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Fe$_2$O$_3$ - ZnO Based Gas Sensors

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Abstract: Thick films of pure ZnO, Fe$_2$O$_3$ added ZnO and Fe$_2$O$_3$ modified ZnO were prepared by screen printing technique. Gas sensing performances of these films were tested for NH$_3$, LPG, CO$_2$, C$_2$H$_5$OH, H$_2$ and Cl$_2$. All these films were observed to be highly or most sensitive to NH$_3$. Gas response profiles along with the response and recovery times of the sensors are presented. Structural, microstructural and elemental analysis were carried out. The effects of microstructure and surface misfits on the sensitivity, selectivity, response and recovery of the sensor were studied and discussed. Copyright © 2009 IFSA.

Keywords: Pure ZnO, Fe$_2$O$_3$ added ZnO, Fe$_2$O$_3$ modified ZnO, NH$_3$-gas sensor, Gas response, Selectivity, Response time, Recovery time

1. Introduction

Many semiconductor oxides like ZnO, Fe$_2$O$_3$, SnO$_2$, Ga$_2$O$_3$, BaTiO$_3$ etc. [1-10] have been known to detect the polluting, toxic and inflammable gases. The gas sensing characteristics of the materials can be improved by surface functionalization or incorporating few additives [11, 12] into the oxide films. Ferric oxide ($\alpha$-Fe$_2$O$_3$) have already reported [13-25] by many researchers as a gas sensing material. ZnO and Fe$_2$O$_3$ are the n-type semiconductors [26]. Fe$_2$O$_3$ occurs as haematite. The oxides of iron are giant molecule compounds [27] in which either the ferrous or ferric ions are present. Pure - Fe$_2$O$_3$ has a poor electrical conductivity and gas sensitivity. Catalysts like Pt, Pd, Ag, Ru and Cu are often added [7, 12] to the base material to improve the gas response and selectivity. As 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 [28-32] in nature. The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. It is therefore, needed to monitor ammonia gas and to develop the ammonia gas sensor. Among various
additives tested, $\alpha$-Fe$_2$O$_3$ is an outstanding promoter in enhancing the catalytic activity and gas sensing properties of ZnO for NH$_3$ detection.

2. Experimental Procedure

2.1. Sensors’ Fabrication/Preparation of Starting Material Powders

(a) Sensors from Pure ZnO (Unmodified ZnO): AR grade Pure ZnO was made available commercially and was used to prepare thick films sensors and referred to as S0.

(b) Sensors from Fe$_2$O$_3$ added ZnO powders: These powders (referred to as S1, S2, S3) were prepared in various weight percentages (such as 50:50, 67:33 and 33:67) from AR grade ammonium ferric sulfate NH$_4$Fe(SO$_4$)$_2$, 12H$_2$O and AR grade zinc sulfate (ZnSO$_4$, 7H$_2$O) precursors.

(c) Sensors from Fe$_2$O$_3$ modified ZnO powders: Thick films of AR grade zinc oxide powder were prepared. These films were surface modified by dipping them into a 0.001 M aqueous solution of ammonium ferric sulfate (NH$_4$Fe(SO$_4$)$_2$, 12H$_2$O) for different intervals of time (viz. 2, 5, 15 and 30 min) and were dried at 90°C under an IR lamp, followed by calcination at 500°C for 24 h in air ambient. The ammonium ferric sulfate dispersed on the film surface was oxidized in calcination and sensor elements with different mass% of Fe$_2$O$_3$ were obtained. These sensors are referred to as S4, S5, S6 and S7.

(d) Silver contacts were made to all samples by vacuum evaporation for electrical measurements.

2.2. Characterization

The structure of the films was analyzed with X-ray diffractogram (RIGAKU DMAX 2500) using CuK$\alpha$ radiation with a wavelength 1.5418Å. 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). Gas sensing characteristic of each sensor was studied using a static gas sensing system.

3. Results

3.1. Gas Sensing Performance Pure ZnO

3.1.1 Gas response of S0: Pure ZnO

The gas response of S0 was studied by varying operating temperature and exposing it to NH$_3$, LPG, CO$_2$, C$_2$H$_5$OH, H$_2$ and Cl$_2$ gases. (Fig.1).

Sensor S0 showed highest gas response to H$_2$ (28.3) at 400°C. The response of S0 to NH$_3$ gas was relatively low (17) at 400°C.

3.1.2 Response and Recovery Time of S0

Response time of S0 was 60 s and recovery time was 90 s. (Fig. 2).
3.2. Gas Sensing Performance of α-Fe$_2$O$_3$ Added ZnO - S1, S2, S3

3.2.1. Gas Response of S1, S2 and S3

Fig. 3 depicts the gas responses of S1, S2 and S3 to various gases. Sensor S2 showed highest sensitivity of 573 for 300 ppm NH$_3$ at 350°C. The sensor was also highly selective to NH$_3$ against LPG, CO$_2$, C$_2$H$_5$OH, H$_2$ and Cl$_2$ gases.

![Fig. 1. Max gas response of S0.](image1)

![Fig. 2. Transient response of S0 to NH$_3$ gas.](image2)

![Fig. 3. Gas response.](image3)
3.2.1 Response and recovery time of S2

The response and recovery times of S2 sensors are represented in Fig. 4. The response was quick (~ 25 s) the recovery was also fast (~ 80 s).

