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Procedia Materials Science 6 (2014) 1798 – 1804

Procedia Materials Science

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3rd International Conference on Materials Processing and Characterization (ICMPC 2014)

Characterizations of ultrasonically prepared nanostructured ZnO powder and NH_3 sensing performance of its thick film sensor

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Abstract

In the present investigation nanostructured ZnO powder was prepared using ultrasonic atomization method. An aqueous solution of Zn $(NO_3)_2$ *$6H_2O$ was atomised using ultrasonic atomizer. The prepared nanostructured ZnO powder was collected using a simple but novel trapping system. The powder was characterized using XRD, TEM, SEM and EDAX. Nanostructured thick-film sensors of this powder were prepared by using the simple screen printing technique. The gas sensing performance of this film was tested. The sensor was found to be most sensitive to NH_3.

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Keywaords: Ultrasonic atomizer technique, Nanostructured ZnO, Thick film, NH_3 sensor

1. Introduction

Now a days, nanostructured ZnO has attracted much interest, due to important applications in different fields, such as optoelectronics, photocatalysis, photovoltaic conversion, piezoelectricityand gas sensing devices by Patil and Bari (2010). Various techniques, such as metal organic chemical vapour deposition by Ohya and Niwa (2001), sol–

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Selection and peer review under responsibility of the Gokaraju Rangaraju Institute of Engineering and Technology (GRIET)
doi:10.1016/j.mspro.2014.07.210

gel by Bari and Patil (2009) , dc magnetron sputtering by Chawla and Kaur (2007), and spray pyrolysis by Shinde and Lokhande (2007) etc. have been used to prepare nanostructured ZnO. Among these, ultrasonic atomization is convenient and simple technique for the preparation of a variety of inorganic and organic materials by Patil and Bari (2011). Gas monitoring devices are in demand for a rapidly growing range of applications. Metal-oxide-based chemical sensors have been used for the detection of toxic pollutant gases, combustible gases and organic vapors by Patil and Bari (2012). As ammonia is utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, etc., a leak in the system would be a catastrophe for humans and animals alike. Ammonia is harmful and toxic by Close and Catlin (1980) in nature. The exposure of ammonia causes chronic lung disease, irritation and even burning the respiratory track, etc. It is therefore, needed to monitor ammonia gas and to develop the ammonia gas sensor.

In this paper, we have developed ultrasonic atomization technique to prepare nanostructured ZnO powder. This powder was studied using X-ray diffraction, TEM, SEM and EDAX. This nanostructured ZnO powder was used to fabricate the thick film sensor using screen printing technique and tested for different conventional gases. Nanostructured ZnO thick film sensor was observed to be sensitive to NH_3 gas.

2. Experimental

2.1. Ultrasonic atomization technique for preparation of nanostructured ZnO powder

Ultrasonic atomization technique was composed of three major components: (1) Ultrasonic atomizer, (2) Two zone reaction furnace and (3) Glass traps to collect nanostructure powder as shown in Fig. 1.

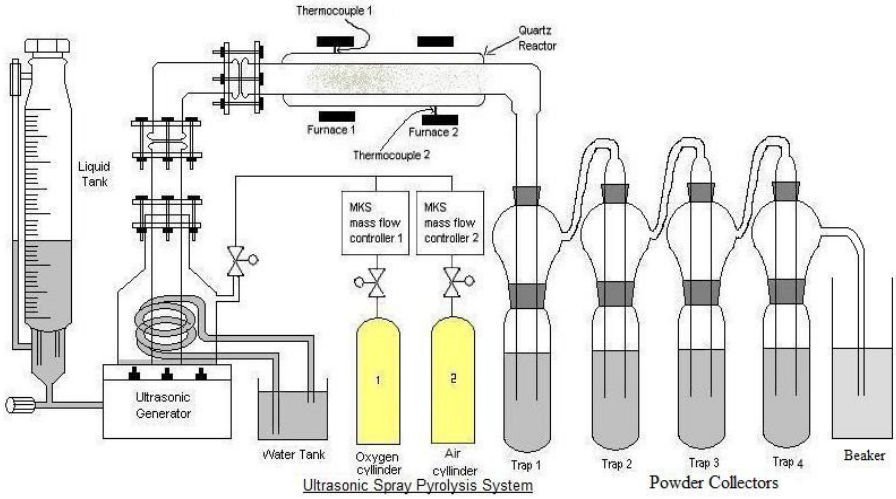

Fig. 1. Ultrasonic atomization tecnique.

