-}80^0$ (2θ) range using Cuk_α radiation. Fig. 1 shows the XRD pattern of undoped and Nb_2O_5 doped ZnO thick films of different concentrations. The peaks in XRD patterns observed for ZnO, Nb_2O_5. All the (hkl) planes are matched with JCPDS data for ZnO and Nb_2O_5. The XRD patterns showed that film samples are polycrystalline in nature. It has been observed that (101) reflections are of maximum intensity, which indicates that ZnO films have preferred orientation in the (101) plane. XRD peak broadening is low for pure ZnO films whereas peak broadening is high for 3 wt. % doped films. Therefore the particle size of 3 wt. % doped films was observed as minimum and for pure films, it was observed as maximum.

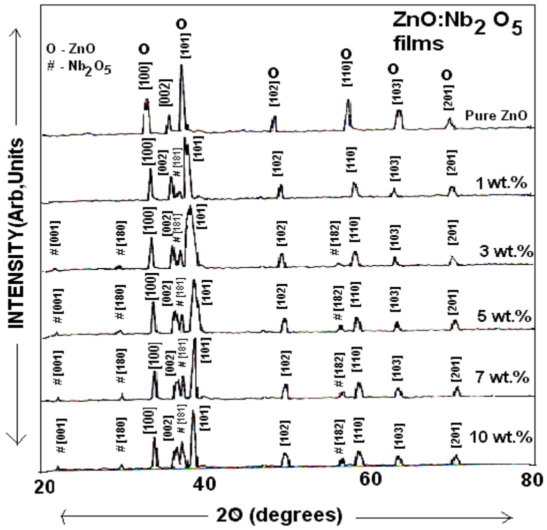


Fig.1. XRD pattern of pure ZnO and ZnO: Nb_2O_5

films fired at 700^{o}C

3.3 Surface morphology analysis

It is well known that the gas sensing properties of a metal oxide thick film strongly depends on its morphological features. A high surface area facilitates the chemisorptions process by increasing the adsorption and desorption rates [30]. Fig. 2 indicates the SEM images of pure and x wt. % of Nb_2O_5 (x = 1, 3, 5, 7 and 10 wt. %) thick films. Fig. 2-(a) shows the microstructure of pure ZnO thick film. It showed that the microstructure is nearly uniform with negligible open porosity. Fig.2-(c) shows the microstructure of 3% Nb_2O_5 doped ZnO thick film which was most sensitive. It showed that the grain size decreases giving large effective surface area. The larger surface area gives more response to react with the target gas. The film seems to be highly porous for oxygen adsorption. The specific surface area was calculated by using equation 1.The specific surface area increases as the size of the grains decreases [29]. Table-2 presents the particle size and surface area of ZnO thick films doped with different wt. % of Nb_2O_5.

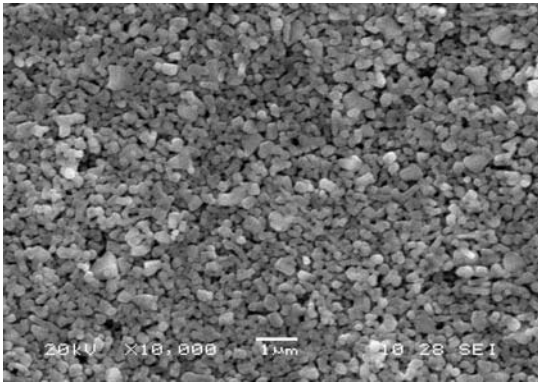


Fig.2a.SEM of Pure ZnO film.

