Proceedings of the Technical Sessions, 39 (2023) 28-35
Institute of Physics, Sri Lanka

Doped ZnO Thin Films for Detection of Harmful Gases in Environment

R.A.U.D. Ranasinghe and P.W.S.K. Bandaranayake
Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka
umadinir@sci.pdn.ac.lk

1. ABSTRACT

Ammonia, nitric oxide, and carbon monoxide gases harm human health and the environment. The present study investigate doped zinc oxide thin films to detect reducing gases such as NO, NH_3, and H_2 gas to construct low-cost and environmentally safe gas sensors. Thin films of pure zinc oxide (ZnO) and aluminum or ferric-doped ZnO were synthesized on thin alumina sheets using zinc acetate, 2-methoxy ethanol, and monoethanolamine. XRD and SEM characterized the structure and surface morphology of crystalline films. The bandgap energy for pure ZnO thin films was detected as 3.40 eV, and the lowest bandgap energy of 3.38 eV was observed for Al-doped thin films. The sensor response for pure ZnO thin film is 24% for H_2 gas, 33% for NO gas and 13% for NH_3 gas at 100 ppm. The sensor responses for Al-doped ZnO thin film are 83% and 49% at 500 ppm NH_3 level at 200 °C and at room temperature of 30 °C, respectively. The maximum sensor response was observed for Al-doped ZnO thin films at all concentrations of ammonia gas compared to pure and Fe-doped ZnO thin films. In future, these gas sensors will be useful in detection of various reducing gases releasing from factories and laboratories.

2. INTRODUCTION

Monitoring of concentration of harmful gases such as sulfur dioxide, ammonia, and carbon monoxide in the ambient atmosphere is vital for controlling environmental pollution. Ammonia is a colorless, toxic gas with a strong odor. Further, it is mainly emitted from agricultural fertilizers and manufacturing plastics, dyes and fabrics [1]. Exposing a high concentration of ammonia may cause immediate burning of the eyes, nose, and respiratory tract, lung cancers or even death. NO is a colorless gas that dilates blood vessels raising blood supply and lowering blood pressure. H_2 is a colorless, odorless, non-toxic and highly combustible gas mainly used in fuel cells to generate electricity, heat and power.

Metal oxide gas sensors detect various types of gases by measuring the change in metal oxide resistance due to gas absorption. Some advantages of metal oxide gas sensors are low cost, high sensitivity, quick response and simplicity in fabrication.

The gas sensing mechanism of metal oxide gas sensors is associated with adsorption of atmospheric oxygen onto the oxide surface, modifying the concentration of charge in the material, leading to a change in the carrier density and electrical conductivity. The negative charge in the oxygen species causes upward band bending, reducing conductivity compared to the flat band situation. When oxygen molecules are adsorbed on the surface of the metal oxide, they would extract electrons from the conduction band and trap electrons at the surface in the form of ions. This will lead to band bending and an electron-depleted region. Then, the reaction of these oxygen species with the reducing gases reverses the band bending, resulting in increased electric conductivity [2]. When thin metal oxide film is exposed to ambient air,

oxygen molecules are captured by electrons seizing from the conduction band of the metal oxide. As a result, the potential barrier's width changes, leading to increased resistance.

$$O_{2(air)} + e^-_{(ZnO\ surface)} \rightarrow O^-_{2(ZnO\ surface)}$$

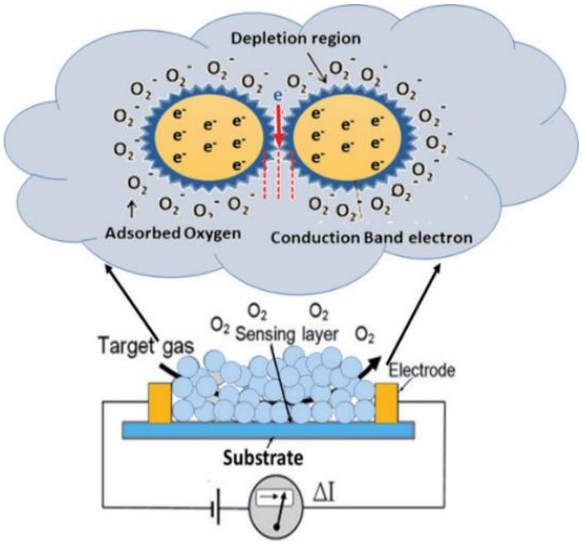

Figure 1: The response mechanism of the metal oxide gas sensor [3].

