

Room Temperature Ammonia Gas Sensing Using MnO₂-Modified ZnO Thick Film Resistors

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Abstract

Pure ZnO thick film, prepared by screen-printing technique, was almost insensitive to NH₃. Pure ZnO thick films were surface modified with MnO₂ by dipping them into 0.01 M aqueous solution of manganese chloride (MnCl₂) for different intervals of time and fired at 500°C for 12 h. The grains of MnO₂ would disperse around the grains of ZnO base material. The MnO₂ modified ZnO films dipped for 30 min were observed to be sensitive and highly selective to NH₃ gas at room temperature. An exceptional sensitivity was found to low concentration (50 ppm) of NH₃ gas at room temperature and no cross sensitivity was observed even to high concentrations of other hazardous and polluting gases. The effects of surface microstructure and MnO₂ concentrations on the sensitivity, selectivity, response and recovery of the sensor in the presence of NH₃ and other gases were studied and discussed. The better performance could be attributed to an optimum number of surface misfits in terms of MnO₂ on the ZnO films.

Keywords: MnO₂ Modified ZnO, Thick Films, Room Temperature Sensing, NH₃-Gas Sensor

1. Introduction

Ammonia is produced and utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, food processing, medical diagnosis, fire power plants etc. A leak in the system can result the health hazards. Ammonia is harmful and toxic [1-5] in nature. Therefore all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentration levels. Detection of low concentration of ammonia is not only important from the points discussed above but also, it is very important from the view of chemical pollution in the production of silicon devices in clean rooms. It is therefore necessary to monitor ammonia gas and to develop the ammonia gas sensors. Efforts are made to develop the ZnO -based gas sensors, which should detect ammonia at room temperature.

Among various materials ZnO [6-8] is the most promising semiconductor to detect toxic and hazardous gases. In fact pure ZnO was reported to have poor gas sensitivity. Various ammonia sensors reported basically work at higher temperature (> 300°C) [9-11], but it is not convenient to work at such high temperature while sensing. The room temperature sensors are therefore necessary.

Few room temperature ammonia sensors are already available [12,13], but having comparatively low response. The electrolytic techniques using diaphragm electrodes are generally used for the detection of ammonia. However, this method is expensive and does not have sufficient response and selectivity for ammonia [14,15]. Another technique utilizes a Pd-metal oxide semiconductor MOS device. This device is sensitive to ammonia but it suffers from poor selectivity. A few sensor models are also available for detecting ammonia gas. They are Figaro gas sensor model TGS 824 (detection range 300 ppm) and Sierra gas monitor model CM 99-447 (electrochemical type, detection range 200 ppm).

Despite of high sensitivity, selectivity and long-term stability, the main drawback of such sensors is that they are operated at high temperature (>300°C). Also, the noble metal additives like Pt, Pd, Au, and Ag to a base material like ZnO, for the modification, increases the cost of the sensors. Therefore the applicability of these sensors remains limited. Hence the sensors operable at room temperature with low cost metal additives must be developed for large applicability. In the present work, the efforts are made to develop a room temperature sensor with a low cost additive (MnO₂) using dipping technique—a simplest method of modification.

2. Experimental Procedure

2.1. Powder and Paste Preparation

AR grade (99.9% pure) zinc oxide powder was ball milled to ensure sufficiently fine particle size. The fine powder was calcined at 1100°C for 24 h in air and re-ground. The thixotropic paste was formulated as explained elsewhere [16,17]. The ratio of inorganic to organic part was kept as 75: 25 in formulating the paste. The paste was then used to prepare thick films.

2.2. Thick Film Preparation

The thixotropic paste was screen printed on a glass substrate in desired patterns. Fluidity of the paste depends up on extent of organic part, which goes in its formulation, *i.e.*, on solid to liquid ratio. Paste must exhibit a certain degree of yield such that after flow occurs under squeegee pressure, it should stiffen and remain in position to have sharp line definitions of patterns to be printed. In other words, it should exhibit thixotropic properties. The films prepared were fired at 500°C for 12 h. These films were surface modified by dipping them into a 0.01 M aqueous solution of manganese chloride ($MnCl_2$) for different intervals of time such as 5 min, 15 min, 30 min and 45 min, and were dried at 90°C, followed by firing at 500°C for 12 h in ambient air. The particles of manganese chloride dispersed on the films would be transformed to manganese oxide (MnO_2) during firing process, and sensor elements with different mass% of MnO_2 were obtained. These surface modified films are termed as MnO_2 modified films. Silver contacts were made by vacuum evaporation for electrical measurements.