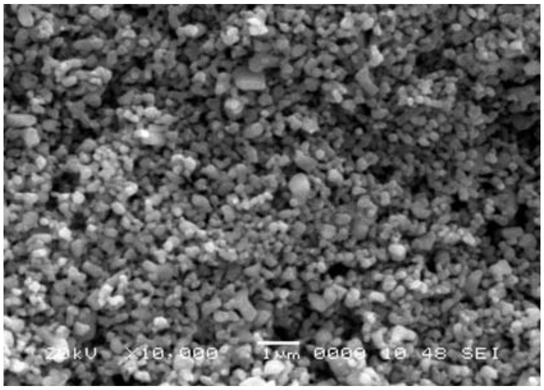


Fig.2b.SEM of 1 wt. % Nb_2O_5: ZnO film

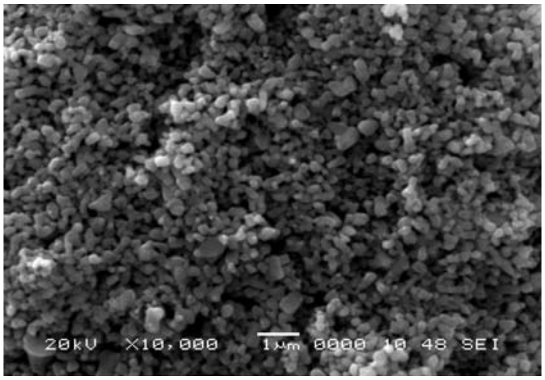


Fig.2c.SEM of 3 wt. % Nb_2O_5: ZnO film.

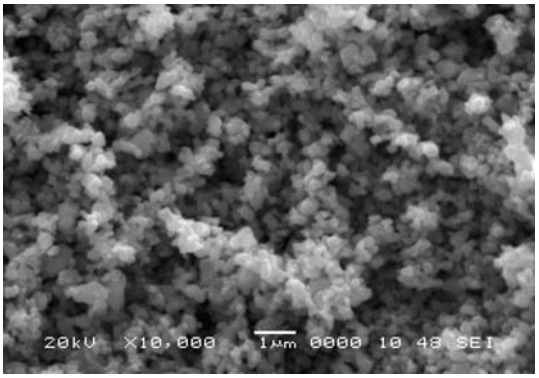
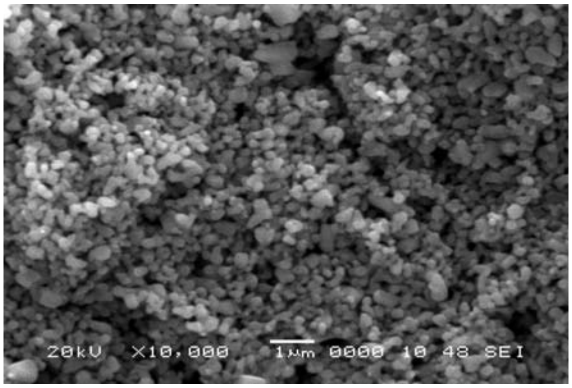


Fig.2d.SEM of 5 wt. % Nb_2O_5: ZnO film.



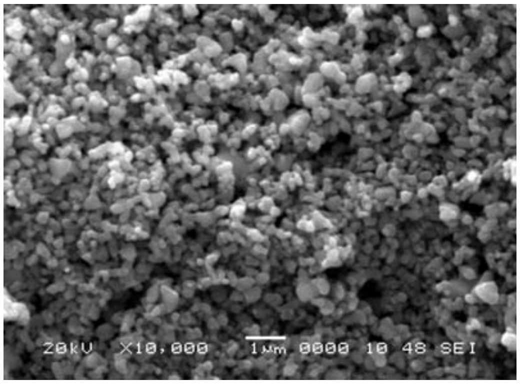


Fig.2e.SEM of 7 wt.% Nb_2O_5: ZnO film

Table 2: Particle size and surface area of ZnO- Nb_2O_5 composite thick films

wt. % of Nb_2O_5	Particle size in nm	Specific Surface Area in m^2/g
Pure ZnO	381	2.752
1	363	2.921
3	244	4.364
5	272	3.932
7	318	3.777
10	323	3.347