When reducing or oxidizing gas is exposed to the metal oxide thin film surface, it interacts with surface-adsorbed oxygen, releasing electrons to the surface. It results in a reduction in the width of the potential barrier and resistance. Therefore, gas sensing response increases.

Zinc oxide (ZnO) is one of the most widely used gas sensing materials due to its low cost, nontoxicity, chemical stability, and high thermal conductivity. Crystalline ZnO is an *n*-type semiconductor with a wide band gap between 3.1-3.4 eV and an excitation binding energy of 0.06 eV in the II-VI semiconductor group. [4] The crystal structure of ZnO is a hexagonal wurtzite structure. It is used in various applications such as cosmetics, gas sensors, field effect transistors, optoelectronic devices, pharmaceuticals, and glass industries.

There are many gas parameters for gas sensing applications, such as sensor response, sensitivity, adsorption ability, response time, and recovery time.

The sensor response is the ratio between the resistances of the sensor in the presence of the gas to the resistance in the air. That is given by equation 1.

$$R = \frac{R_a - R_g}{R_a} \tag{1}$$

where,

R - Sensor response
R_a - Resistance in the air and
R_g - Resistance in the presence of gas.

Response time is the time required to raise 90% of the baseline resistance in the presence of the gas [5] and recovery time is the time required to return resistance to 10% of baseline resistance after removing the gas [5].

As mentioned above, ZnO is a low cost and nontoxic semiconducting metal oxide that can be used for gas sensing applications. The possibility of doping ZnO with various types of cations

to alter the electronic structure for improving the adsorption of ammonia gas is the focus of the project. Then thin films of doped ZnO can be prepared on a suitable substrate by the sol-gel method. The widely used substrate to deposit films in the laboratory is common borosilicate glass slides. However, the adhesion of these oxides to the glass surface is not very good and hence reduces the durability of the films in the ambient environment. Therefore, to improve the film adhesion different substrates are used.

By identifying all these problems, the project is focused on analyzing NH_3, NO and H_2 gas sensing properties such as sensor response, response time and recovery time using low cost, nontoxic and chemically stable doped ZnO semiconductor material.

The objectives of my project are,

1) Synthesis of doped ZnO thin films which is the main and active part of the sensors, using sol-gel method.
2) Characterization of the films using XRD, SEM and optical techniques.
3) Analysis of gas sensing properties of doped ZnO sensors.

3. MATERIALS AND METHODS

$Zn(CH_3COOH)_2.2H_2O$ (98.0% DAEJUNG Chemicals & Metals, Korea), monoethanolamine (99% BDH Chemicals, England), 2-methoxy ethanol (99% BDH Chemicals, England), laboratory reagent grade aluminium acetate and ferric nitrate were used as the starting materials.

Pure ZnO, Al-doped ZnO, and Fe-doped ZnO thin films were synthesized using the sol-gel method. $Zn(CH_3COOH)_2.2H_2O$) was used as a precursor, 2-methoxy ethanol as the solvent, and monoethanolamine as the stabilizer. Aluminium acetate and ferric nitrate were used as doping materials to prepare Al-doped ZnO and Fe-doped ZnO, respectively. They were coated on alumina sheets and annealed at 400 °C for 1 hour.

