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Preparation and Study of NH_3 Gas Sensing Behavior of Fe_2O_3 Doped ZnO Thick Film Resistors

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Abstract: The preparation, characterization and gas sensing properties of pure and Fe_2O_3-ZnO mixed oxide semiconductors have been investigated. The mixed oxides were obtained by mixing ZnO and Fe_2O_3 in the proportion 1:1, 1:0.5 and 0.5:1. Pure ZnO was observed to be insensitive to NH_3 gas. However, mixed oxides (with ZnO: Fe_2O_3 =1:0.5) were observed to be highly sensitive to ammonia gas. Upon exposure to NH_3 gas, the barrier height of Fe_2O_3-ZnO intergranular regions decreases markedly due to the chemical transformation of Fe_2O_3 into well conducting ferric ammonium hydroxide leading to a drastic decrease in resistance. The crucial gas response was found to NH_3 gas at 350^0C and no cross response was observed to other hazardous and polluting gases. The effects of microstructure and doping concentration on the gas response, selectivity, response and recovery of the sensor in the presence of NH_3 gas were studied and discussed.

Keywords: ZnO, Fe_2O_3, Cross response, Thick film resistor, NH_3 gas sensor

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1. Introduction

Environmental pollution [1-4] is a burning global issue; pollution has raised its ugly head high in the global environment. Ammonia is utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, etc. A leak in the system can result the health hazards. Ammonia is harmful and toxic [5-9] in nature. The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. Therefore all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentrations. It is therefore, necessary to monitor ammonia gas and to develop the ammonia gas sensor. Efforts are made to develop the ZnO based NH_3 gas sensors.

Among the various materials ZnO [10-14] is the most promising semiconductor to detect the toxic and hazardous gases. It has been studied that α- Fe_2O_3 [15-18] was used as gas sensing element. In fact pure α- Fe_2O_3 was reported to have poor gas sensitivity. Some well-known materials for NH_3 gas sensing are ZnO, modified-ZnO (viz. Fe-ZnO, Pd-ZnO, and Ru-ZnO) [13, 14], molybdenum oxide [19], polyaniline [20], polypyrrole [21], Au and MoO_3-modified WO_3 [22, 23], Pt and SiO_2-doped SnO_2 [24] etc.

2. Experimental

2.1. Thick film preparation

AR grade (99.9 % pure) ammonium ferric sulfate $NH_4Fe(SO_4)_2,12H_2O$ was mixed to zinc sulfate ($ZnSO_4$, $7H_2O$) in ratios 1:1, 1: 0.5 and 0.5: 1. The mixture was dissolved in double distilled water and then heated slowly up to 100^0C for 10 h. The mixture is then calcined at 500^0C for 5 hours. The final products were ball milled to ensure fine powder. Thick films of, so obtained powder, were prepared by adopting the procedure explained elsewhere [13, 25].

