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Humidity sensing properties of Ce-doped nanoporous ZnO thin film prepared by sol-gel method

Mansoor Anbia, Seyyed Ebrahim Moosavi Fard

(Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology, Farjam Street, Narmak, Tehran 16846, Iran)

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Abstract: The humidity sensitive characteristics of the sensor fabricated from Ce-doped nanoporous ZnO by screen-printing on the alumina substrate with Ag-Pd interdigital electrodes were investigated at different sintering temperatures. The nanoporous thin films were prepared by sol-gel technique. It was found that the impedance of the sensor sintered at 600 ºC changed more than four order of magnitude in the relative humidity (RH) range of 11%–95% at 25 ºC. The response and recovery time of the sensor were about 13 and 17 s, respectively. The sensor showed high humidity sensitivity, rapid response and recovery, prominent stability, good repeatability and narrow hysteresis loop. These results indicated that Ce-doped nanoporous ZnO thin films can be used in fabricating high-performance humidity sensors.

Keywords: humidity sensing; nanoporous ZnO; Ce-doped; rare earths

Humidity sensors, due to the recognized importance of vapor concentration, have been widely used in medicine, agriculture, industrial plants, environment monitoring, storage and human comfort[1–3]. The ideal humidity sensors should possess the characteristics such as high sensitivity, good chemical and physical stability, no hysteresis, short response time, excellent repeatability[4,5]. Among the different types of humidity sensors, ceramic humidity sensors based on porous and sintered oxides have received much attention due to their chemical and physical stability and wide range of working temperature[6–9]. Furthermore, the nanoporous thin film types having the nanosized grains and nanoporous structure are optimal candidates for humidity sensors because of the miniaturization of the sensing element and large surface area[10–14] that facilitates the adsorption of water molecules.

So far, many investigations have been carried out for monitoring humidity sensing properties of ZnO. Humidity sensing properties of nanorod ZnO have been investigated by Zhang et al.[15], and their results have shown that the resistance of ZnO nanorod devices increases more than two orders of magnitude, when exposed to moisture of 97% RH. Humidity sensing properties of Pd-doped ZnO nanotetrapods have been investigated by Wang et al.[16], and they have found that Pd doping can improve sensitivity and linearity of sensor. Humidity sensing properties of quartz crystal microbalance (QCM) coated by flower-like ZnO nanostructures and annealed ZnO nano-sized clusters were also investigated by Zhou et al.[17] and Yadav et al.[18], respectively.

Rare earths have been immensely used to modify the properties of functional materials due to their unique physicochemical activity[19–23]. Cerium is a major element in the useful rare earth family. Gas-sensing properties of Ce-doped ZnO thin-film sensors were investigated by Ge et al. and they found that 5 at.% Ce-ZnO thin-film sensors show good selectivity to alcohol at 370 ºC[24].

In this paper, we reported the preparation, characterization and humidity sensing properties of Ce-doped ZnO thin film prepared by sol-gel method at humidity range of 11%–95% at room temperature. Pluronic P123 was used as the organic template to make the nanoporous structure. The results offered an effective approach to understand and design ZnO-based humidity sensing thin films.

1 Experimental

1.1 Materials

Zinc nitrate, $Zn(NO_3)_2·6H_2O$, cerium sulfate, $Ce(SO_4)_2·4H_2O$, triblock copolymer pluronic P123 ($EO_{20}PO_{70}EO_{20}$, where EO is ethylene oxide and PO is propylene oxide, MW 5800, Aldrich), acetic acid, HCl and ethanol were of analytical grade.

1.2 Preparation of samples

The nanoporous thin films were prepared by sol-gel technique. In the typical experiment, 0.5 mol zinc nitrate and 0.002 mol cerium sulfate were dissolved in 120 ml HCl and vigorously stirred. 36 g P123 was dissolved in 150 ml ethanol and 50 ml acetic acid (P123 was added to make the nanoporous structure). Then, solutions were mixed and stirred for 12 h. Then, the solution was aged for 5 d at 50 ºC.

