

Gas sensing performance of nanocrystalline ZnO prepared by a simple route

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The nanocrystalline powders of pure and Al^{3+} -doped ZnO with hexagonal structure were prepared by a simple hydrothermal decomposition route. The structure and crystal phase of the powders were characterized by X-ray diffraction (XRD) and the microstructure by transmission electron microscopy (TEM). All the compositions exhibited a single phase, suggesting a formation of solid solution between Al_2O_3 and ZnO. DC electrical properties of the prepared nanoparticles were studied by DC conductivity measurements. The indirect heating structure sensors based on pure and doped ZnO as sensitive materials were fabricated on an alumna tube with Au electrodes. Gas-sensing properties of the sensor elements were measured as a function of concentration of dopant, operating temperature and concentrations of the test gases. The pure ZnO exhibited high response to NH₃ gas at an operating temperature of 200 °C. Doping of ZnO with Al^{3+} increased its response towards NH₃ and the Al^{3+} -doped ZnO (3.0 wt% Al_2O_3) showed the maximum response at 175 °C. The selectivity of the sensor elements for NH₃ against different reducing gases like LPG, H₂S and H₂ was studied. The results on response and recovery time were also discussed.

Keywords: nanocrystalline zinc oxide; H₂S; gas sensor; selectivity; recovery time

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1. Introduction

Gas sensors have been widely used in the field of industry, agriculture, electronics and daily life. They play a positive role in inspecting and monitoring harmful and inflammable gases. Semiconducting metal oxides are widely used as inexpensive and robust materials for sensing toxic, hazardous and combustible gases and vapors in safety and automotive applications. The semiconducting metal oxides used in these applications are ZnO, SnO₂, In₂O₃, Fe₂O₃, NiO, etc. [1–11]. Very interesting seems to be zinc oxide (ZnO), an n-type semiconductor with a hexagonal crystalline wurtzite-type structure and space group P63mc. The importance of ZnO is due to its unusual physical properties

such as high conductance, chemical and thermal stability, wide and direct band gap of 3.37 eV and a high excitation binding energy of 60 MeV. Moreover, it is harmless to the environment [12-16]. Zinc oxide (ZnO) has emerged as one of the most promising materials due to its optical and electrical properties, high chemical and mechanical stability together with its abundance in nature. The effect of preparation conditions and/or doping on the electrical properties of ZnO-based thin films have been intensively studied because of their interesting possibilities of application such as transparent electric conductor, electroacoustic transducer, etc. [17, 18]. Appropriate donor doping can produce the electronic defects that increase the influence of oxygen partial pressure on the conductivity. Nanto et al. showed that a lower operating temperature may be achieved by the doping effect, and a significant re-

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sistance change can be obtained in the doped ZnO rather than in the undoped ZnO sensor, which results in its higher sensitivity [19].

Generally, nanometer-sized materials have been widely studied in recent years due to their good gas sensitivity caused by high surface activity. Ultra fine particles of metal oxide powders with controlled and narrow size distribution can be obtained using various techniques. The first step in keeping full control of the microstructure of the material is to control the preparation method of the starting powders. Desired crystalline properties of metal oxides can be achieved by selecting a proper fabrication process.

Ammonia is harmful and toxic in nature. The exposure to ammonia causes chronic lung disease, irritating and even burning respiratory track, etc. Therefore all industries working with ammonia should have a detection system for hazardous ammonia concentrations. Consequently, it is essential to monitor ammonia gas and to develop the ammonia gas sensors. In this paper, pure and Al₂O₃-doped ZnO nanocrystalline powders prepared by hydrothermal decomposition route have been reported. The ZnO doping is achieved by replacing Zn^{2+} atoms with the atoms of an element of higher valence like aluminum. Its gas sensing properties to ammonia (NH₃) were investigated. The results revealed that 3.0 wt% Al-doped ZnO was very promising for detection of low concentration, up to 50 ppm of NH₃ at rather lower operating temperatures.

