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Hydrogen sensors based on ZnO nanoparticles

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Abstract

Hydrogen sensing characteristics of thick films of nanoparticles (~35 nm diameter) of ZnO, 3% Co doped ZnO, 1% Pt-impregnated ZnO and 1% Pt-impregnated 3% Co–ZnO have been investigated. The last composition exhibits the highest sensitivity for 10–1000 ppm H_2, reaching values upto 1700 as well as good response and recovery times at 125 °C or lower. The sensor is not affected significantly upto 50% relative humidity.

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Keywords: A. Nanoparticles; A. ZnO; D. Chemical sensors

1. Introduction

ZnO is known to be useful for sensing gases particularly H_2, CO and ethanol [1–4]. Since the sensitivity of the bulk material is not sufficiently high, Wang et al. [5] employed ZnO nanorods coated with Pd to detect H_2 down to 10 ppm, with a relative response of 2.6% at 10 ppm and a recovery time of less than 20 s at 25 °C. Jiaqiang et al. [6] employed ZnO nanorods, prepared by the hydrothermal process, and found a sensitivity of ~50 for 1000 ppm of H_2 at 330 °C. There are a few other reports on the gas-sensing characteristics of different nanostructures of ZnO, but the H_2 sensing characteristics have not been adequately examined. We have investigated thick films of pure and Co doped ZnO nanoparticles for sensing H_2, specially after impregnating the nanoparticles with Pt. We have doped the ZnO nanoparticles with 3% Co^{2+} since the energy gap of ZnO is lowered upto this level of doping [7]. We have impregnated the nanoparticles with 1% Pt in view of the reported beneficial effect of Pt on the gas sensing characteristics of ZnO [8]. We find that Co-doping improves the sensitivity of ZnO, but impregnation of Pt further improves the sensitivity as well as the response and recovery times. The sensing characteristics are not affected significantly even when the relative humidity goes upto 50%.

2. Experimental

ZnO nanoparticles were synthesized by the sol–gel technique starting with zinc acetate. An aqueous solution of ammonia was used to hydrolyze the zinc acetate and yield a gel. The gel so obtained after 2 h, was dried at 100 °C for 10 h to obtain the xerogel of the material. The xerogel was calcined at 250 °C for 3 h and ground to form a powder. The powder was slowly heated to 400 °C for 30 min to decompose the organic matter completely. The same procedure was used to prepare the powders of ZnO doped with 3 mol% of Co. Powders of the various ZnO samples were characterized by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscope (TEM). To fabricate thick film sensors, an appropriate quantity of diethyleneglycol was added to the ZnO powder and the mixture ground to form a paste. The paste was coated on to an alumina substrate (5 mm × 20 mm, 0.5 mm thick) attached with a comb-type Pt electrode on one side, the other side having a heater. The films were dried and annealed at 600 °C for 1 h. The annealing had little effect on the particle size as seen from electron microscopic images. The oxide films were doped in the solution of 0.08 M-chloroplatinic acid to obtain a coating of ~1% Pt, as revealed by EDAX analysis. The films were again annealed at 600 °C for 30 min. The film thickness was generally in the 1–5 μm range.

The gas sensing characteristics were measured with an apparatus consisting of a test chamber, sensor holder, a Keithley multimeter-2700, a Keithley electrometer-6517A, mass flow controllers and a data acquisition system. The test gases were allowed to flow through a pipe network of diameter

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of 3 mm to a test chamber of volume of 8.8 cm^3 via a two-way valve. The ZnO nanoparticulate films were tested for H_2 sensing in the temperature range 30–125 °C. The gas flow was maintained at 100 sccm by using mass flow controllers. By monitoring the output voltage across the sensor, the resistance of the sensor was measured in dry air and in the test gas. A load resistor R_L was connected in series with the sensor element R_S. The input circuit voltage V was applied across R_L and R_S. The resistance of the sensor material was obtained by measuring the voltage drop across the element. The gas sensitivity (response magnitude) of the sensor was obtained by the relationship $S = R_{air}/R_{gas}$ where R_{air} is the resistance of the thick film sensor in dry air and R_{gas} is the resistance in the test gas. The resistance of the sensors was of 1.2–10 MΩ range in dry air at 30–125 °C. The response time was taken as the time required for the variation in conductance to reach 90% of the equilibrium value after the test gas was injected and the recovery time is taken as the time necessary for the sensor to attain a conductance 10% above the original value in air.

