10. Preparation, Characterization of Nanostructured Zno Powder and Sensing Performance of its Thick Film Sensor

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Abstract

Nanostructured ZnO powder was prepared by ultrasonic atomization technique. As prepared powder was characterized by X-ray diffractogram, Scanning Electron Microscopy, Transmission Electron Microscopy and Energy Dispersive Analysis of X-rays. The powder was used to prepare thick films using screen printing technique. The sensing system was used to test the sensing performance of the nanostructured ZnO thick-film sensors on the exposure of conventional gas (Ammonia, LPG, Hydrogen, Ethanol, Carbon-Dioxide and Chlroine)) and simulants of chemical warfare agents (dimethyl methyl phosphonate, 2-chloroethyl ethyl sulfide and 2-chloroethyl phenyl sulphide). The nanostructured ZnO thick-film sensor was found to be most sensitive to Ammonia (conventional gas) and Dimethyl Methyl Phosphonate (simulant of chemical warfare agents) respectively.

Keywords: Ultrasonic Atomization, Zno, Thick Films, Sensor

1. Introduction

Metal oxide semiconductor is used to detect the hazardous and toxic gases [1]. ZnO thin films have been prepared by various technique such as metal organic chemical vapour deposition [2], dc magnetron sputtering [3], sol–gel [4] and spray pyrolysis [5] etc. Among these techniques, ultrasonic spray pyrolysis is convenient and simple technique. Now a days

nanostructured sensors are in demand for a rapidly growing range of variety of applications. Small in size, low power consumption, long life and easy fabrication are the main advantage of chemical sensors. Conventional gasses like ammonia is harmful and toxic [6] in nature. The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. The threat of attack and terrorist groups using chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) is on the rise [7]. Thus, there exists an urgent need for reliable detectors and sensors for these classes of gas and chemicals. For this purpose, the development of highly sensitive, selective, reliable, and compact sensing devices to detect flammable, toxic chemical and biological agents is of major importance. Over the last decades, Thick and thin film metal oxides have been widely studied for various gases [8].

In the present study, the nanostructured ZnO powder prepared from ultrasonic atomization technique. Thick film of this powder was prepared using screen printing technique. Thick film was characterized by XRD, TEM, SEM and EDAX. The conventional gas and simulant sensing performance of this film was tested.

2. Experimental

The nanostructured ZnO powder was prepared by ultrasonic atomization and decomposition technique, the procedure of which has been explained elsewhere [9]. The thixotropic paste of nanostructured zinc oxide powder was formulated and thick films were prepared using screen printing technique on glass substrate in the desired pattern explain elsewhere [10]. The films were fired at 500°C for 30 min to remove the binder permanently.

3. Characterizations
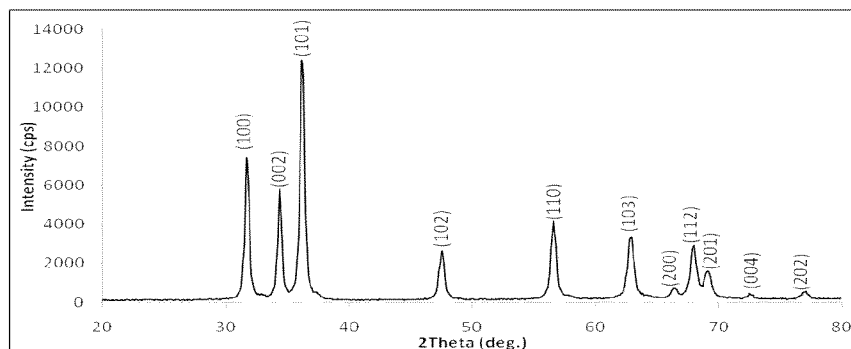
3.1 X-ray diffractogram

Fig. 1. X-ray diffractogram of nanostructured ZnO powder

Fig.1 shows the x-ray diffractogram of nanostructured ZnO powder. The observed peaks are matching well with the standard JCPDS data of ZnO [11]. The broad peaks are due to nanocrystalline nature of ZnO. The average grain size calculated from Scherrer's formula was about 19 nm.