2. Experimental details

2.1. Preparation of pure and Al-doped ZnO nanocrystalline powders

All the chemicals used in this work were of AR grade (> 99.9 %). In a typical experiment of synthesis, appropriate quantity of zinc nitrate (Zn(NO₃)₃·6H₂O) was grounded for 30 min in an agate mortar pestle and then dissolved in double distilled water. The aqueous solution was stirred for about 30 min and subsequently transferred to Teflon lined stainless steel autoclave. The temperature of the autoclave was raised slowly to 180 °C and maintained for 10 h. Thereafter, the autoclave was allowed to cool naturally to room temperature and the resulting product was washed several times with deionized water and absolute ethanol to remove the possible residues. Then the product was kept for drying at 100 °C in an oven for 12 h, which was followed by calcination at 600 °C for 6 h. Depending on the required Al-doping concentration, appropriate amount of Al (NO₃)₃·6H₂O salt was added to the aqueous solution of zinc nitrate. In the present study, doping concentration of aluminum was varied from 1.0 to 5.0 wt%.

2.2. Characterization of pure and doped ZnO

The crystal phases of calcinated samples were analyzed using X-ray diffractometer (model: Philips X'pert) with Cu K_{α} radiation ($\lambda = 1.54059$ Å). The average grain size (D) was calculated according to the Debye-Scherrer formula

$$D = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where *B* is the full width at half-maximum intensity (in radians) of a peak at an angle θ , *K* is a constant depending on the line shape profile, λ is the wavelength of the X-ray source. The lattice parameters of the prepared powder samples were calculated from the XRD peaks by indexing corresponding peaks in a cubic space group P63mc, using least square refinement. The morphology of the synthesized powders was examined using a transmission electron microscopy (TEM).

2.3. Sensor fabrication and measurement of gas sensing properties

The calcinated pure and doped ZnO powders were mixed with α -terpineol as a binder to form a paste. The paste was coated onto an alumina tube on which two gold leads had been installed at each end. The alumina tube was about 8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter. A small Ni–Cr alloy coil was positioned throughout the tube as a heater, which provided operating temperatures from 50 to 400 °C, The temperature was controlled by adjusting the heating power. In order to improve their stability and repeatability, the gas-sensing elements were heated at 500 °C for 5 days in air. The description of the schematic sensor assembly and the circuitry for the sensor characteristics measurement was reported in our earlier publication [20]. The sensor response to a test gas, *S*, is defined as [21]:

$$S = \frac{\Delta R}{R_a} = \frac{|R_a - R_g|}{R_a} \tag{2}$$

where, R_a and R_g are the sensor resistances in air and in presence of test gas respectively.

The time taken by the sensor to attain 90 % of the maximum change in resistance upon exposure to the gas was measured as a response time. The time taken by the sensor to get back to 90 % of the original resistance was measured as a recovery time. It is worth mentioning here that pure and doped ZnO nanoparticles are both n-type material whose resistance decreases in a reducing gas atmosphere.

3. Results and discussion

3.1. Material characterization

The XRD patterns of pure ZnO and Al³⁺-doped ZnO are provided in Fig. 1(a - d). XRD patterns are indexed to hexagonal structure of ZnO (JCPDS Card No. 01-079-2206). The peaks corresponding to any intermediate compound or pure Al_2O_3 are not observed, indicating the formation of a solid solution between Al₂O₃ and ZnO for all the concentrations of dopant investigated in this study. However, with the introduction of dopant we observed a change in the preferential orientation. Fig. 1(a - c) shows the <1 0 1> direction as the preferred growing orientation for the undoped ZnO, 1.0 wt% Al^{3+} -doped ZnO and 3.0 wt% Al^{3+} doped ZnO powders, but this direction changes to <0 0 2> for 5.0 wt% Al³⁺-doped ZnO powder sample. This effect can be attributed to the role of the dopant in the nucleation process. The lattice parameters of the prepared powder samples were calculated from the XRD peaks by using least square refinement. Further, average grain size has been calculated with Debye-Scherer formula. The calculated values of lattice parameters and average grain size with respect to Al-dopant concentration are presented in Table 1. It can be seen that there is a decrease in the lattice parameters of Al-doped samples as compared with pure ZnO, which may be due to lower ionic size of Al^{3+} than the host Zn^{2+} .



Fig. 1. XRD patterns of (a) pure ZnO, (b) ZnO: 1.0 wt% Al₂O₃, c) ZnO: 3.0 wt% Al₂O₃, and (d) ZnO: 5.0 wt% Al₂O₃, calcinated at 600 °C.