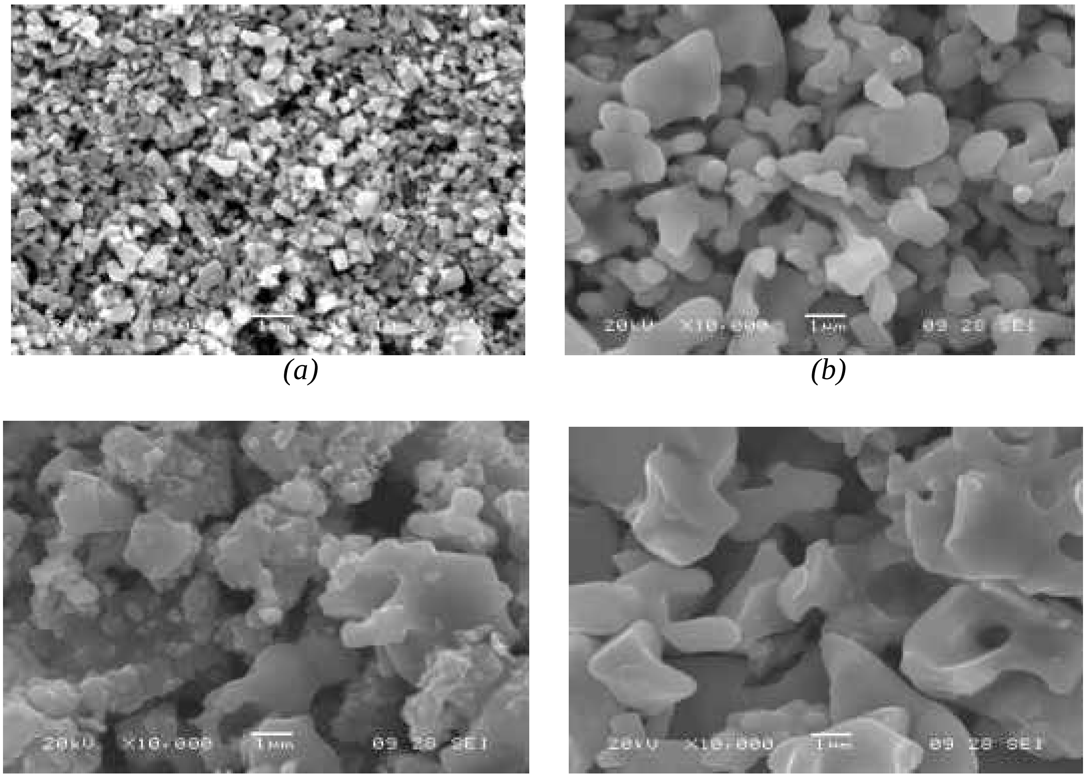
2.2. Characterization

The microstructure and chemical composition of the films were analyzed using a scanning electron microscope (JOEL JED 2300) coupled with an energy dispersive spectrometer (6360 LA). Thickness measurements were carried out using a Taylor- Hobson (Talystep, UK) system. Electrical and gas sensing characteristics were measured using a static gas sensing system.

3. Materials Characterization

3.1. Microstructure-SEM

Fig.1 depicts the SEM images of unmodified ZnO and Fe_2O_3-modified ZnO films. Unmodified ZnO film (Fig. 1a) consists of randomly distributed grains with smaller size and shape distribution. Fig. 1b depicts the microstructure of a most sensitive Fe_2O_3-modified film (with ZnO: Fe_2O_3 = 1:0.5) consisting of giant grains of Fe-species associated with smaller grains of ZnO. This film shows more porosity, giving largest effective surface area. This enables larger surface for the gas to react giving more response. Fig. 1c consists of large number of giant grains of Fe-species associated with ZnO as compared to the grains associated with Fig. 1b. The smaller grains of Zn-species are distributed randomly with giant grains of Fe-species. Fig. 1d consists of even larger grains of Fe-species in association with ZnO as compared to the grains associated with Fig. 1c. The smaller grains of Zn-species are entirely covered with giant grains of Fe-species. The decreased porosity in figures 1c-d tends to reduce the gas response.



(a) *(b)*

(c) *(d)*

Fig.1. Micrographs of (a) Unmodified, (b) Fe_2O_3-modified (ZnO: Fe_2O_3 = 1: 0.5), (c) Fe_2O_3-modified (ZnO: Fe_2O_3 = 1:1) and (d) Fe_2O_3-modified (ZnO: Fe_2O_3 = 0.5:1) samples.

3.2. Thickness measurement

The thicknesses of the films were observed to be in the range from 30 to 40 µm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

3.3. Thermoelectric power measurements

The n-type semiconductivity of thick films of ZnO and Fe_2O_3-doped ZnO were confirmed by measuring thermoelectromotive force of the thick film samples. The ZnO and Fe_2O_3-doped ZnO were observed to be n-type material

4. Electrical Properties

4.1. I-V characteristics

Fig.2 depicts the I-V characteristics of the Fe_2O_3-modified ZnO films. It is clear from the symmetrical I-V characteristics that the silver contacts on the film were ohmic in nature.

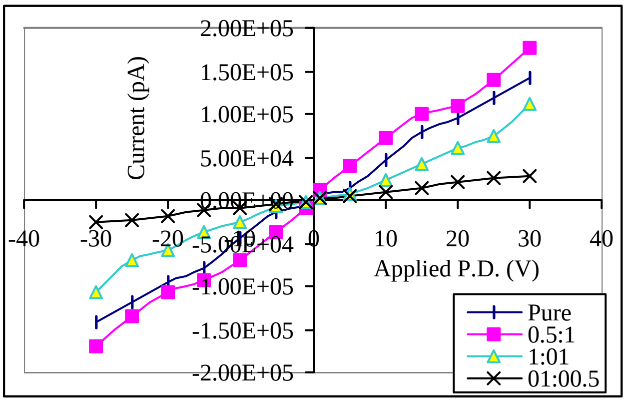


Fig. 2. I-V characteristics.