3. Results and discussion

In Fig. 1(a) and (b), we show typical transmission electron microscope (TEM) images of ZnO and 3% Co doped ZnO nanoparticles, respectively. The images show nanoparticles along with a few nanorods (∼10%). Fig. 1(c) shows the TEM image of the 3% Co doped ZnO nanoparticles after Pt impregnation. The particle size distribution histograms of all the three types of ZnO nanoparticles are shown in Fig. 1(d). From the TEM studies, the average size of the different types of ZnO nanoparticles is found to be 35 ± 15 nm.

The sensitivity of the thick films of ZnO nanoparticles for 1000 ppm of H_2 varied between 40 and 65 in the 80–125 °C range. The sensitivity, however, increased considerably on impregnating the nanoparticles with 1% Pt. In order to ensure

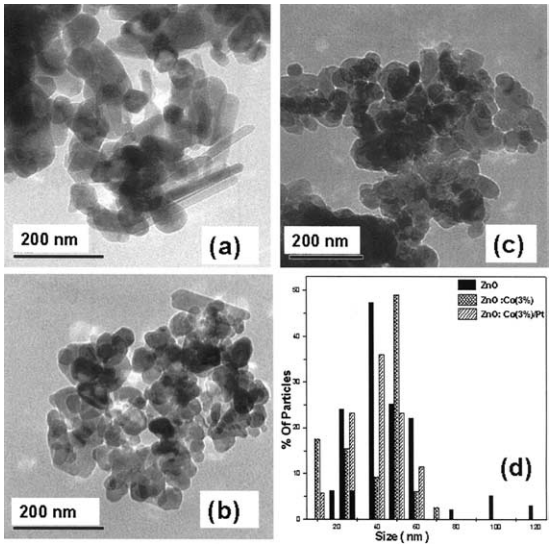

Fig. 1. TEM images of (a) ZnO, (b) ZnO doped with 3% Co before annealing and (c) ZnO doped with 3% Co and 1% Pt impregnation after annealing at 600 °C (d) Histograms of the particle size distributions of ZnO, ZnO:Co (3%) and ZnO:Co (3%)/Pt nanoparticles.

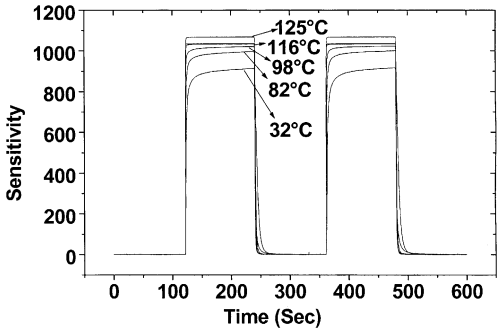

Fig. 2. Gas sensing characteristics of ZnO impregnated with Pt for 1000 ppm of H_2.

that the increased sensitivity is not due to the Pt nanoparticles alone, we examined the gas sensing characteristics of Pt nanoparticles by impregnating 0.08 M chloroplatinic acid on the graphite and silicon powders. Pt/graphite and Pt/Si nanoparticles showed sensitivities of 5 and 3, respectively, for 1000 ppm of H_2 at 125 °C.

Hydrogen sensing characteristics of the thick films of ZnO nanoparticles impregnated with Pt are presented in Fig. 2. The sensitivity was 912 at 32 °C and 1065 at 125 °C, with response and recovery times of 3 and 4 s, respectively. Doping the ZnO nanoparticles with 3% Co increases the sensitivity to 60–335 in the 80–125 °C range. On impregnation of the 3% Co-doped ZnO nanoparticles with Pt, the performance was significantly enhanced. In Fig. 3, we show the sensor characteristics of the films of 3% Co doped ZnO particles impregnated with Pt. These films exhibit a sensitivity of 1720 at 125 °C. Thus, the Pt impregnated samples show good sensitivity even at lower temperatures. The response and recovery times for 3% Co doped ZnO were 4.5 and 7 s, respectively. ZnO: 3%Co/Pt exhibits response and recovery times of 3 and 4 s, respectively.

In Fig. 4(a), we show the variation of the sensitivity with the concentration of H_2 at 125 °C for the thick nanoparticle films of ZnO, ZnO/Pt and 3% Co doped ZnO impregnated with Pt. The sensitivity is 150 and 180, respectively, for ZnO/Pt, ZnO: 3% Co/Pt at 10 ppm of H_2 while pure ZnO (without Pt) shows a sensitivity of 17. Fig. 4(b) shows the variation of the response and recovery times with temperature for ZnO:3% Co/Pt for

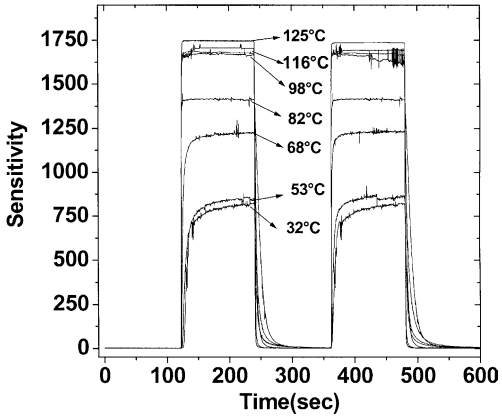

Fig. 3. Gas sensing characteristics of ZnO doped with 3% Co and impregnated with Pt for 1000 ppm of H_2.