0.5M aqueous solution of zinc-nitrate (Zn $(NO_3)_2$ *$6H_2O$, Merck extra pure) was prepared in double distilled water. The stock solution was stored in a cylindrical vessel, which was connected to the ultrasonic generator through a tube. When the solution was allowed to pass to generator, it was converted into aerosol. The aerosol generated from generator was pushed forward through quartz reactor. The quartz reactor was placed in a tubular two-zone furnace. The temperature of drying zone (1^{st} zone) was kept at 150^oC and pyrolysis zone (2^{nd} zone) was at 1000^oC. The carrier air-flow rate was optimized to prevent compositional segregation in order to obtain uniform and direct droplets of starting solution and to control decomposition of these droplets. Generally, the density of droplets in the aerosol is constant at the same solution characteristics and ultrasound frequency. Aerosol would pass 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.

3. Characterizations

3.1. X-ray diffractogram

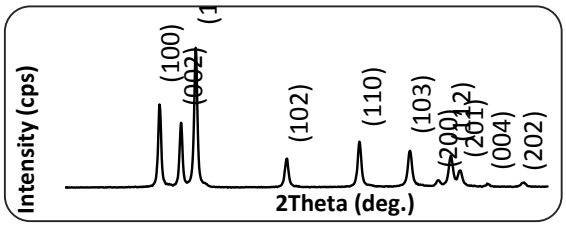

Fig. 2. XRD of nanostructured ZnO powder.

Fig. 2 shows the X-ray diffractogram of the as prepared nanostructured ZnO powder. The observed peaks match well with the standard JCPDS data of ZnO (JCPDS data card no. 5-664). The broad peaks are due to nanostructured in nature of ZnO.

3.2. Scanning electron microscopy

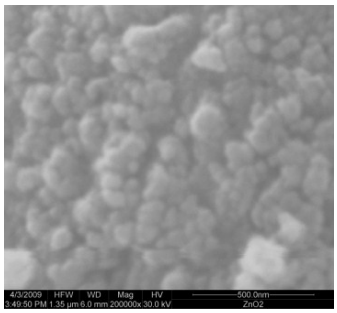

Fig. 3. SEM images of nanostructured ZnO powder

Scanning electron micrograph is shown by using topography of the film surface. The morphology of the particles was roughly spherical in shape. The average particle size was about 30 nm. Larger particles may be due to agglomeration of smaller crystallites as shown in Fig.3.

3.3. Transmission electron microscopy

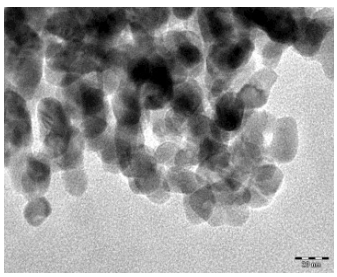

Fig. 4. TEM images of nanostructured ZnO powder

The TEM technique was used to know the exact grain size, shape and, distribution of the crystallites associated with the powder. It is clear from TEM image (Fig. 4) that there are uniformly distributed spherical-shaped grains with the average grain size of 20 nm. It is clear from TEM images that basically there are nanocrystallites. Aggregates of these crystallites give nanoparticles having larger diameters as indicated in SEM (Figure 3).

3.4. Energy dispersive analysis of x-rays

Table 1. Elemental composition of nanostructured ZnO powder

Element	at %	mass %
Zn	59.46	86.50
O	38.94	13.50
ZnO	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 Table1. It is clear from table that as-prepared ZnO powder was observed to be oxygen deficient

4. Fabrication of nanostructured ZnO thick film sensor

The thixotropic pastes were formulated by mixing lab-prepared nanocrystalline zinc- oxide powder (1 gm) with solution; of ethyl cellulose (100 mg) as a temporary binder in organic solvents of 15-20 drop of BCA to formulate the paste. (BCA is mixture of butyl cellulose, butyl carbitol acetate and turpineol).The ratio of inorganic and organic part was kept at 75:25 in formulating the paste. These pastes were screen printed by Patil and Bari (2010) on glass the substrate in the desired pattern of sensors. These sensors were sintered at 500^{o}C for ½ h. to remove the binder permanently.

5. Sensing performance of nanostructured ZnO sensor

5.1. Gas response

The gas response (R) is defined as the ratio of the change in conductance of the sensor on exposure to the target gas to the original condutance in air and is given by following relation

$$R\% = (I_g - I_a)/ I_g \times 100$$

where, I_a is conductance of sensor in air and I_g is conductance of sensor in a target gas.