4.2 Electrical conductivity

Fig.3 shows the variation of log (conductance) with temperature. The conductance values of all samples increase with operating temperature. They are nearly linear from 150^{0}C to 250^{0}C. The increase in conductance with increasing temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of the Fe_2O_3-modified ZnO. It is observed from Fig.3 that the electrical conductance of the pure ZnO was larger than Fe_2O_3-modified ZnO films in air ambient. It may be due to the intergranular potential barrier. Pure ZnO has only one kind of grains arranged uniformly. The modified films cause the formation of heterogeneous intergrain boundaries of Fe_2O_3-ZnO. Thus increased barrier height of the intergranular region of modified ZnO may be responsible to decrease in conductance.

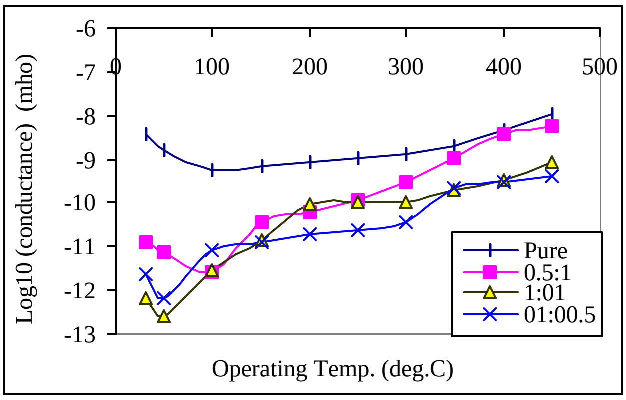


Fig.3. Conductance-temperature profiles of Fe_2O_3-modified samples in air.

5. Sensing Performance

5.1. Sensing characteristics

The relative response to a target gas is defined as the ratio of the change in conductance of a sample upon exposure of the gas to the original conductance in air. The gas response can be written as:

$$\text{Gas Response} = \frac{G_g - G_a}{G_a} = \frac{G}{G_a}$$

where G_a is the conductance in air and G_g is the conductance in a sample gas.

Specificity or selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of different gases. Response time (RST) was defined as the time required for a sensor to attain the 90% of the maximum increase in conductance after the exposure of test gas on the sensor surface, while recovery time (RCT) as the time taken to get back 90% of the maximum conductance in air.

5.2. Response of unmodified ZnO films

Fig. 4 shows the variation of gas response of unmodified ZnO to 1000 ppm NH_3 gas with operating temperature. The response was observed to increase with temperature up to 400^0C and then decrease with a further increase in temperature. The response of unmodified ZnO was very poor (17) to NH_3 gas at 400^0 C.

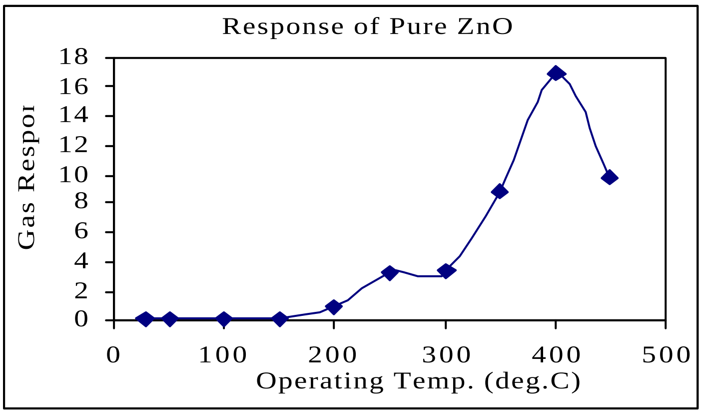


Fig. 4. Variation of response with temperature.

5.3. Gas response of Fe_2O_3-modified ZnO

5.3.1 Gas response and NH_3 gas concentration

The variation of response of Fe_2O_3-modified (1: 0.5) sample with NH_3 gas concentration is represented in Fig.5. It is clear from the figure that the gas response goes on increasing with gas concentration up to 300 ppm at 350^0C. The rate of increase in response was relatively larger up to 300 ppm and smaller beyond 300 ppm. Thus, the active region of the sensor would be up to 300 ppm.