The synthesized doped ZnO thin films were characterized using XRD (Bruker D8 advance X-ray diffractometer), SEM (Ziess evo LS 15 scanning electron microscope), and optical techniques (Shimadzu UV-1800 UV-Visible scanning spectrophotometer) to confirm the successful synthesis of ZnO. Ammonia gas was prepared using an ammonia solution in a laboratory-built setup and used to investigate the ammonia gas response of the films. Nitric oxide was produced by mixing copper foil and conc. HNO_3 (69%, LOBA Chemie Pvt. Ltd, India) together and passed through the water, and Hydrogen gas was produced using alumina foil, NaOH, and DI water by passing it through the water.

4. RESULTS AND DISCUSSION

4.1 XRD Analysis

The synthesized doped ZnO thin films were characterized by X-ray Diffractometer (XRD) to determine the crystallographic structure. The study reveals that the (1 0 1) plane shows high intensity, and the (2 0 0), (0 0 4), and (2 0 2) planes show low intensities. The observations

show the formation of high-quality ZnO crystalline phases since all peaks are sharp and distinguishable.

The XRD pattern of Al-doped ZnO thin film shows the highest intensity peak corresponds to (1 0 1) plane at 2θ = 36.26° as shown in Fig. II. There are no other additional peaks were observed in the XRD pattern of Al-doped ZnO than in the XRD pattern of pure ZnO. Therefore, it concludes that Al^{3+} ions are substituted into Zn^{2+} sites interstitially in the ZnO lattice without changing the hexagonal structure. This verifies the successful synthesis of Al-doped ZnO thin films. Also, it can be observed that peaks are slightly shifted in the Al-doped ZnO compared to Pure

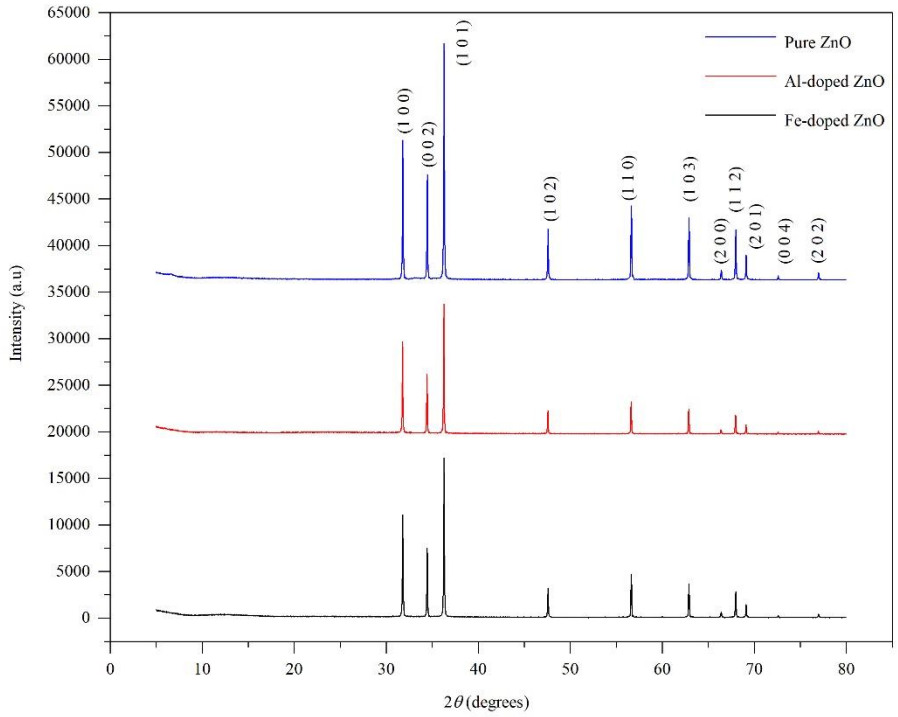

Figure 2: XRD pattern for pure ZnO, Al-doped and Fe-doped ZnO .

