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Ammonia and DMMP Sensor based on Nanostructured ZnO Thick Films

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Abstract

Nanostructured zinc oxide powder was prepared using the ultrasonic atomization technique. This powder was collected using simple indigenous glass trapping system attached to ultrasonic system. Thick films of this powder were prepared using simple screen printing technique. The films were characterized using XRD, TEM, SEM and EDAX to know structure, size of crystallites, microtopography and elemental analysis respectively. The conventional gas and simulants of chemical warfare agents sensing performances of these films were tested. The thick film sensor was found to be most sensitive to NH_3 (conventional gas) and DMMP (simulant of chemical warfare agents) respectively. The results were discussed and interpreted.

Keywords: Ultrasonic Atomization; Nanocrystalline ZnO; Thick Films; Sensor, Response; Response-Recovery Time

Introduction

ZnO is the most promising semiconductor to detect the toxic and hazardous gases [1]. Variety techniques have been used to prepare ZnO nanostructures: like sol–gel [2], metal organic chemical vapour deposition [3], dc magnetron sputtering [4], and spray pyrolysis [5] etc. Compared with these methods, ultrasonic spray pyrolysis is convenient and simple technique. Monitoring devices like sensors are in demand for a rapidly growing range of applications. Long life, small in size, low power consumption and easy fabrication are the main advantage of chemical sensors. Ammonia is harmful and toxic [6] 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.

The threat of attack from rogue nations 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 chemicals, to enable people to safely leave a contaminated zone or to protect themselves. Semiconducting metal oxide sensors are one of the most widely studied groups of chemiresistive gas sensors. Several materials are fabricated to enhance the sensing characteristics of the SMO CWA sensors with high sensitivity to toxic, combustible gases and CWA [8]. 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 [9].

In the present study, the nanocrystalline ZnO powder prepared from ultrasonic atomization technique. As prepared powder was studied using XRD, TEM, SEM and EDAX to know structure, size of crystallites associated with powder, microtopography and elemental analysis respectively. Thick film of this powder was prepared using screen printing technique. The conventional gas and simulant sensing performance of this film was tested.

Experimental

Preparation of Nanocrystalline ZnO Powder and Thick Film Preparation

The nanocrystalline ZnO powder was prepared by ultrasonic atomization and decomposition technique, the procedure of which has been explained elsewhere [10]. The thixotropic paste of nanocrystalline zinc oxide powder was formulated and thick films were prepared using screen printing technique on glass substrate in the desired pattern explain elsewhere [11]. The films were fired at 500^{o}C for 30 min to remove the binder permanently.

Characterizations

X-ray Diffractogram (XRD)

(Figure 1) shows the x-ray diffractogram of ZnO thick film. The observed peaks are matching well with the standard JCPDS data of ZnO [12]. The broad peaks are due to nanocrystalline nature of ZnO. The average grain size calculated from Scherrer‟s formula was about 19 nm.

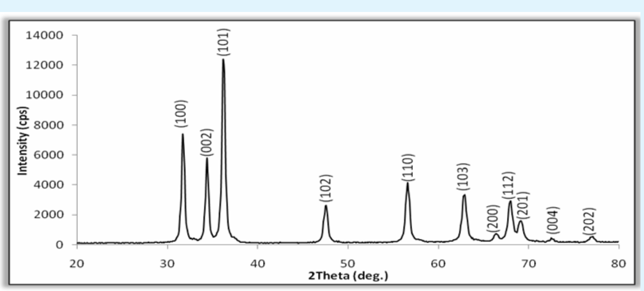

Figure 1: X-ray diffractogram of nanocrystalline ZnO thick film.

Scanning Electron Microscopy (SEM)

Scanning electron micrograph, in Figure 2 is showing topography of the film surfaces. 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.

