Synthesis of nanocrystalline ZnO powder using ultrasonic atomization technique and application of its thick films for highly toxic gases

L. A. Patil

Nanomaterials Research Lab., Department of Physics, Pratap College, Amalner, 425 401, India
plalachand_phy_aml@yahoo.co.in

ABSTRACT

Nanocrystalline ZnO powder was prepared using ultrasonic atomization technique. Thick films of this powder were prepared using simple screen printing technique. Pt-modified-ZnO (platinum activated) films were obtained by dipping pure ZnO films into an aqueous solution of chloroplatnic acid for different intervals of time, followed by firing at 500^{o}C for 30 min. The sensing performance of the unmodified (pure) and Pt-modified ZnO(Pt-ZnO) films was tested on exposure of CWA (chemical warfare agents) simulants, such as, dimethyl methyl phosphonate (DMMP), 2-chloroethyl ethyl sulfide (CEES) and 2-chloroethyl phenyl sulfide (CEPS). Both pure ZnO and Pt-ZnO films showed higher response to DMMP than the responses to CEES and CEPS. Enhanced oxygen adsorption capability due to surface platinum would be the reason of higher response and good selectivity to DMMP. The simulant response, selectivity, response time and recovery time of the sensors were measured and presented. The role played by surface platinum species in the simulant sensing performance is discussed.

Keyword: Ultrasonic atomization, Nanocrystalline ZnO powder, thick films, Pt-modified ZnO films, CWA simulant sensing, DMMP sensor.

1 Introduction

Chemical Warfare agents are highly toxic and their use is restricted. Research on the environmental fate of CWAs is often conducted using simulant compounds [1-3]. Semiconducting metal oxide sensors are one of the most widely studied groups of chemiresistive gas sensors. Several materials are employed to enhance the sensing characteristics of the SMO gas sensors. Among these ZnO is an interesting chemically and thermally stable *n*-type semiconductor of wurtzite structure with a large-band gap energy of 3.37 eV at low temperature and 3.3 eV at room temperature [30], and with high sensitivity to toxic and combustible gases [4-10].

2 Experimental

2.1. Preparation of nanocrystalline ZnO powder

The nanocrystalline ZnO powder was prepared by ultrasonic atomization technique as shown in fig. 1.

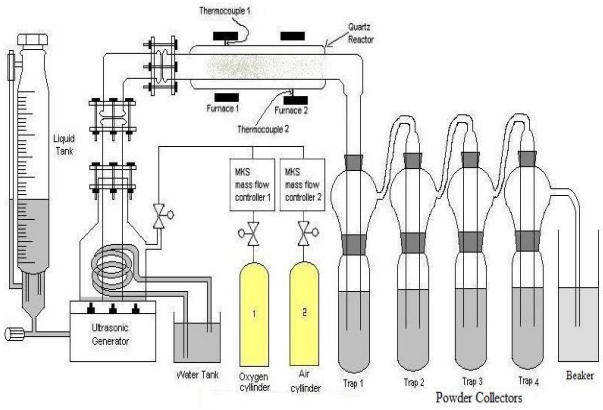

Figure 1: Ultrasonic atomization technique for the preparation of nanocrystalline ZnO powder.

Ultrasonic atomizer (**Figure 1**) was used to convert the zinc nitrate ($Zn(NO)_3 \cdot 6H_2O$) solution(0.5 M) into fine aerosol which was passed through the process of heating, solvent evaporation, pyrolysis, reaction with compressed air and finally formation of the fine particles. The glass traps were used to collect the powder. This powder was then filtered with the ceramic filter. The powder sample was refered as P1.

2.2 Paste formulation and preparation ZnO thick films

The thixotropic paste was formulated by mixing the nanocrystalline zinc oxide powder with solution of ethyl cellulose (a temporary binder) in mixture of organic solvents, such as, butyl cellulose, butyl carbitol acetate and turpineol, etc. The ratio of inorganic and organic part was kept at 75:25 in

formulating the paste. The paste was screen printed [11,12] on glass substrates in the desired pattern to obtain the sensors. These films were fired at 500°C for 30 min to remove the binder permanently. The films fabricated from as prepared nanocrystalline zinc oxide powder were termed as 'unmodified ZnO films' and referred to as S1. Thickness of the films was measured using a Taylor-Hobson (Talystep, UK) system. The thickness of the films was observed to be in the range of 10 to 13μm.

2.3.Preparation of Pt-modified nanocrystalline ZnO thick films

The Pt- modified nanocrystalline ZnO thick films were obtained by dipping them into a 0.001M aqueous solution of chloroplatnic acid ((H_2PtCl_6) 6 H_2O) for different dipping time intervals of 1, 2, 3, 4 & 5 min and referred respectively as S2, S3, S4, S5 and S6.