3.4. Gas – sensing characteristics

Fig. 3 shows the gas sensitivity of pure ZnO and different wt. % Nb_2O_5 doped ZnO thick films fired at 700°C exposed to 1000 ppm of Ethanol vapour with operating temperatures. The sensitivity of pure ZnO thick film to ethanol vapour was found to be 17.07 % at 350°C. Pure ZnO is notably less sensitive than doped ZnO.The sensitivity of 3 wt. % Nb_2O_5 doped ZnO film was observed to be 84% at 300°C which is higher than other dopant concentrations. Fig. 4-(a) shows histograms indicating the selectivity of 3wt. % of Nb_2O_5 doped ZnO thick film for different gases against Ethanol vapours. Fig. 4-(b) shows variation of sensitivity of 3wt. % of Nb_2O_5 doped ZnO thick film for different gases with operating temperatures. The films showed highest selectivity to Ethanol vapours at 300°C against other tested gases viz: NH_3, LPG. H_2S, CO_2, NO_2. Figure 5 shows the variation of sensitivity of the 3% Nb_2O_5 doped ZnO film with Ethanol vapour concentrations (in ppm) at 300°C temperature. The response and recovery times of 3wt. % Nb_2O_5 doped ZnO thick films are represented in Fig. 6. The response was quick (~ 18 sec) to 1000 ppm of Ethanol while the recovery time was fast (~ 25 sec).

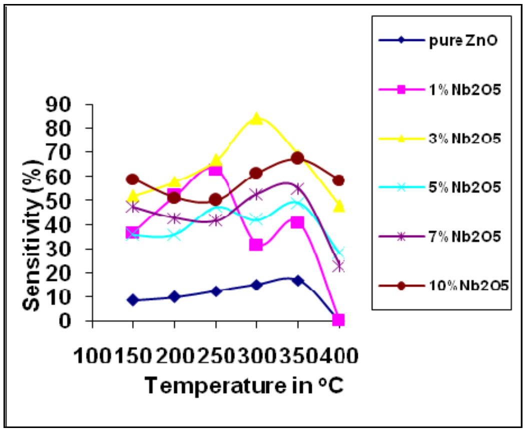


Fig.2f.SEM of 10 wt.% Nb_2O_5: ZnO film.

Fig.3 Gas sensitivity of pure and doped films for 1000 ppm ethanol vapours

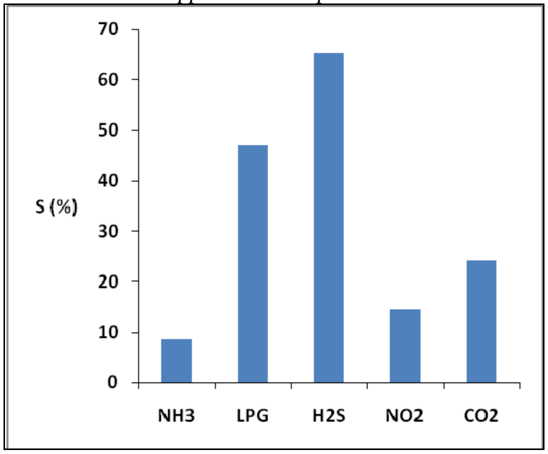


Fig.4(a) Selectivity of 3wt. % of Nb_2O_5: ZnO film for different gases against ethanol vapours

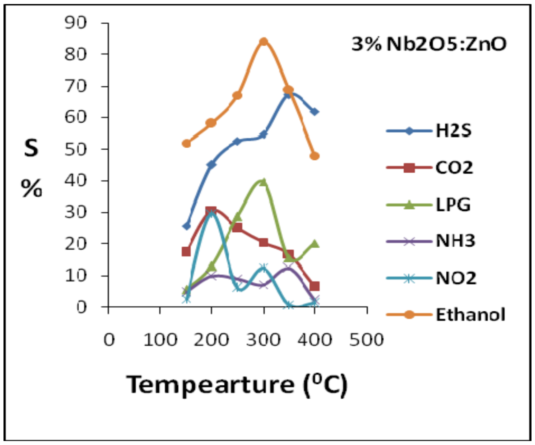


Fig.4(b) Variation of sensitivity of 3wt. % Nb_2O_5 doped ZnO thick film for different gases