2.3. Characterizations

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). The polycrystalline structures of the films were analyzed with X-ray diffractogram (RIGAKU DMAX 2500) using CuK_{α} radiation with a wavelength 1.5418Å. 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.

2.4. Details of the Gas Sensing System

There were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample un-

der test, up to required operating temperatures. The current passing through the heating element was monitored using a relay with adjustable ON and OFF time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and current was measured by a digital Pico-ammeter. Air was allowed to pass into the glass dome after every NH_3 gas exposure cycle.

3. Materials Characterizations

3.1. Structural Properties (X-Ray Diffraction Studies)

Figure 1 depicts the XRD of MnO_2 -modified ZnO film. The observed peaks are matching well with ASTM reported data of ZnO. The sharp peaks of the XRD pattern correspond to ZnO and are observed to be microcrystalline in nature. The average grain size was determined using Scherrer formula and was estimated to be 190 nm. The crystals show anisotropy because different directions within the repeating pattern interact differently with incident radiations. In case of dipped films, no peaks corresponding to MnO_2 were observed, which may be due to its very small mass% dispersed on the surface of ZnO thick films.

3.2. Microstructure-SEM

Figure 2 depicts the SEM images of unmodified (pure) and two MnO_2 -modified ZnO films (dipped for 30 min, which was most sensitive and for 45 min, the longest dipping time). The pure ZnO film (**Figure 2(a)**) consists of randomly distributed grains with smaller size and shape distribution. **Figure 2(b)** depicts the microstructure of MnO_2 -modified ZnO film (30 min) consisting of

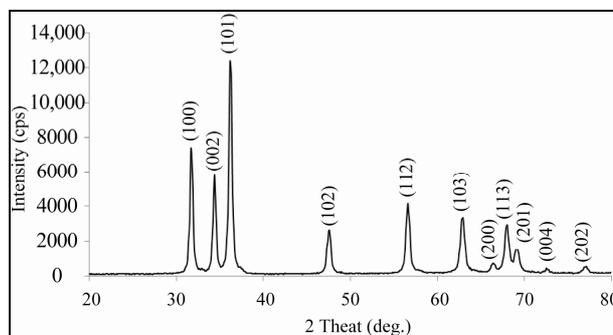
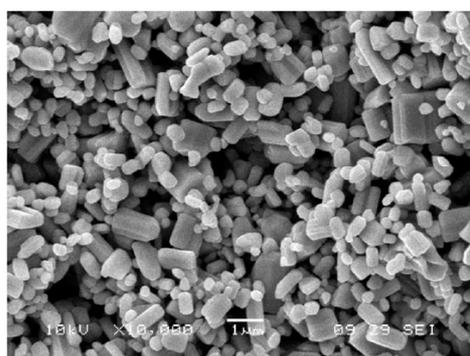


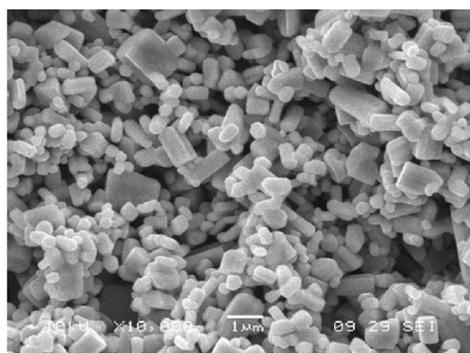
Figure 1. XRD of MnO_2 -modified ZnO (30 min).



(a)



(b)



(c)

Figure 2. (a) Micrographs of pure ZnO sample; (b) Micrographs of MnO₂-modified (30 min) ZnO sample; (c) Micrographs of MnO₂-modified (45 min) ZnO sample.

some larger particles distributed around smaller grains. **Figure 2(c)** depicts the microstructure of MnO₂-modified ZnO film (45 min) consisting of some larger particles distributed around smaller grains, which may be more as compared with the grains in **Figure 2(b)**.