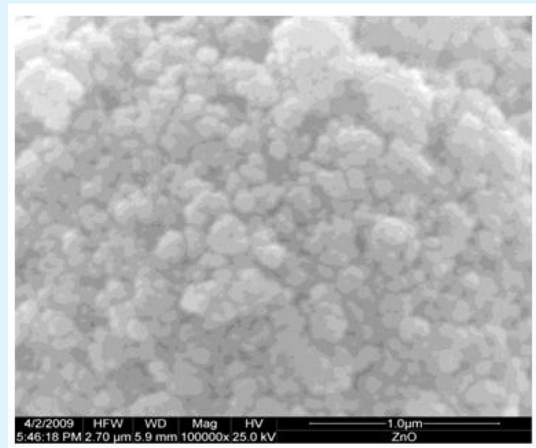

Figure 2: SEM images of the nanocrystalline ZnO thick film.

Energy Dispersive Analysis of X-rays (EDAX)

Elemental compositions of nanocrystalline ZnO thick film (Table 1).

	Observed		Stoichiometric	
Element	mass %	at %	mass %	at %
Zn	86.5	59.46	80.34	50
O	13.5	38.94	19.66	50
ZnO	100	100	100	100

Table 1: Elemental compositions of nanocrystalline ZnO thick film.

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.

Transmission Electron Microscopy (TEM) and Electron Diffraction

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 (Figure 3) that there are uniformly distributed spherical or elliptical shaped grains with the average grain size of 20 nm.

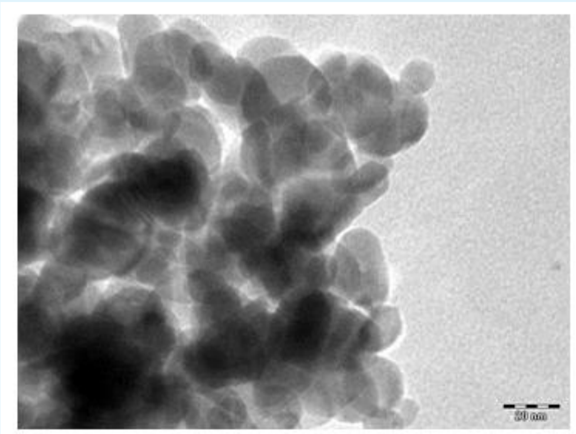

Figure 3: TEM images of the nanocrystalline ZnO thick film.

Sensing performance of the sensors

Measurement of Response

Response (S) is defined as the ratio of the change in conductance of the sensor on exposure of the conventional gas /simulant to the original conductance in air. It is given as:

$$S = (I_g - I_a) / I_a$$

where I_a and I_g are the conductances of the sensor on exposure of air and conventional gas/simulant respectively.

Gas Response with Operating Temperature of Sensor

Figure 4 shows the variation of gas response with operating temperature of nanocrystalline 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°C as compared to responses of C_2H_5OH & Cl_2 at 400°C, LPG & H_2 at 350°C and CO_2 at 300°C.

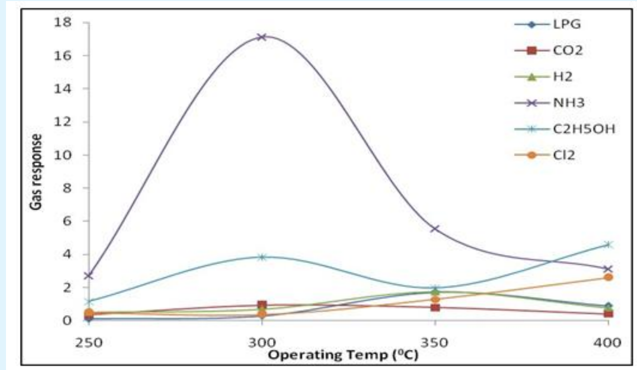

Figure 4: Variation of gas response with operating temperature of nanocrystalline ZnO.