![Fig. 4. Response and recovery times of S2.](image)

3.3. Gas Sensing Performance of $\alpha$-Fe$_2$O$_3$ Modified ZnO - S4, S5, S6 and S7

3.3.1. Gas Response of S4, S5, S6 and S7

Fig. 5 shows gas responses of S4 through S7 to 300 ppm of NH$_3$ gas and 1000 ppm of other gases at 350$^\circ$C. These sensors showed relatively higher sensitivity and selectivity to NH$_3$ in comparison to LPG, Cl$_2$, CO$_2$, C$_2$H$_5$OH and H$_2$ gases.

![Fig. 5. Gas response of S4 - S7 to various gases.](image)

Fig. 6 (a) and (b) depict gas responses of S4-S7 sensors on exposure of 50 ppm and 300 ppm of NH$_3$ respectively tested at various operating temperatures of 300, 350, 400 and 450$^\circ$C. S5 showed highest
NH\textsubscript{3} gas response of 3572 to 300 ppm and 179 to 50 ppm at 350\textdegree C. Sensor S5 was also highly selective to NH\textsubscript{3} gas.

3.3.2. NH\textsubscript{3} Gas Response Profile

It is clear from Fig. 7 that gas response goes on increasing with operating temperature, reaches to maximum at 350\textdegree C and then decreases further with increase operating temperature.

3.3.3. Response and Recovery Times

The response time of S5 sensor is quick (~30 s) and the recovery is fast (~ 90 s) tested at 300 ppm ammonia gas. (Fig. 8).
Fig. 8. Transient response of the S5 sensor.

Summary Table

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<th>Samples</th>
<th>NH₃ Gas sensing performance</th>
<th>Gas, Temp</th>
<th>S</th>
<th>Conc. ppm</th>
<th>T_{Res} (s)</th>
<th>T_{Rec} (s)</th>
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<td>Pure ZnO</td>
<td>NH₃ 400°C</td>
<td>17</td>
<td>1000</td>
<td>60</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-doped ZnO</td>
<td>NH₃ 350°C</td>
<td>573</td>
<td>300</td>
<td>25</td>
<td>80</td>
<td></td>
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<tr>
<td>Fe₂O₃-modified ZnO</td>
<td>NH₃ 350°C</td>
<td>3572/179</td>
<td>300/50</td>
<td>30</td>
<td>90</td>
<td></td>
</tr>
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</table>

S-Sensitivity, T_{Res}-Response time, T_{Rec}-Recovery time

4. Discussion

4.1. Scanning Electron Micrographs of S0, S2 and S5

It is clear from SEM images that the average particle size of S2 is largest and of S0 is smallest. S2 and S5 are modified films and S0 is unmodified. Average particle size of S2 is larger than S5. Therefore, S5 is more porous than S2. Higher the porosity is, higher the effective area to react the gas is. This may be one of the reasons of highest sensitivity of sensor S5. Though the average particle size and in turn the porosity of S0 is smaller than S5, former shows smaller sensitivity to NH₃. It may be due to lack of misfits on the surface of S0 as it is not added or modified with Fe₂O₃. (Fig. 9).

The gas response could be explained using adsorption-desorption type of sensing mechanism. It is observed that the oxygen adsorption on the ZnO surface occurs at different temperature ranges [39, 40]. The conversion is as follows:
During oxidation of the gas, the electrons are released soon and become free to carry the current (Eq. 1).

\[
2 \text{NH}_3 + 7 \text{O}^- \rightarrow 2 \text{NO}_2 + 3 \text{H}_2\text{O} + 7 e^-
\]  

When ammonia reacts with 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 possible reactions would take place.

Fe$_2$O$_3$ is used for surface modification of the films due to some of the following reasons. Fe$_2$O$_3$ is the transition-metal oxide. Properties of transition-metal oxide stems from the different bonding properties associated with $d$ orbital. These include the existence of variable oxidation states. Trends in the stability of different oxidation states are very important in surface chemistry, as they control both the types of defect that may be formed easily, and the type of chemisorptions that may take place. The range of band gap energy of transition metal oxides (Cr$_2$O$_3$, WO$_3$, NiO, Fe$_2$O$_3$) is 2-3 eV. It is relatively lower as compared to SnO$_2$ and ZnO like materials. Therefore, transition-metal oxides are more sensitive to the change of outside ambient and these types of oxides could be more preferable for the use in gas sensors. Fe$_2$O$_3$ has an electron configuration of $d^5$. Electron configuration of SnO$_2$ and ZnO is $d^{10}$. Activity of oxides with electron configuration of $d^5$ is much higher than the activity of oxides with electron configuration of $d^{10}$. Fe$_2$O$_3$ is n-type semiconductors and provide an opportunity of oxygen's chemosorption.

Fig. 10. NH$_3$ gas sensing mechanism.

5. Summary

Pure ZnO thick films showed highest response to H$_2$ and not to NH$_3$ gas.
1. The bulk properties of pure ZnO were conveniently customized by adding Fe$_2$O$_3$ in ZnO or by modifying the sensor surface using dipping technique which in turn improve the gas sensing performances.
2. Fe$_2$O$_3$ modified ZnO showed highest response to NH$_3$ gas.
3. Fe$_2$O$_3$ modified ZnO improved response time and recovery time to NH$_3$ gas.

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References

Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in Sensors & Transducers Journal will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. Sensors & Transducers Journal is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

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