3.3. Thickness Measurement

The thicknesses of the films were observed to be in the range from 30 to 35 μm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

3.4. Quantitative Elemental Analysis

The quantitative elemental compositions of MnO₂-modified ZnO films were analysed using an energy dispersive spectrometer and mass% of Zn, O, MnO₂ and ZnO are represented in **Table 1**. Pure ZnO is expected to be stoichiometric and showing insulating properties. The fine powder of pure ZnO calcined at higher temperature (1100°C for 24 h) losses oxygen, resulting in deficiency of oxygen. Stoichiometrically expected mass% of Zn and O (in ZnO) are 80.34 and 19.66, respectively. The mass% of Zn and O in each samples were not as per the stoichiometric proportion, leading to semiconducting nature (**Table 1**). It is clear from **Table 1** that, the mass% of MnO₂ goes on increasing with the dipping time, reaches to maximum and decreases further. The film dipped for 30 min was found to be most oxygen deficient. This may be the reason of showing most sensing performance for this film.

4. Electrical Properties of the Sensor

4.1. I-V Characteristics

Figure 3 depicts the I-V characteristics of the pure and MnO₂ modified ZnO films. It is clear from the symmetrical I-V characteristics that the silver contacts on the films were ohmic in nature.

Table 1. Elemental analysis of pure and MnO₂ modified ZnO films.

Elemental Mass %	Dipping time (min)				
	0 (Pure)	5	15	30	45
Zn	91.95	89.20	88.32	91.23	89.23
O	08.05	10.62	11.36	08.01	10.12
ZnO	100.00	99.82	99.68	99.24	99.35
MnO ₂	00.00	00.18	00.42	00.76	00.65
ZnO-MnO ₂	100.00	100.00			

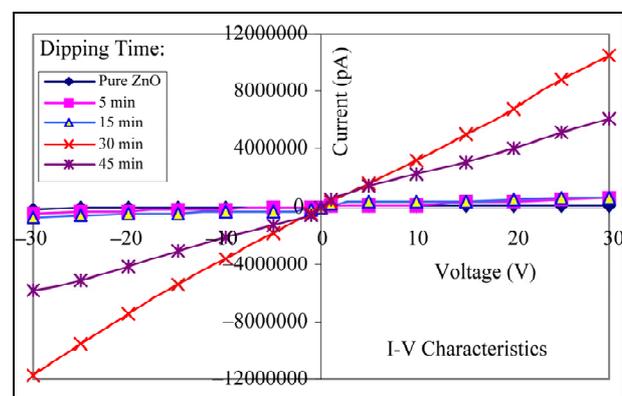


Figure 3. I-V characteristics of pure and MnO₂ modified ZnO films.

4.2. Electrical Conductivity

Figure 4 shows the variation of log (conductivity) with reciprocal of temperature. The conductivity values of all samples increase with operating temperature. They are nearly linear to $1/T$ in the range from 100°C to 250°C . The increase in conductivity with increasing temperature could be attributed to the negative temperature coefficient of resistance and semiconducting nature of the MnO_2 modified ZnO films. The conductivity increases during 250°C to 350°C and suddenly increases above 350°C . It is observed from **Figure 4** that the electrical conductivity of the pure ZnO film was larger than modified ZnO films in dry air. It may be due to the intergranular potential barrier. Pure ZnO has only one kind of grains, where in the case of activated films there would be two types of the grains MnO_2 and ZnO. The modification causes the formation of heterogeneous intergrain boundaries of MnO_2 -ZnO. Thus increased barrier heights of the intergranular regions of modified ZnO may be responsible to decrease the conductivity.

5. Sensing Performance of the Sensor

5.1. Measurement of Gas Response, Selectivity, Response and Recovery Time

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

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

where G_a = conductance in air and G_g = conductance in a target 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 exposure of the sensor surface to a test gas, while recovery time (RCT) as the time taken to get back 90% of the maximum conductance [17] in air.

5.2. Sensing Performance of Pure ZnO Thick Films

5.2.1. Effect of Operating Temperature

Figure 5 shows the variation of response of pure ZnO thick film to 1000 ppm NH_3 gas with operating tempera

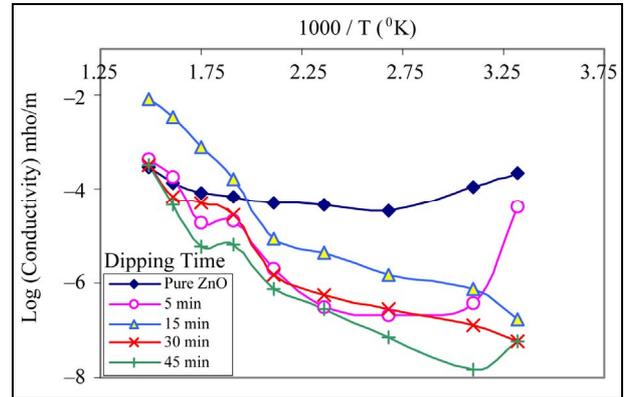


Figure 4. Conductivity-temperature profiles of MnO_2 modified ZnO samples.