The average crystallite size calculated from XRD data substantiates the TEM results. The TEM images of pure and 3.0 wt% Al^{3+} -doped ZnO powders calcinated at 600 °C are provided in Fig. 2 and the corresponding diffraction patterns are shown in the Fig. 3. The small amount of agglomerations can be observed in the TEM micrographs. The diffraction patterns illustrating spot patterns of the hexagonal structure of ZnO indicate that the ZnO nanoparticles are highly crystalline, which is in good agreement with the XRD data.

The formation of ZnO wurtzite structure in the synthesized pure and Al-doped ZnO powders was further supported by FT-IR spectra as shown in Fig. 4. The absorption peaks at about 3431 and 1590 cm⁻¹ are attributed to the stretching vibration of the O–H bond and the bending vibration of H–O–H from water molecules, respectively. The absorption band at ~ 490 cm⁻¹ is the stretching mode of ZnO [22–24].

Al ₂ O ₃ concentration (wt%)	Lattice parameters (Å)	Average grain size (nm)
0	a = b = 3.2499 (9); c = 5.2056 (2)	78
1.0	$a=b=3.2497\left(2\right)$; $c=5.2060\left(3\right)$	75
3.0	$a=b=3.2495\ (2)\ ;\ c=5.2058\ (3)$	65
5.0	a = b = 3.2491 (2) ; $c = 5.2054$ (3)	69

Table 1. Lattice parameters and average grain size of ZnO-Al₂O₃ solid solution.



Fig. 2. TEM photographs of (a) pure ZnO and (b) 3.0 wt% Al₂O₃-doped ZnO, calcinated at 600 °C.



Fig. 3. Selected area electron diffraction patterns of (a) pure ZnO and (b) 3.0 wt% Al₂O₃-doped ZnO, calcinated at 600 °C.

3.2. doped ZnO nanoparticles

The gas-sensing properties of pure and Aldoped ZnO sensors were studied. Fig. 5 shows the

Gas sensing behavior of pure and Al- gas sensitivity of a thick film made from undoped ZnO nanoparticles to different reducing gases like LPG, H₂S and H₂ with a constant concentration of 500 ppm. It was found that the ZnO nanoparticles exhibited a higher response for NH₃ at an



Fig. 4. IR spectra of (a) pure ZnO, (b) ZnO: 1.0 wt% Al_2O_3 , c) ZnO: 3.0 wt% Al_2O_3 , and (d) ZnO: 5.0 wt% Al_2O_3 , calcinated at 600 °C.

operating temperature of 200 °C as compared with other tested reducing gases.



Fig. 5. Sensor response of pure ZnO towards different reducing gases as a function of operating temperature.

It is well known that the gas sensitivity usually depends on dopants and the sensor operating temperature. The appropriate selection of an additives may enhance gas response to both reducing and oxidizing gases and also improve selectivity of gas response. However, this effect does not have an universal character. Optimizing effect depends on many factors, such as the nature of tested gas, the type and concentration of additives [25]. The responses of pure and Al-doped ZnO samples as a function of operating temperature towards 500 ppm NH₃ are shown in Fig. 6. The response of the sensors to NH₃ varies with the amount of Al₂O₃ and operating temperature. The 3.0 wt% Al³⁺-doped ZnO samples exhibit the utmost response to NH₃ at 175 °C. Furthermore, the sensor response depends on the content of Al in the thick films. As 3.0 wt% Al³⁺-doped ZnO sample has smaller crystallite size amongst the investigated samples, the increase in response of this sample towards NH₃ may be attributed to the specific surface area effect of the nanoparticles [26]. This can be explained as follows: it is possible that Al_2O_3 doping not only decreases the particle size but also increases the catalytic activities of the powder. One of the probable explanations for the decrease in optimal operating temperature by 25 °C may be the reduction in the particle size with the doping concentration. In nanosized particles the surface-to-bulk ratio is much larger than that of coarse micro-grained materials, which yields a large interface between the oxide and the gaseous medium. The larger surface area generally provides more adsorptiondesorption sites, which can enhance the reactivity at lower temperature and thus provide the higher sensitivity at lower operating temperature. The reduction in the grain size allows the space charge to cover large volume of the grain and the large number of grain boundaries and peripheries. This leads to large variation in the barrier and resistance, which helps to significantly enhance gas detection [27-29].