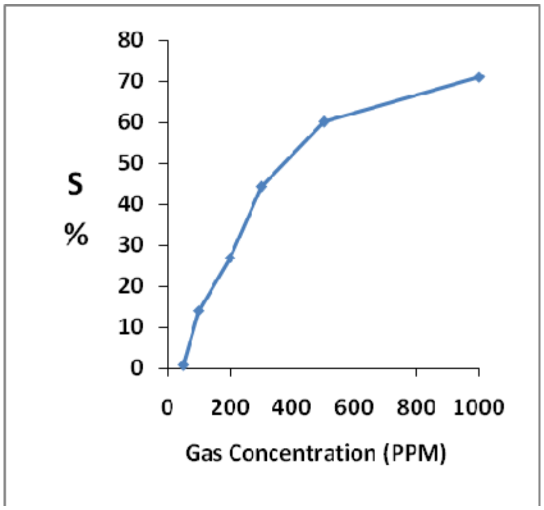


Fig.5. Variation of gas sensitivity with gas concentration

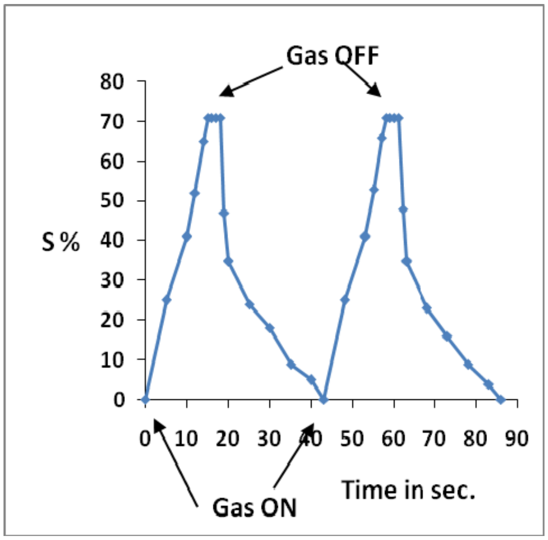


Fig.6 Response and recovery time of 3% Nb_2O_5 doped ZnO film.

The higher response may be attributed to the optimum porosity and largest effective surface area available to react with the gas. The response could be attributed to the adsorption–desorption type of sensing mechanism. The amount of oxygen adsorbed on the surface would depend on the number of Nb_2O_5 misfits to adsorb the oxygen which in turn would oxidize the exposed gas.

When the optimum amount of Nb_2O_5 (3 wt. %) is incorporated on the surface of the ZnO film, Nb species would be distributed uniformly throughout the surface of the film. As a result the initial resistance of the film is high and this amount would also be sufficient to promote the catalytic reaction effectively and the overall change in the resistance on the exposure of ethanol vapour leading to an increase in the sensitivity. When the amount of Nb_2O_5 on the surface of the film is less than the optimum, the surface dispersion may be poor and the sensitivity of the film is observed to be decreased since the amount may not be sufficient to promote the reaction more effectively. On the other hand, as the amount of Nb_2O_5 on the surface is more than the optimum, the Nb atoms would be distributed more densely. Therefore the initial resistance of the film would decrease and the overall change in the resistance on the exposure of ethanol vapour would be smaller leading to lower response [13].

This film was exposed to different gas concentrations of ethanol. The sensitivity values were observed to have increased continuously by increasing the gas concentration up to 1000 ppm. The response was highest for 1000 ppm of Ethanol vapour. The monolayer of the gas molecules formed on the surface could cover the whole surface of the film. The excess gas molecules would remain idle and would not reach the surface active sites of the film. So, the response at higher concentrations of the gas was not expected to increase in large extent [25].