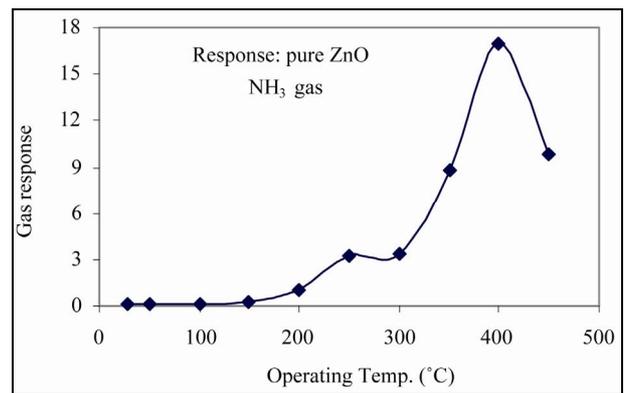


Figure 5. Variation of response of pure ZnO film with temperature.

ture. The gas response increases with operating temperature, reaches maximum at 400°C and then decreases with a further increase in temperature. The response of pure ZnO to NH_3 gas is 17 at 400°C . The response of pure ZnO to NH_3 gas is related, generally, to the oxygen adsorption on the surface of the film. If the film surface chemistry is favorable for adsorption, the response and selectivity would be enhanced. The oxygen adsorption is poor for pure ZnO and shows poor response to NH_3 . In addition to this, ZnO requires relatively larger operating temperature to adsorb the oxygen ions, and therefore it would have responded at higher operating temperature. To improve the sensing performance of ZnO, it is essential to modify pure ZnO.

5.2.2. Selectivity

It is observed from the **Figure 6** that the pure ZnO shows maximum response to H_2 at higher temperature ($\sim 400^{\circ}\text{C}$). Also, it shows comparatively same response to NH_3 , ethanol and Cl_2 gases. Thus, it is less selective to a particular gas among the different gases. This is the main drawback of pure ZnO thick film sensor.

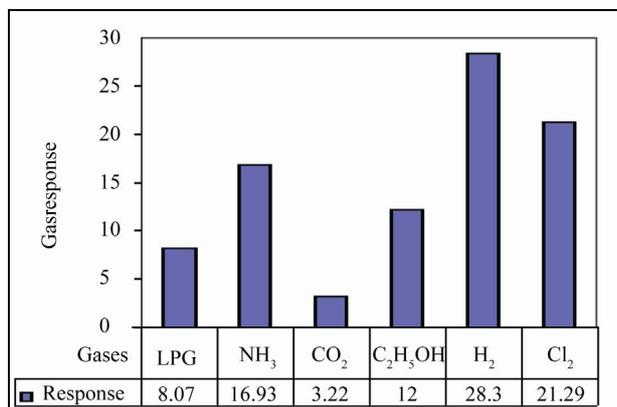


Figure 6. Selectivity of pure ZnO thick film sensor.

5.3. Sensing Performance of MnO₂ Modified ZnO Thick Films

5.3.1. Effect of Operating Temperature

Figure 7 depicts the variation of response to NH₃ gas (50 ppm) with operating temperature of MnO₂ modified ZnO thick films. The largest response of MnO₂ modified ZnO was observed to be 100 at room temperature. The ammonia response at room temperature is expected to monitor by adsorption of moisture on the modified ZnO film. The cumulative effect would decrease the film resistance, giving a response to ammonia gas at room temperature. At room temperature, there would be no oxygen adsorption. Therefore the oxygen adsorption-desorption mechanism is not employed to sense the NH₃ gas. When raising the temperature above room temperature, the moisture from the film surface evaporates and hence the response would decrease further.