The XRD pattern of Fe-doped ZnO thin film is shown in figure 2. No additional peaks were observed, indicating Fe^{3+} ions are substituted into Zn^{2+} sites successfully. This proves the successful doping of Ferric. Also, Fe was recognized using XRF. Moreover, peaks are slightly shifted compared to pure ZnO. All peak intensities of both Al-doped and Fe-doped ZnO are less compared to pure ZnO. Therefore, results indicate that doping ZnO with Al and Fe decreases the intensities of all peaks.

4.2 Morphologic Properties

SEM was used to characterize the surface morphology of the thin films. The observation shows a closely packed arrangement of crystallites, as shown in figure 3. Al-doped ZnO and Fe-doped ZnO thin films show small rod-shaped crystallites compared to pure ZnO thin films. Also, some holes are present, indicating porosity and no cracks.

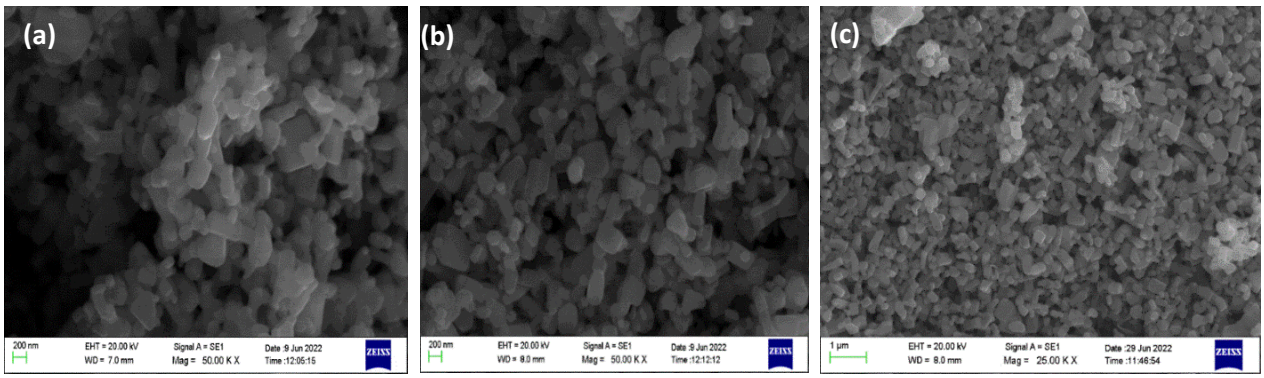

Figure 3: SEM images for (a) Pure ZnO (b) Al-doped ZnO (c) Fe-doped ZnO.

4.3 UV-VISIBLE SPECTROSCOPY

The optical absorption spectra of thin films were accessed using a UV-Visible spectrometer. Figure 4 shows the absorbance variation of pure and doped ZnO with wavelength. Fe-doped and Al-doped ZnO thin films absorb less than pure ZnO thin films.

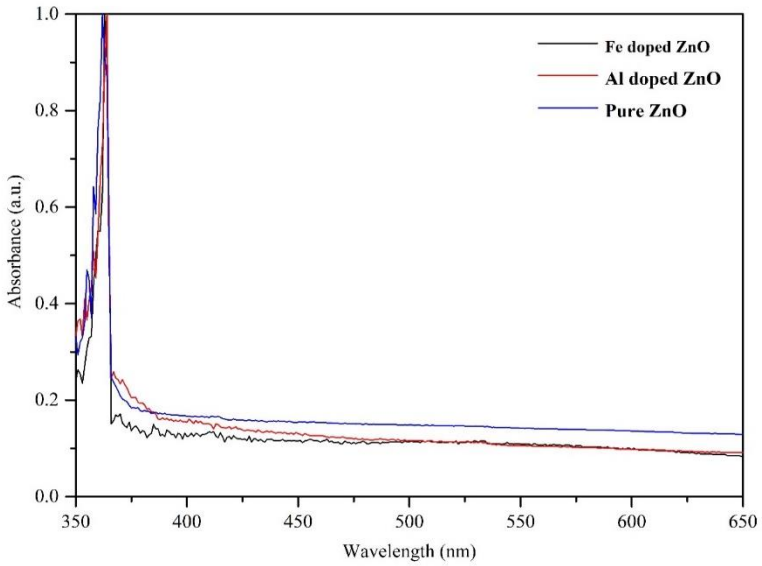

Figure 4: Absorbance of ZnO thin films.