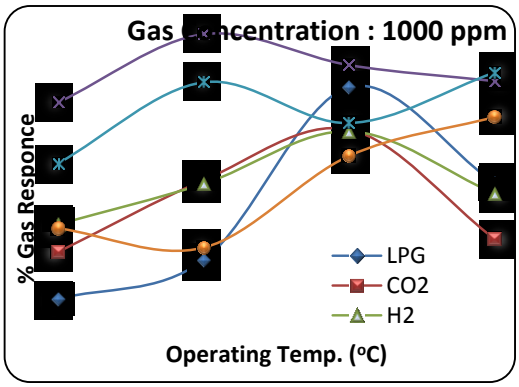

Fig. 5. Gas response with operating temperature of nanostructured ZnO thick film sensor.

Fig. 5 shows the variation of gas response with operating temperature of the nanocrystalline ZnO sensor for 1000 ppm LPG, H_2, CO_2, NH_3, C_2H_5OH and Cl_2. It is clear from the figure that the largest response to NH_3 at 300^0C is shown compared to responses of C_2H_5OH & Cl_2 at 400^0C, LPG & H_2 at 350^0C and CO_2 at 300^0C. The sensor reported in this paper show reasonably better sensitivity at lower operating temperatures. The enhancement of sensitivity at a relatively lower operating temperature may be due to the nanostructured nature of ZnO powder employed to fabricate the thick film sensors.

5.2. Selectivity

Selectivity is defined as the ability of a sensor to respond to certain gas in the presence of other gases.

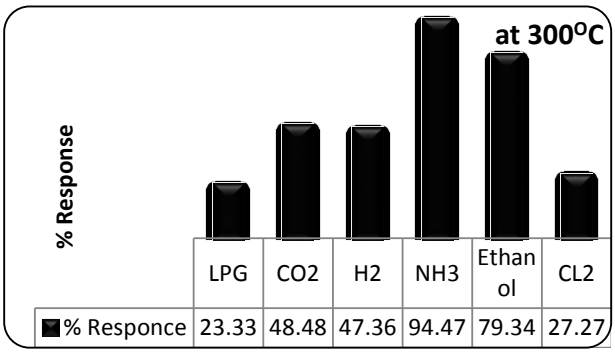

Fig. 6. Selectivity of nanostructured ZnO thick film sensor for different gases.

It is observed from figure 6 that the sensor is selective to NH_3 gas against LPG, H_2, CO_2, C_2H_5OH and Cl_2.

5.3. Response and recovery time

The time taken for the sensor to attain 90% of the maximum increase in conductance on exposure of the target gas is known as the response time. The time taken by the sensor to get back 90% of the maximum conductance when the flow of gas is switched off is known as recovery time.

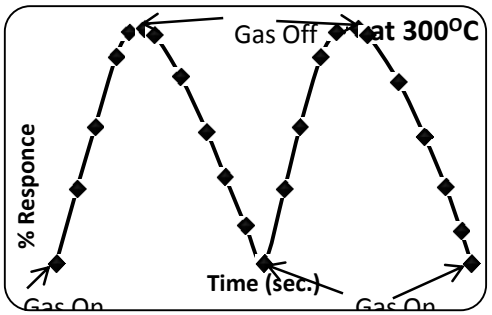

Fig. 7. Response and recovery of nanostructured ZnO thick film sensor

Fig. 7 shows the response and recovery of the nanocrystalline ZnO thick-film sensor. The response was quick (~17 s) and the recovery was fast (~37 s). The negligible quantity of the surface reaction products and their high volatility explain the quick response and fast recovery to NH_3.

6. Conclusion

1) The ultrasonic atomization technique is used to prepare nanostructured ZnO powder.
2) The technique is simple and inexpensive and it may be useful for the production of nanostructured metal-oxide powders.
3) XRD analysis confirmed that the powder to be that of ZnO with wurtzite structure.
4) The SEM image showed roughly spherical particles with an average size of 29 nm.
5) The average grain size calculated from XRD was 19 nm and from TEM, it was 20 nm.
6) The response of nanocrystalline ZnO-based sensor was observed to be largest to NH_3.
7) The sensor showed good selectivity to NH_3 gas against LPG, H_2, CO_2, C_2H_5OH, and Cl_2 gases.
8) Response time was moderate at 17 sec and the recovery time was 37 sec for NH_3 gas.

Acknowledgements

The authors are thankful to the Head, Department of Physics and Principal, Pratap College, Amalner for providing laboratory facilities for this work. The financial support for this work from the Department of Information Technology (DIT) and Defence Research and Development Organization (DRDO), Government of India, New Delhi are gratefully acknowledged. One of the authors (ARB) also thankful to Principal and staff of Arts, Commerce and Science College, Bodwad.

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