5.3.2. Active Region of the Sensor

The variation of gas response of MnO₂ modified (30 min) ZnO sample with NH₃ gas concentration at room tem-

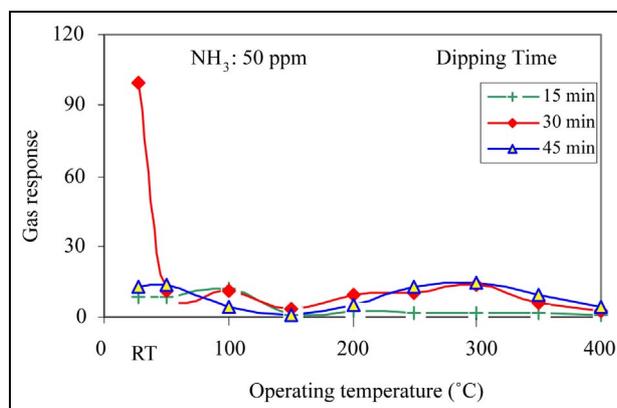


Figure 7. Variation of gas response with operating temperature.

perature is represented in Figure 8. This film was exposed to varying concentrations of NH₃. For the MnO₂ modified ZnO samples, the response values were observed to increase continuously with increasing the gas concentration up to 50 ppm at room temperature. The rate of increase in response was relatively larger up to 50 ppm, but smaller during 50 and 100 ppm. Thus, the active region of the sensor would be up to 50 ppm. At lower gas concentrations, the unimolecular layer of gas would be formed on the surface of the sensor, which could interact more actively giving larger response. The multilayers of gas molecules on the sensor surface, at the higher gas concentrations, would result into saturation in response beyond 50 ppm gas.

5.3.3. Effect of Dipping Time

The response of MnO₂ modified ZnO films to 50 ppm NH₃, as a function of the dipping time is shown in Figure 9. The sample dipped for 30 min in 0.01 M aqueous solution of manganese chloride was observed to be the most sensitive film at room temperature. It showed the response of 100 to 50 ppm NH₃ gas at room temperature. Elemental analysis (Table 1) shows that the mass% of MnO₂ goes on increasing with dipping time, reaches

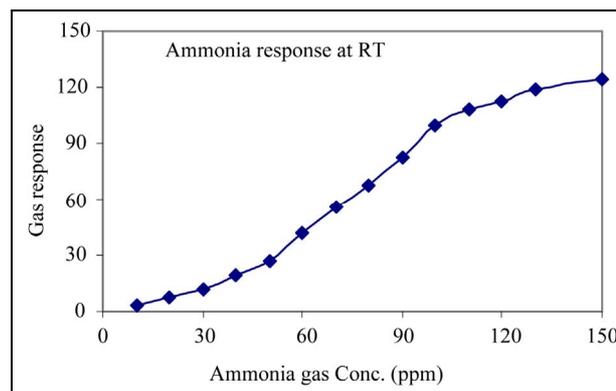


Figure 8. Variation in response with NH₃ gas concentration.

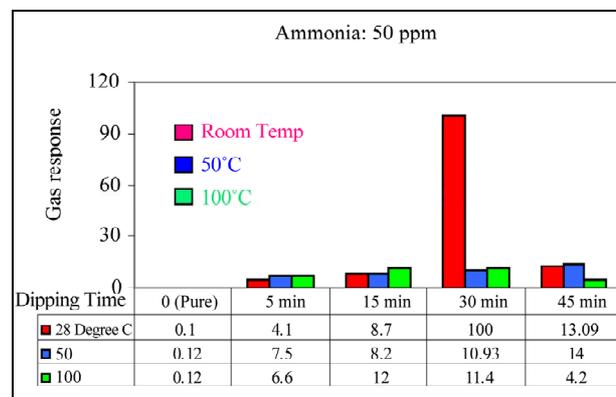


Figure 9. Variation of gas response with dipping time.

maximum (0.76) at 30 min dipping time and decreases with further increase in dipping time. The higher response of this sample may be attributed to the maximum number of MnO₂ grains dispersed on the surface of thick film as islands. This would create maximum number of MnO₂-ZnO heterojunctions. If the amount of MnO₂ dispersed on the film surface was smaller, then the number of MnO₂ islands on the surface would be less and less number of MnO₂-ZnO heterojunctions would be formed. This would facilitate the weak interaction of target gas, giving smaller response. It doesn't mean that if MnO₂ covers the whole surface of ZnO thick film, it will give more response to NH₃ at room temperature. If this may be the case, MnO₂ grains would mask the whole surface of ZnO thick film, which resists the gas to reach to interstitial sites of thick film, giving less response.