Optical absorbance can be used to study optical energy bandgap and optical energy transitions of ZnO thin films. Using Tau's rule, band gap energies can be calculated, and calculated values of band gap energies are 3.40 eV, 3.38 eV, and 3.39 eV for pure ZnO, Al-doped ZnO, and Fe-doped ZnO thin films respectively. Pure ZnO's calculated band gap energy is much closer to the standard value. Also, observations conclude that band gap energy decreases with doping [6].

4.4 Gas Detection

The observations show maximum sensor responses of around 25% for pure ZnO thin film and around 30% for Fe-doped ZnO thin film, while Al-doped ZnO thin film shows around 83% of sensor response when ammonia concentration is 500 ppm. The variations of sensor response to different ammonia gas concentrations for pure, Al-doped, and Fe-doped ZnO thin films are

shown in Figure 5. The magnitude of sensor response increases with an increase in ammonia gas concentrations for all three types of thin films. Moreover, it reveals that higher sensor response values are recorded for Al-doped thin films at all concentrations of ammonia gas due to its crystalline structure suitable for diffusion and high interaction with ammonia gas.

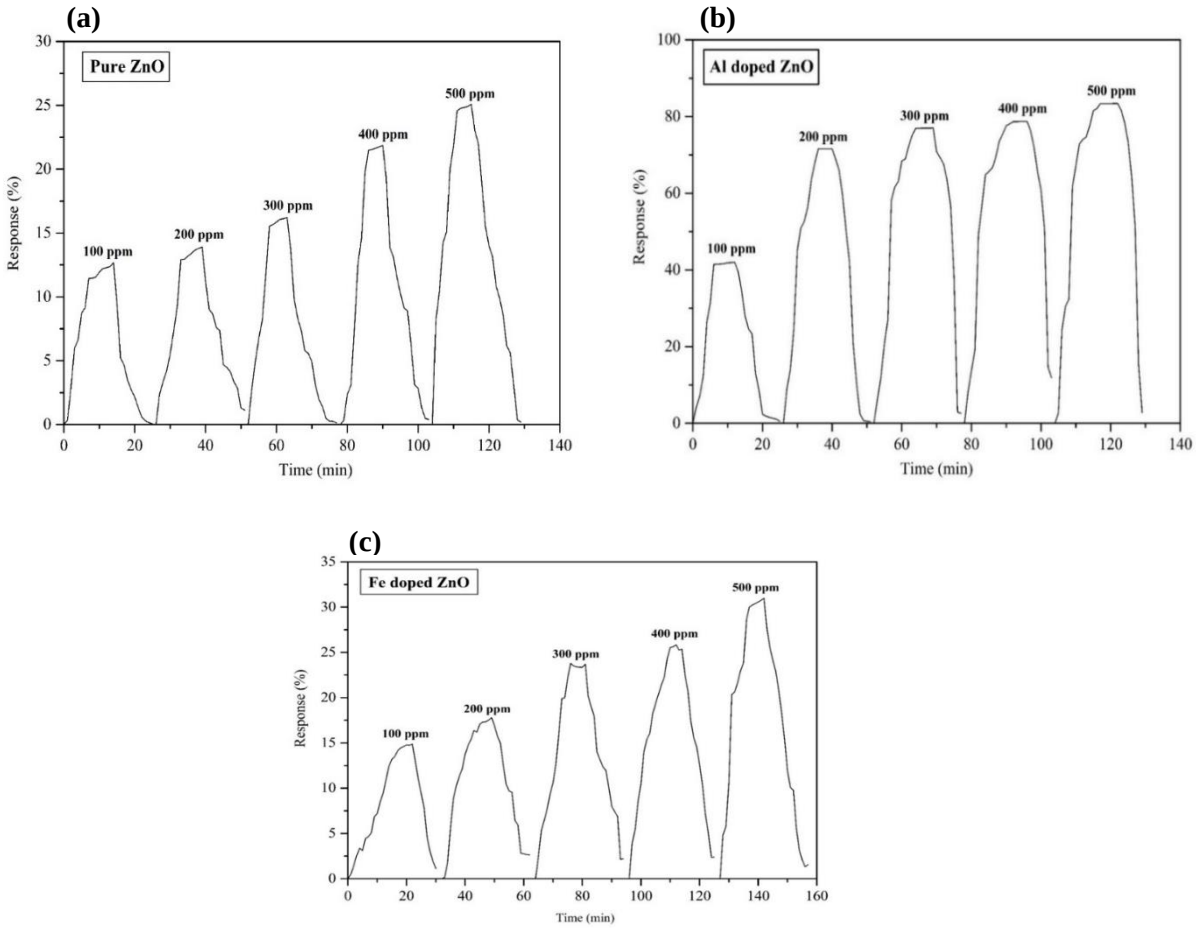

Figure 5: Response of (a) pure ZnO (b) Al-doped ZnO (c) Fe-doped ZnO with NH_3 concentrations.

Figure 6 shows that the ammonia gas sensor response varies with time at different operating temperatures of Al-doped ZnO thin films. The most significant response, about 83%, and the lowest response, about 49%, have been observed at an operating temperature of 200 °C and room temperature, respectively. Moreover, ammonia gas responses are 56%, 64%, and 73% at operating temperatures of 50 °C, 100 °C, and 150 °C, respectively. The observations reveal that the sensor response of ammonia gas increases with operating temperature. As the temperature increased, the sensor resistance decreased due to free carriers generated in the semiconductors.

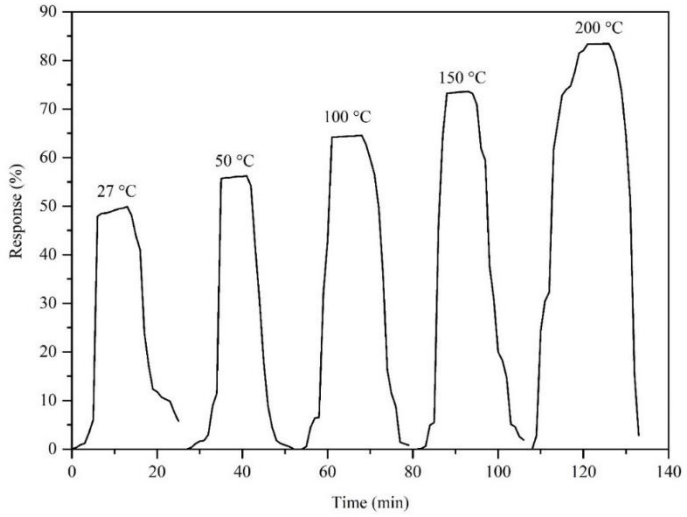

Figure 6: Gas response vs. time plots at different temperatures for Al-doped ZnO at ammonia the concentration of 500 ppm