Simulant Response with Operating Temperature

Figure 5 shows the variation of simulant responses with operating temperature of nanocrystalline 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. The same sensor could be used to detect DMMP and CEES simulants just by tuning the corresponding operating temperature. Different simulant have different chemical activity with the sensor surface at particular temperature, i.e., different simulants have different energies of adsorption and desorption and also different energy required to decompose different simulants. Good simulant response may be due to nanocrystalline nature of ZnO.

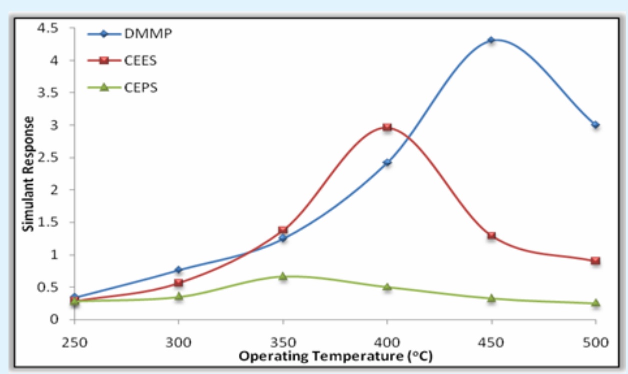

Figure 5: Variation of simulant response with operating temperature of nanocrystalline ZnO film.

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. Figure 6 shows the response and recovery of the nanocrystalline 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.

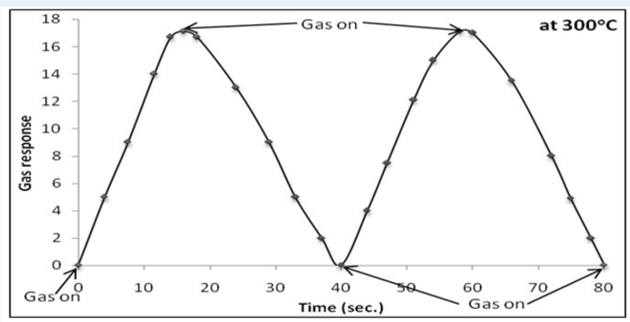

Figure 6: Response and recovery of nanocrystalline ZnO thick film sensor.

Figure 7 shows the response and recovery of pure nanocrystalline ZnO thick film to DMMP. The 90% response and recovery levels were attained within ~3 and ~7 seconds respectively.

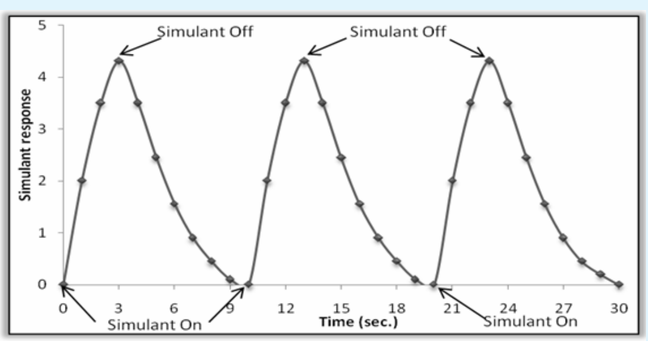

Figure 7: Response and recovery of nanocrystalline ZnO thick film sensor.

Conclusions

1. Ultrasonic atomization technique was used to prepared nanostructured ZnO powder
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 29.75 nm.
4. Average grain size calculated from XRD was 19.25 nm and from TEM it was 20.10 nm.
5. The response of nanocrystalline ZnO based sensor was observed to be largest to NH_3 at 300°C.
6. The sensor showed very quick response (17s) and fast recovery time (37s) to NH_3 gas.
7. The response of nanocrystalline ZnO thick film sensor to DMMP at 450°C was larger than the response to CEES. Response to CEPS was observed to be smallest.
8. The quick response (3s) and fast recovery (7s) were the important features of the nanocrystalline ZnO sensor.
9. The nanocrystalline ZnO could be a promising candidate as a sensor for detecting conventional gas and simulants of chemical warfare agents.

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