5.3.4. Selectivity for NH₃ against Various Gases

Figure 10 depicts the selectivity of the MnO₂ modified ZnO sensor for NH₃ (50 ppm) gas at room temperature. The sensor showed crucial selectivity to NH₃ gas against LPG, CO₂, C₂H₅OH, H₂ and Cl₂ gases at room temperature.

6. Response and Recovery of Sensors

Figure 11 shows dynamic response of a sample, which is highly sensitive to NH₃. The sensor showed rapid response (~10 s) and fast recovery (~50 s) to NH₃ gas. Fast response and speedy recovery are the important qualities of this sensor.

7. Discussion

Gas sensing mechanism is generally explained in terms of conductance change either by adsorption of atmospheric oxygen on the surface at higher temperature and / or by direct reaction of lattice oxygen or interstitial oxygen with test gases. In the former case, the atmospheric oxygen adsorbs on the surface by extracting electrons from the conduction band to form superoxides or peroxides, which are mainly responsible for the detection of the test gases.

The surface reaction processes can explain the selective ammonia response of the sensor at room temperature. It is well known that the thick film of MnO₂ modified ZnO consists of a largest number of grains of MnO₂ distributed on the surface. Upon exposure to ammonia, a remarkable decrease in the resistance of the sensor was observed [12], which may be due to the surface reaction of ammonia with physisorbed H₂O or by proton conductivity via NH₄⁺ cations. MnO₂ may generate the solid acidity on solid bases such as ZrO₂ and ZnO. The solid

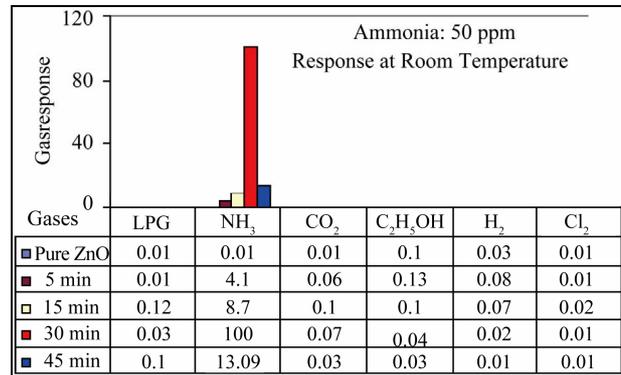


Figure 10. Selectivity to NH₃ gas from the mixture of gases.

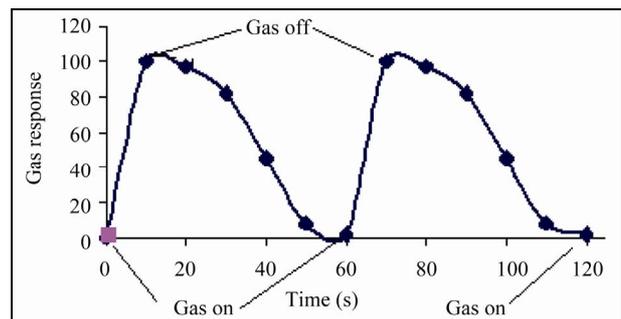


Figure 11. Response and recovery of Sensor on exposure of NH₃.

acidity on the sensor surface would form NH₄⁺ cations, which constitutes the proton conductivity leading to a crucial decrease of the resistance. This would decrease the barrier height among the MnO₂-ZnO grains.



Ammonium hydroxide NH₄OH produced during the surface reaction is volatile in nature. The high volatility of NH₄OH explains the quick response and fast recovery of the sensor.

8. Summary

From the results obtained, the following statements can be made for the sensing performance of MnO₂-activated ZnO sensors.

- 1) Pure ZnO thick films were observed to be less sensitive to NH₃ gas even at higher temperature.
- 2) Surface properties of the pure ZnO thick film surfaces were conveniently customized (without affecting bulk properties) by modifying it with dipping technique.
- 3) MnO₂ modified ZnO sensors showed crucial response to NH₃ gas at room temperature.
- 4) The sensor was highly selective to NH₃ gas (50 ppm) against other toxic gases of higher concentrations (1000 ppm).

The sensor showed very rapid response (~10 s) and recovery (~50 s) to NH₃ gas.

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