The quick response may be due to faster oxidation of gas. Its high volatility explains its quick response and fast recovery to its initial chemical status.

3.5 Sensor mechanism

The gas sensitive mechanism of a semiconductor metal oxide sensor is based on the resistance change of some semiconductor oxides, due to oxidation or reduction of the semiconductor oxide itself, according to the gases of the surrounding atmosphere. In the presence of test gases, the electrical conductivity of porous semiconductor thick film sensor changes due to two main reactions occurring on the surface [4, 31]. These reactions are the adsorption of atmospheric oxygen on the surface and the direct reaction of lattice oxygen or interstitial oxygen with test gases. In the first reaction, atmospheric oxygen molecules are physisorbed on the surface sites, which while moving from site to site, get ionized by taking an electron from the conduction band and are thus ionosorbed on the surface as O^-_{ads} [4, 32]. This causes decrease in conductance of sensor material. The resulting reaction is,

$$O_2 + 2e^- \rightarrow 2O^-_{ads} \qquad (3)$$

In ZnO films, electrons are also extracted from the interstitial zinc atoms Zn_i^{2+} which act as an electron donor [4, 33]. The interstitial zinc atoms in such cases are ionized via the following reversible reaction,

$$Zn_i^{2+} \leftrightarrow Zn_i^{+} + e^-$$

In the second step the reducing gas (R) present in air ambient reacts with the chemisorbed oxygen, thereby releasing an electron back to the conduction band and increasing the conductance of the semiconductor,

$$R + O^-_{ads} \rightarrow RO + e^- \qquad (4)$$

At higher temperature RO desorbs.

The catalyst used dispersed on the surface of the grains of the sensor material activates the reducing gas and allows it to spill over onto the sensor material. Thus the resulting change in conductance in Eq. (4) is enhanced

Nb_2O_5 doped ZnO thick films consist of number of grains of Nb_2O_5 (misfits) and ZnO connected to each other through grain boundaries. This leads to the formation of barrier height among the grains and increases the resistance in the absence of the target gas [34].

The drastic increase in electrical conductivity of Nb_2O_5 doped ZnO could be attributed to the charge-carrier generation mechanism resulting from the electronic defects [31] and can be described as,

$$Nb_2O_5 \; ZnO \longleftrightarrow 2Nb_{Zn} + 2Oo + 3/2\, O_2\,(g)$$

$$Nb_{Zn} \longleftrightarrow Nb^{3+}{}_{Zn} + 3e \qquad (5)$$

These generated electrons and donor levels in the energy band gap of ZnO will contribute to an increase in conductivity. When ethanol reacts with oxygen, a complex series of reactions take place, ultimately converting the ethanol to carbon dioxide and water as,

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

This shows an n-type conduction mechanism. Thus on oxidation, number of electrons in conduction band increases which increases the conductivity. The temperature (thermal energy) at which the gas response is maximum is the actual thermal energy required to activate the material for progress in reaction. However the response decreases at higher operating temperature, as the oxygen adsorbates are desorbed from the surface of the sensor [31]. Also at higher temperature, the carrier concentration increases due to intrinsic thermal excitation and Debye length decreases. This may be one of the reasons for decreased gas response at higher temperature [35].

4. Conclusions

From the results obtained, following conclusions can be drawn for the sensing performance of Nb_2O_5 doped ZnO thick films

(1) It has become possible to make thick film gas sensors using screen printing method

(2) Pure ZnO thick films showed low response to Ethanol vapours

(3) 3wt. % Nb_2O_5 doped ZnO thick films showed highest response to ethanol at 300^0C.

(4) The sensitivity increases in proportion to the test gas concentration

(5) The sensor has good selectivity to ethanol against LPG, NH_3, H_2S, CO_2 and NO_2 at 300^0C.

(6) The sensor showed very rapid response and recovery to ethanol.

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