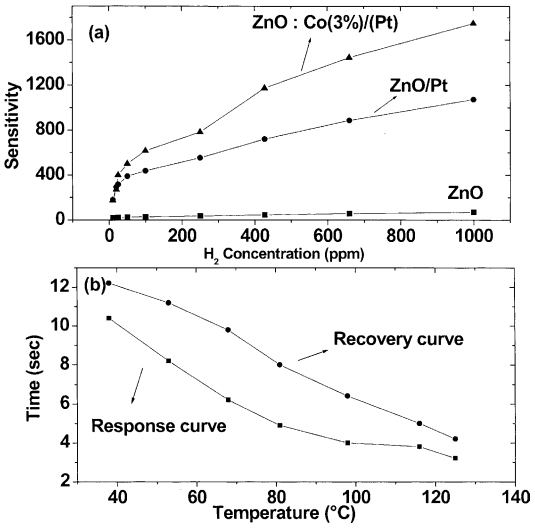

Fig. 4. Variation of sensitivity (a) with concentration of H_2 and (b) variation of response and recovery times for ZnO:Co(3%)/Pt.

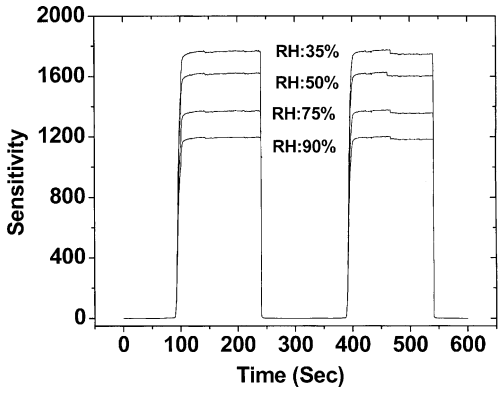

Fig. 5. Effect of humidity on ZnO:Co (3%)/Pt sensors for 1000 ppm of H_2 at 125 °C.

1000 ppm of H_2. We see that these characteristics are satisfactory even at 60 °C.

An important aspect of such oxide-based sensors relates to the effect of humidity on the sensing characteristics. For this purpose, we examined the effect of humidity on several of the thick film sensors prepared by us. We show typical results on the effect of humidity on the H_2 sensing characteristics of ZnO:3% Co/Pt sensors in Fig. 5. The sensitivity is not affected up to 50% of relative humidity in the thick film sensor. In the case of ZnO:3% Co/Pt, the sensitivity remains 1100 even at a relative humidity of 90%. We, therefore, conclude that the H_2 sensing characteristics for ZnO:3% Co/Pt remains good even in the presence of moisture.

In order to ensure that the sensors prepared by us were stable, we carried out measurements repetitively by measuring the sensing characteristics several times. The sensitivity remained the same even after carrying the measurements over 1000 cycles. The mechanism of H_2 sensing by the ZnO nanostructures reported here would involve the defect structure of the semiconducting oxide described in the literature [9–14].

4. Conclusions

ZnO nanoparticles impregnated with Pt and/or doped with Co show very good sensitivity for H_2 at relatively low temperatures. Thus, the sensitivity for 1000 ppm H_2 reaches values of over 1000 and 1500 for Pt impregnated ZnO and 3% Co doped ZnO at 125 °C or lower. The response and recovery times are generally well within 10 s in the regime of high sensitivity. The ZnO nanoparticle sensors are stable over several cycles for long periods, thereby demonstrating their practical utility as H_2 sensors. Furthermore, the performance is not sensitive to humidity upto 50% relative humidity. To our knowledge, the ZnO-based H_2 sensors designed here are superior to those reported in the literature, including those in the recent report on Pt-coated ZnO films [15].

We have employed nanoparticles with an average diameter of 35 nm. The sensitivity does not normally get affected down to a particle size of ∼10 nm, but increases when the size is much smaller [16]. We have not prepared such small particles in the present study. It may be worthwhile to investigate the H_2 sensing characteristics of ZnO nanoparticles with average diameters 10 nm and less, but it should also be noted that the long-term stability of very small nanoparticles is somewhat doubtful.

Acknowledgements

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