3. Chracterization:

3.1Structural properties of the powder

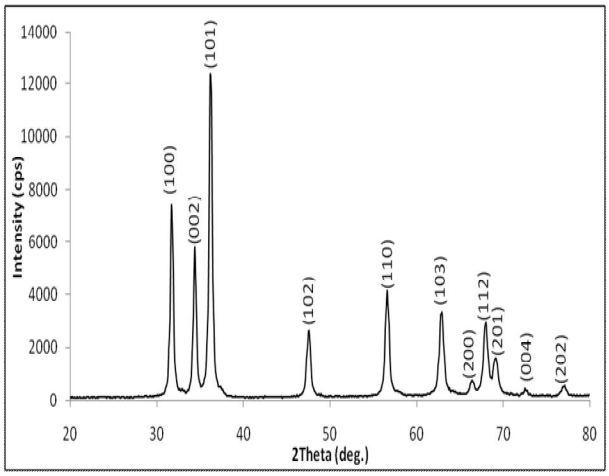

Figure 2. X-ray diffractogram of nanocrystalline ZnO powder

X-ray (CuKα, 1.5418Å) diffractogram (**Figure 2**) confirmed the powder to be of ZnO powder (JCPDS data of ZnO [48].). The average grain size of nanocrystalline ZnO powder, calculated from Scherer's formula, was found to be 19 nm.

3.2. Microstructure using TEM

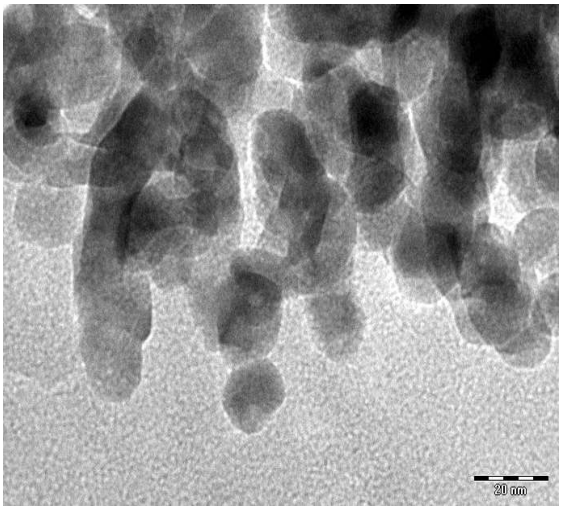

Figure 3. TEM image of the nanocrystalline ZnO: Sample S1

It is clear from TEM image (**Figure 3**) that there are spherical shaped fine grains. The average grain size was observed to be 20 nm.

4. Response of the sensors to various simulants:

4.1 Response of Pure ZnO films to DMMP, CEPS and CEES simulants

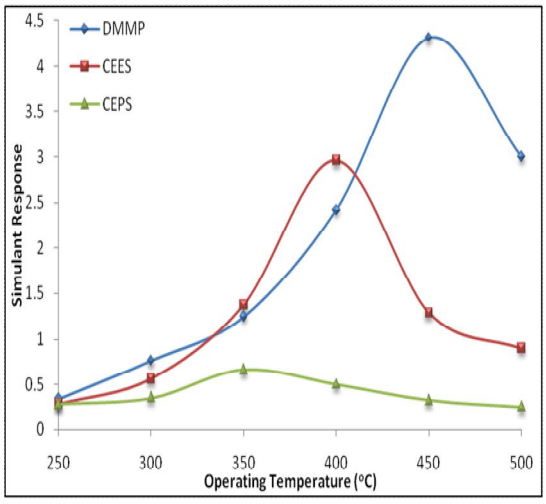

Figure 4. Variation of response with operating temperature of sample S1.

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4.2 Selectivity of sample S1 to to DMMP, CEPS and CEES simulants

Simulant response (S) is defined as:

$S = (I_g - I_a)/ I_a$, where I_a and I_g are the current flowing through the sensor resistor in air and in a simulant medium respectively.

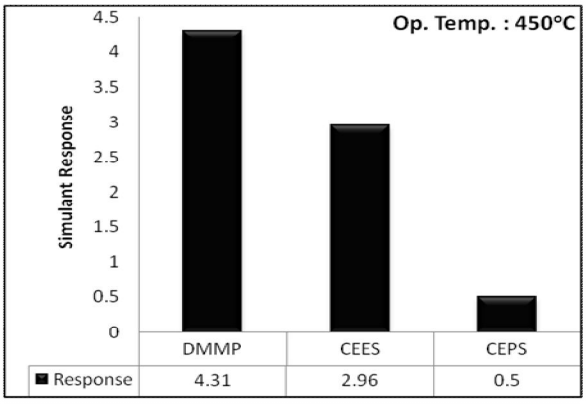

Figure 5. Selectivity of sample S1 to different simulants

The variation of simulant response with operating temperature is shown in figure 6. It is clear from figure that pure ZnO gives better response to DMMP at 450°C than the response to CEES & CEPS. The response to CEES is slightly larger than the response to DMMP at 400°C. Thus same sensor could be used to detect DMMP as well as CEES by tuning the corresponding temperatures(Figures 4 & 5).