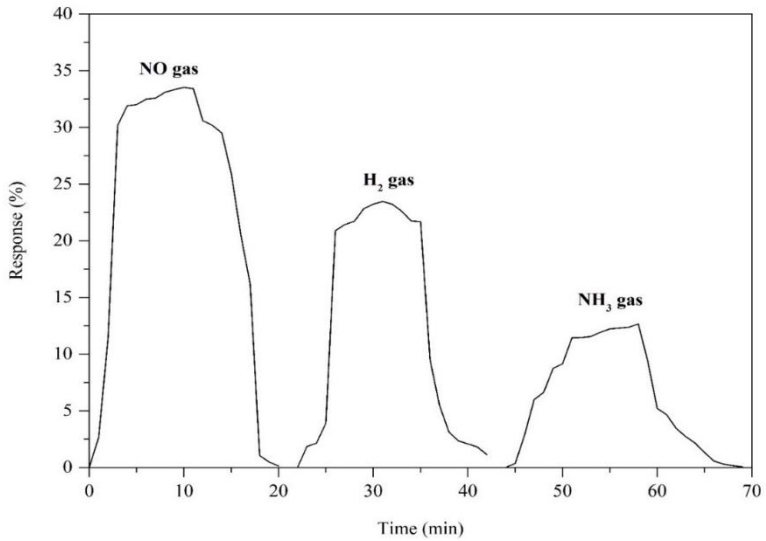

Figure 7: Gas response for pure ZnO for NO, H_2, and NH_3 gas concentrations at 100 ppm

Figure 7 shows the sensor response of NO and H_2 gases at 100 ppm for pure ZnO thin films. NO gas has about 33% of the sensor response, while H_2 has around 24%. The observations reveal that NO and H_2 gases have a higher sensor response than ammonia gas at 100 ppm at an operating temperature of 200 °C.

5. CONCLUSIONS

The ZnO thin films were synthesized using the low-cost sol-gel method. The doped ZnO thin films show small rod-type crystallites. XRD verifies the hexagonal wurtzite structure of ZnO. Non-availability of other peaks in the XRD pattern confirms the successful synthesis of Al-doped and Fe-doped ZnO. The energy band gaps of thin films were calculated using Tauc's plots. The energy band of pure ZnO is 3.40 eV and is larger compared to doped ZnO thin films with 3.38 eV and 3.39 eV band gap energies for Al-doped ZnO and Fe-doped ZnO, respectively. The calculated band gap energies are much closer to the standard values, and it verifies a decrease in band gap energies with doping. Different ammonia concentrations (100-500 ppm) were used to study the influence of pure and doped ZnO thin films on sensor response, response time, and recovery time. Al-doped ZnO thin films showed a maximum sensor response of around 83%, and the sensor response increased with the ammonia concentration and doping material. Also, NO and H_2 gases have a higher sensor response than ammonia gas at 100 ppm for pure ZnO.

6. REFERENCES

[1] D. Kwak, Y. Lei, and R. Maric, *Ammonia Gas Sensors: A Comprehensive Review*, Talanta **204**, pp.713-715 (2019)

[2] S. K. Gupta, A. Joshi, and K. Manmeet, *Development of Gas Sensors Using ZnO Nanostructures*, J. Chem. Sci. **122**, p.57 (2010)

[3] E. Rodríguez, J. L. Arqués, R. Rodríguez, M. Nuñez, M. Medina, T. L. Talarico, I. A. Casas, T. C. Chung, W. J. Dobrogosz, L. Axelsson, S. E. Lindgren, W. J. Dobrogosz, L. Kerkeni, P. Ruano, L. L. Delgado, S. Picco, L. Villegas, F. Tonelli, M. Merlo, J. Rigau, D. Diaz, and M. Masuelli, *We Are IntechOpen ,* Intech **32**, p.137 (1989)

[4] H. Aydın, F. Yakuphanoglu, and C. Aydın, *Al-Doped ZnO as a Multifunctional Nanomaterial: Structural, Morphological, Optical and Low-Temperature Gas Sensing Properties*, J. Alloys Compd. **773**, p.802 (2019)

[5] A. K. Bal, A. Singh, and R. K. Bedi, *Characterization and Ammonia Sensing Properties of Pure and Modified ZnO Films,* Appl. Phys. A Mater. Sci. Process. **103**, pp.497-503 (2011)

[6] S. Marouf, A. Beniaiche, H. Guessas, and A. Azizi, *Morphological, Structural and Optical Properties of ZnO Thin Films Deposited by Dip Coating Method*, Mater. Res. **20**, p.89 (2017).