3.2 Scanning electronmicroscopy (SEM)

Fig. 2 shows the Scanning electron micrograph of the sample. The morphology of the particles was roughly spherical in shape. The particles are observed to be agglomerated. Determination of particle size was found to be difficult. The microstructure of the film was therefore studied using transmission electron microscopy.
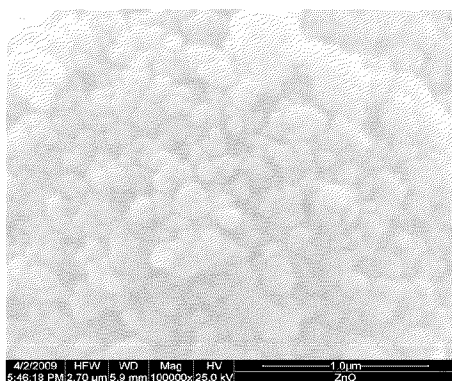

Fig. 2. SEM images of the nanostructured ZnO powder.

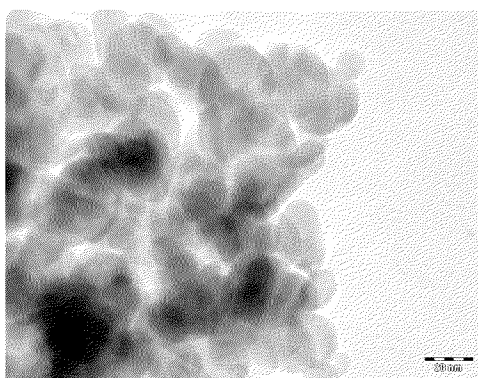**3.3 Transmission electron microscopy (TEM)**

Fig. 3. TEM images of the nanostructured ZnO powder

TEM technique was used to know exact grain size, shape and distribution of the crystallites associated with the powder. It is clear from TEM image (Fig. 3) that there are uniformly distributed spherical shaped grains with the average grain size of 20 nm.

3.4 Energy dispersive analysis of x-rays (EDAX)

Table 1 Elemental compositions of nanostructured ZnO powder

Element	Observed		Stoichiometric	
	mass %	at %	mass %	at %
Zn	86.50	59.46	80.34	50.00
O	13.50	38.94	19.66	50.00
ZnO	100.00	100.00	100.00	100.00

Theoretically expected mass % of Zn and O in stoichiometric ZnO are expected to be 80.3 and 19.7 respectively. The observed values of mass % of Zn and O are represented in Table 1. It is clear from table that as prepared ZnO powder was observed to be nonstoichiometric. The powder was found to be oxygen deficient. Sensing performance of the oxygen deficient films was reported to be better as compared to the stoichiometric counterpart.

4. Sensing Performance of the Sensors

4.1 Response with operating temperature of sensor

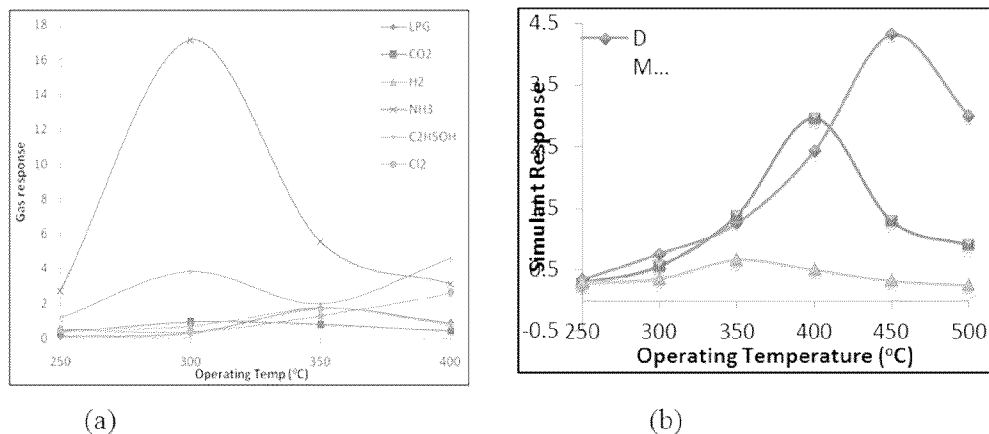(a)   (b)