The working principle of semiconductor gas sensors is based on the conductivity changes of semiconductor materials caused by its interaction with test gas molecules. When gas molecules are adsorbed on the surface of a semiconductor, electron transfer occurs between the semiconductor and the adsorbates. The sensing mechanism of ZnO gas sensors is usually based on the surface properties of the material [30, 31]. At elevated temperatures, adsorption of atmospheric oxygen takes place. The adsorbed oxygen extracts the conduction electrons from the surface region of ZnO grains, leaving positively charged donor ions behind. An electric field develops between the positively charged donor ions and the negatively charged oxygen ions



Fig. 6. Sensor response of Al-doped ZnO to 500 ppm NH₃ as a function of operating temperature.

such as O_2^- , O^- or O^{2-} on the surface [30, 32]. The more the oxygen ions are on the surface, the higher the potential barrier and therefore the higher the resistance [32]. As the concentration of NH₃ gas present in the ambient atmosphere increases, the amount of O_2^- , O^- or O^{2-} decreases due to the reaction with NH₃ molecules, resulting in a decrease in resistance. When temperature is varied at a given concentration of NH₃ gas, usually a peak appears in the sensor response versus operating temperature correlation. The probable reaction is as follows:

$$2NH_3 + 3O^-(ads) \rightarrow 3H_2O(g) + N_2(g) + 3e^-$$
(3)

To know about the selective behavior of $3.0 \text{ wt}\% \text{ Al}^{3+}$ -doped ZnO towards NH₃ at optimal operating temperature, its response to LPG, H₂S and H₂ at a constant concentration of 500 ppm was also studied. The results are exhibited in Fig. 7. From this, we may conclude that a sensor element based on 3.0 wt% Al³⁺-doped ZnO could detect NH₃ at 175 °C with good selectivity.

3.3. Response, recovery and stability

The response-recovery characteristics of the pure and 3.0 wt% Al^{3+} -doped ZnO sensor samples to 500 ppm of NH₃ at their respective optimal operating temperatures are shown in Fig. 8. It can be seen that the response times for pure ZnO and 3.0 wt% Al-doped ZnO sensors are 35 and 21 s, and the recovery times are 160 and 135 s, respectively.



Fig. 7. Sensor response of 3.0 wt% Al₂O₃-doped ZnO to various gases at 175 °C.



Fig. 8. Response characteristics of (A) pure ZnO and (B) $3.0 \text{ wt}\% \text{ Al}_2\text{O}_3\text{-doped ZnO to 500 ppm NH}_3$ ZnO at optimal operating temperature.

The result indicates that the 3.0 wt% Al^{3+} -doped ZnO sensor can meet the practical application in ammonia gas detection. Fig. 9 shows the variation of sensor response with gas concentration.

In order to check the stability of pure and $3.0 \text{ wt}\% \text{ Al}^{3+}$ -doped ZnO sensor samples, their responses to 500 ppm NH₃ at their respective optimal operating temperatures was measured for 90 days, at an interval of ten days. The results are demonstrated in Fig. 10. The sensors exhibit almost constant response to 500 ppm NH₃ indicating their good stability.



Fig. 9. Response vs. H₂S concentration of pure ZnO and 3.0 wt% Al₂O₃-doped ZnO sensor elements at 200 and 175 °C respectively.



Fig. 10. Stability of pure ZnO and 3.0 wt% Al₂O₃doped ZnO sensor elements at 200 and 175 °C respectively.

4. Conclusions

In summary, nanocrystalline powders of pure and Al^{3+} -doped ZnO were prepared successfully by a hydrothermal decomposition route. The asprepared materials were tested for their respective response towards different reducing gases. The sensor made of the 3.0 wt% Al^{3+} -doped ZnO nanoparticles exhibited high response and good selectivity to NH₃ as compared with pure ZnO nanoparticles. Also the sensor realized the detection of NH₃ with response time in seconds with excellent selectivity. The as-prepared 3.0 wt% Al^{3+} -doped ZnO is a promising ammonia-sensing material. Various gassensing responses to different gases may be caused by the adsorption of reducing gases and reaction between the gases and the adsorbed oxygen. All responses of the sensors were stable and repeatable.

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Received 2011-02-15 Accepted 2013-03-14