4.3.Response of Pt-modified nanocrystalline ZnO

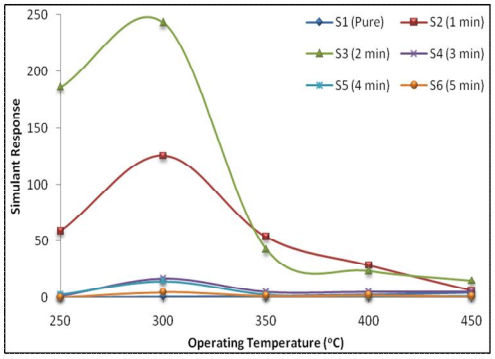

Figure 6. Variation of response with operating temperature

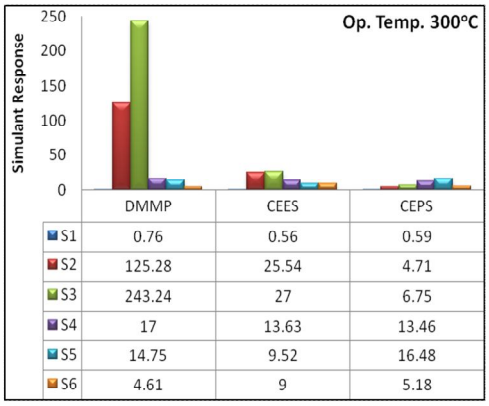

Figure 7. Selectivity of modified nanocrystalline ZnO film.

Pt- modified ZnO thick films showed better response (**Figure 6 & 7)** to DMMP than the response of pure ZnO films. DMMP response of sample S3 (Pt- modified ZnO thick film) was observed to be more than the responses shown by S1, S2, S4, S5 and S6. Pt- modified ZnO thick films showed response to DMMP at relatively lower operating temperature as compared to pure ZnO films. Presence of surface platinum would have enhanced the ability of the surface to adsorb large number of oxygen ions.

4.4. Response and recovery profiles of S3

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

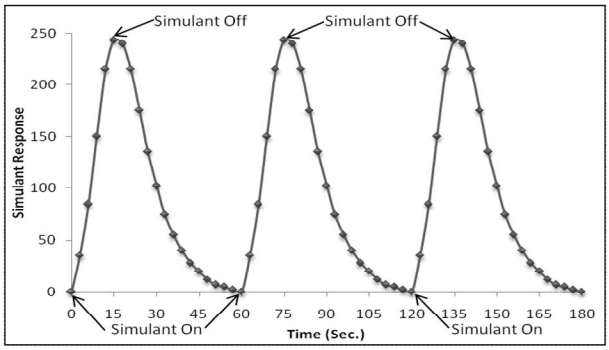

Figure 8. Variation of response with time

Figure 8 shows the response and recovery profile of sample S3 in presence and absence of DMMP (2 ppm). The 90% response and recovery levels were attained within 15 and 45 seconds respectively. Very short response and recovery times are the important feature of the Pt- ZnO sensor.

4.6 Gas Sensing Mechanism: Adsorption, Dissociation and subsequent oxidation of DMMP at higher temperatures

It has been observed that DMMP ($CH_3P(O)(CH_3O)_2$) decomposes on semiconducting metal oxide surface in steps according to: DMMP - MMP – MP, where MMP = methyl methylphosphonate ($CH_3P(O_2)(OCH_3)$) and MP = methylphosphonate (CH_3PO_3) with CH_3OH emitted at each decomposition step. In first step, DMMP would be adsorbed on ZnO surface, partially oxidized due to the interaction with adsorbed oxygen ions and converted into MMP. Subsequently, MMP would be oxidized and converted into MP.

$(CH_3P(O)(CH_3O)_2)_{ads} + O^-_{(ads)} \text{----} (CH_3P(O)_2(OCH_3))_{ads} + (H_3CO)^-_{(ads)}$ ---- (1)

$(CH_3P(O)(CH_3O)_2)_{ads} + 10\ O^-_{(ads)} \rightarrow H_3PO_4 + 3CO_2 + 3H_2O + 10\ e^-$ ------- (2)

In short, DMMP molecules adsorb on film surface, dissociated into MMP and then MP. MMP and MP react with adsorbed oxygen ions, oxidized and converted into volatile constituents: CO_2, H_2O and H_3PO_4. While oxidation, it releases electrons decreasing the resistance of the ZnO based thick film resistor. The above reaction could be summarized as:

5. Conclusions

Pure (unmodified) nanocrystalline zinc oxide was observed to be more sensitive to DMMP than the responses to CEES and CEPS at 450°C. Response of Pt- modified- ZnO to DMMP was observed to be higher than the response of the unmodified ZnO to DMMP. Response of Pt- modified- ZnO to DMMP was observed to be higher than the responses to CEES and CEPS at 300°C. Pt- modified- ZnO could operate at lower temperature (300°C) while unmodified ZnO requires higher operating temperature (450°C). Pt additive (in ZnO) may be advantageous due to the spillover action. Ability to dissociate the molecule would have enhanced due to presence of platinum ions on the film surface. The sensor has good selectivity to DMMP against CEES and CEPS. Selectivity to a particular simulant could be sharpened by the surface modification. The sensor showed quick response (15 s) and fast recovery (45 s).

Acknowledgements

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