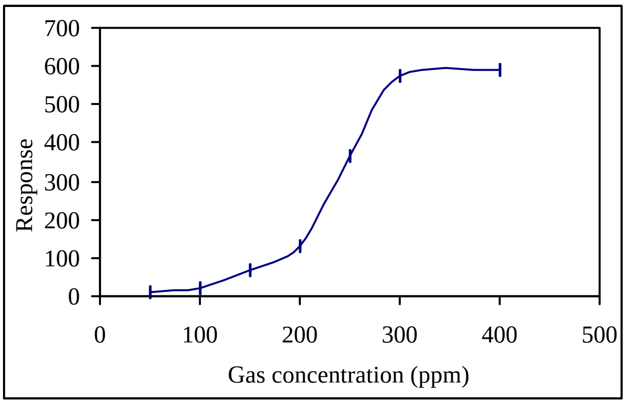


Fig. 5. Variation in response with NH_3 gas concentration.

5.3.2. Response and operating temperature

The response to 300 ppm NH_3 of Fe_2O_3-modified films, as a function of operating temperature is shown in Fig. 6. The sample, with ZnO: Fe_2O_3 ratio equals 1: 0.5 wt %, was observed to be the most sensitive of all. It showed the large response (573) to 300 ppm NH_3 at 350^0C. The response could be attributed to the adsorption-desorption type sensing mechanism. The higher response of this sample as compared to other Fe_2O_3-modified samples may be due to the optimum porosity and largest effective area available to react to gas. For ZnO: Fe_2O_3 ratio 1: 1 and 0.5: 1, the giant molecules of Fe_2O_3 and smaller grains of ZnO form the large intergranular potential barrier. Small amount of oxygen would be adsorbed and reduction of target gas would be weak giving smaller response. For ZnO: Fe_2O_3 ratio 1:0.5, the optimum effective surface area, would adsorb the oxygen in large extent, giving large response.

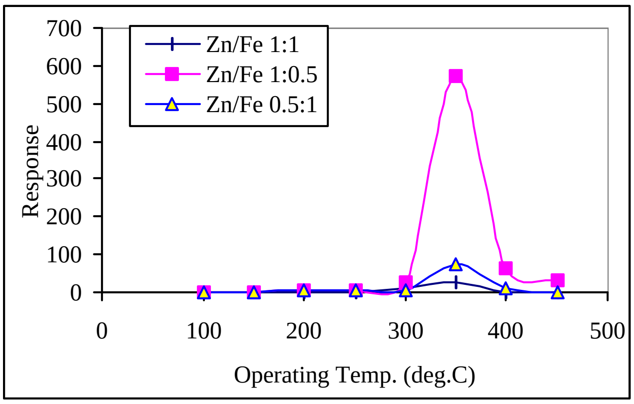


Fig. 6. Variation of response with operating temperature.

5.3.3 Response and mass % Fe_2O_3 modifier

Fig.7 is the histogram indicating the NH_3 (300 ppm) gas response as a function of the amount of á-Fe_2O_3 –modifier. The sensor with 33 mass % of á-Fe_2O_3 was observed to be most sensitive at 350^0C.

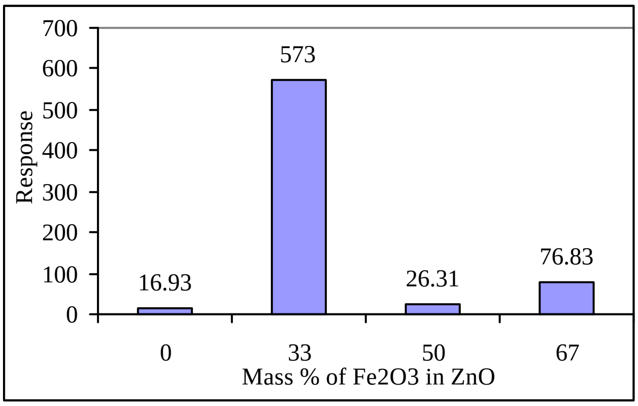


Fig. 7. Response values of different Fe_2O_3-modified samples.

5.3.4. Selectivity for NH_3 against various gases

Fig. 8 depicts the selectivity of Fe_2O_3-modified (ZnO: Fe_2O_3 = 1: 0.5) sensor for NH_3 (300 ppm) gas at 350^0C. The sensor showed high selectivity for NH_3 and could distinguish the NH_3 among all the gases: LPG, CO_2, C_2H_5OH, H_2 and Cl_2.

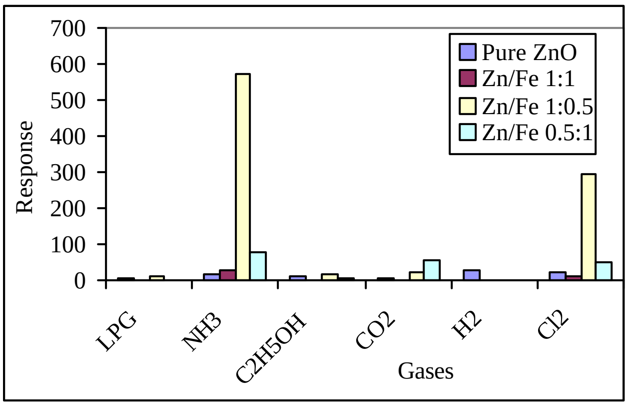


Fig. 8. Selectivity of NH_3 gas from mixture of gases.