Fig. 4. Response with operating temperature: (a) Conventional gas and (b) Simulants of CWA

Figure 4 (a) shows the variation of conventional gas response with operating temperature of nanostructured ZnO sensor (thick film) for 1000 ppm LPG, H_2, CO_2, NH_3, C_2H_5OH and Cl_2. It is clear from figure that nanocrystalline ZnO showed largest response to NH_3 at 300^0C as compared to responses of C_2H_5OH & Cl_2 at 400^0C, LPG & H_2 at 350^0C and CO_2 at 300^0C. Figure 4 (b) shows the variation of simulant responses with operating temperature of nanostructured ZnO thick film on exposure of 2 ppm DMMP, CEES and CEPS. It is clear from figure that pure ZnO gives temperature dependent sensing to various simulants. It shows better response to DMMP than to CEES at $450°C$ while better response to CEES than to DMMP at $400°C$.

4.2 Response and recovery of the sensor.

The time taken for the sensor to attain 90 % of the maximum decrease in resistance on exposure to target is defined as response time. The time taken for the sensor to get back 90 % of original resistance is the recovery time.
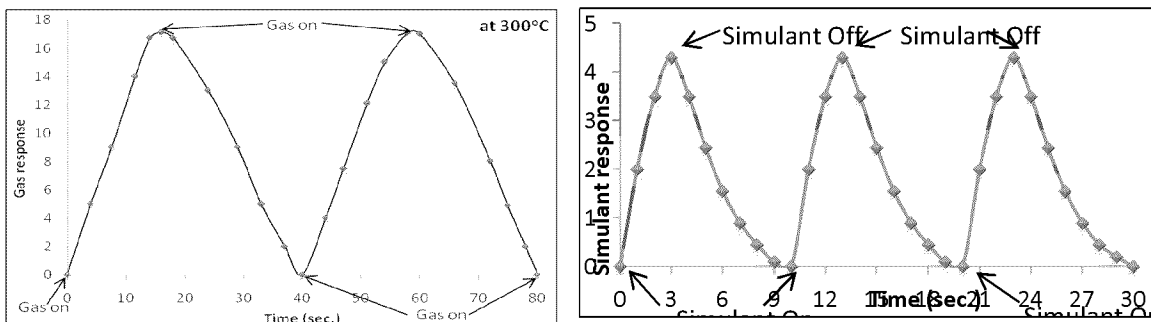

Fig. 5. Response and recovery of nanostructured ZnO thick film sensor: (a) Ammonia and (b) DMMP

Figure 5 (a) shows the response and recovery of the nanostructured ZnO thick film sensor at an operating temperature 300°C. The response was quick (~17 s) and the recovery was fast (~37 s). The neglibale quantity of the surface reaction products and their high volatility explain the quick response and fast recovery to NH_3. Figure 5 (b) shows the response and recovery of pure nanostructured ZnO thick film to DMMP. The 90% response and recovery levels were attained within ~3 and ~7 seconds respectively.

Conclusions

1)   Nanostructured ZnO powder was prepared using ultrasonic atomization technique.

2)   XRD analysis confirmed that the powder to be of ZnO with wurtzite structure.

3)   SEM image showed roughly spherical particles with average size of 29 nm. Average grain size calculated from XRD was 19 nm and from TEM it was 20 nm.

4)   The response of nanostructured ZnO thick film sensor was observed to be largest to NH_3 at 300°C.

5)   The sensor showed very quick response (17s) and fast recovery time (37s) to NH_3 gas.

6)   The response of nanostructured ZnO thick film sensor to DMMP at 450°C was larger than other stimulants.

7)   The quick response (3 s) and fast recovery (7 s) were the important features of the nanostructured ZnO sensor.

8) The nanostructured ZnO could be a promising candidate as a sensor for detecting conventional gas and simulants of chemical warfare agents.

Acknowledgments

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