5.3.5. Response and recovery of the sensor

The response and recovery of the á-Fe_2O_3 -modified (ZnO: Fe_2O_3 = 1: 0.5) sensors are represented in Fig. 9. The response was quick (~ 30 s) to 300-ppm of NH_3, while the recovery was fast (~90 s). The fast response may be due to immediate oxidation of NH_3 gas. The negligible quantity of the surface reaction product and its high volatility explains its fast response to ammonia and quick recovery to its initial chemical status.

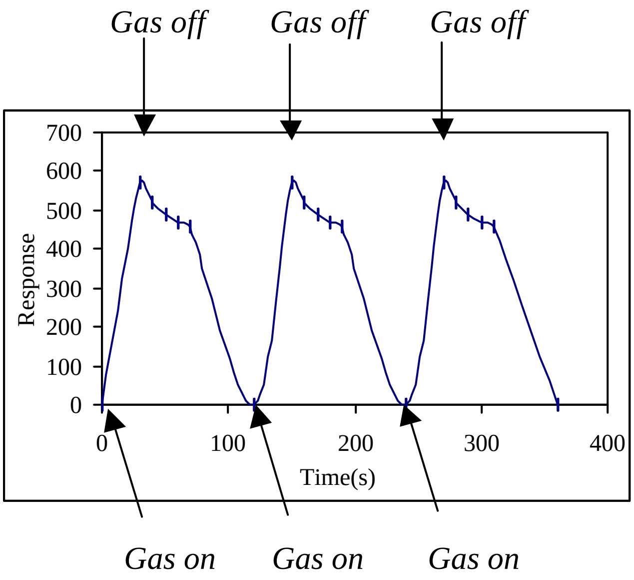


Fig. 9. Response and recovery of the Fe_2O_3-modified sample.

6. Discussion

Gas sensing mechanism is generally explained in terms in conductance either by adsorption of atmospheric oxygen on the surface and / or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. In case of former, the atmospheric oxygen adsorbs on the surface by extracting an electron from conduction band, in the form of super oxides or peroxides, which are mainly responsible for the detection of the test gases. At higher temperature, it captures the electrons from conduction band as:

$$O_{2\,(air)} + 4e^{-}_{(cond.band)} \rightarrow 2O^{2-}_{(film\ surface)}$$

It would result in decreasing conductivity of the film. When ammonia reacts with the surface of the film and adsorbed oxygen on the surface of the film, it gets oxidized to nitrogen oxide gas and ferric ammonium hydroxide, liberating free electrons in the conduction band. The following reaction takes place as:

$$Fe_2O_3 + 5NH_{3\,(gas)} + 4\,O^{2-}_{(film\ surface)} \rightarrow Fe_2\,(NH_4OH)_{3\,(film\ surface)} + 2\,NO_{2(gas)} + 8\,e^{-}_{(cond.band)}$$

This shows n-type conduction mechanism. Thus generated electrons contribute to sudden increase in conductance of the thick film. The Fe_2O_3 misfit regions dispersed on the surface would enhance the ability of material to adsorb more oxygen species giving high resistance in air ambient. On exposure to the NH_3 containing atmosphere, Fe_2O_3 would be converted into ferric ammonium hydroxide and the resistance was observed to decrease in large extent. Therefore, the high response was obtained to 300 ppm NH_3 gas. The high response, high selectivity from mixed gases, fast response and recovery and easy operation of the sensor are the main features achieved in the present investigation.

7. Summary

From the results, following statements can be made for the sensing performance of Fe_2O_3 -modified sensors.

1. Pure ZnO thick films are observed to be insensitive to NH_3 gas.
2. Fe_2O_3-modified ZnO sensors showed high response to 300 ppm NH_3 gas at 350^0C.
3. The bulk properties of pure ZnO were conveniently customized by doping Fe_2O_3 in ZnO.
4. The sensor was highly selective to a trace amount (300 ppm) of NH_3 gas from other toxic gases of higher concentrations.
5. The sensor showed very rapid response (~30 s) and recovery (~90 s) to NH_3 gas.

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