Corresponding author: Mansoor Anbia (**E-mail:** anbia@iust.ac.ir; **Tel.:** +98-21-77240516)
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After aging, the as-prepared Ce-doped gel was divided into three groups and sintered at 600, 700 and 800 ºC for 4 h. The Ce-doped nanoporous ZnO powders were ground and mixed with deionized water in a mass ratio of 100:25 to form a paste. The pastes were screen-printed on the alumina plates (9 mm×3 mm, 0.5 mm thick) with seven pairs of Ag-Pd interdigitated, and then the films were dried in air at 100 ºC for 5 h. The schematic diagram of the humidity sensor is shown as Fig. 1.

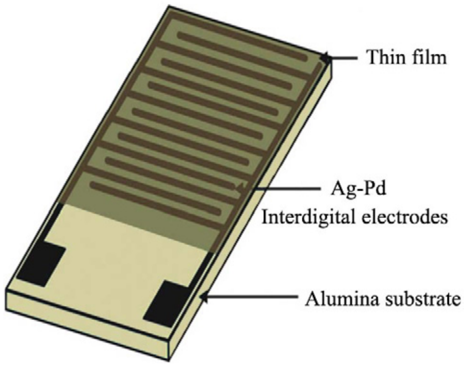

Fig. 1 Schematic diagram of humidity sensor

1.3 Measurements

The characteristic curves of humidity sensitivity were measured on an Agilent model LCR analyzer (E4980A, USA). The impedance measurements were made at 1 V from 40 Hz to 100 kHz. The RH range of 11%–95% was obtained by using saturated salt solutions as the humidity generation sources. Different saturated salt solutions were LiCl, CH_3CO_2K, $MgCl_2·6H_2O$, K_2CO_3, $Mg(NO_3)_2$, KI, KCl, and KNO_3, and their corresponding RH values were 11%, 23%, 33%, 43%, 53%, 69%, 85% and 95% RH, respectively[25]. The humidity and temperature were calibrated by a humidity-temperature digital instrument (HT-3015 type, Lutron, Taiwan).

2 Results and discussion

2.1 Characterization

X-ray powder diffraction (XRD) patterns were obtained on a Philips X'PERT MPD diffractometer using Cu-Kα_1 radiation. Fig. 2 shows the XRD patterns of Ce-doped samples sintered at different temperatures for 4 h. All the diffraction peaks of Ce-doped ZnO can be indexed as a hexagonal wurtzite structure ZnO with lattice constants a=0.3249 nm and c=0.5206 nm according to the Joint committee powder diffraction standards (JCPDS) file No. 36-1451. In the range of 28°–33°, two weaker diffraction peaks indicate that the face-centered cubic (FCC) crystalline structure CeO_2 exists in the films according to the standard JCPDS (No. 75-0390) card. At the same time, it is observed that no composite metal oxide is detected in the films. Scanning electron microscopy (SEM) image was observed using a Tescan VEGA device, (Czech) after gold-plating of the samples. Fig. 3 shows the SEM image of Ce-doped ZnO sintered at 600 °C.

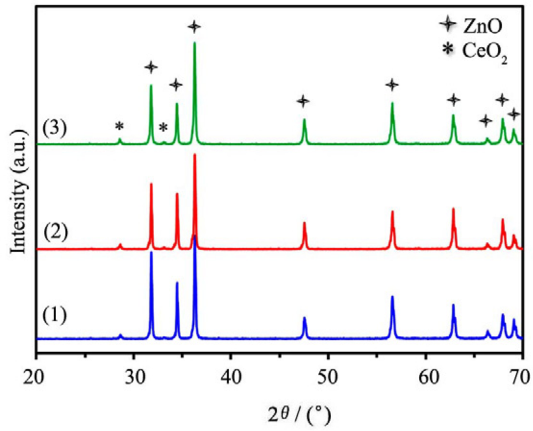

Fig. 2 XRD pattern of Ce-doped ZnO samples sintered at different temperatures
(a) 600 °C; (b) 700 °C; (c) 800 °C

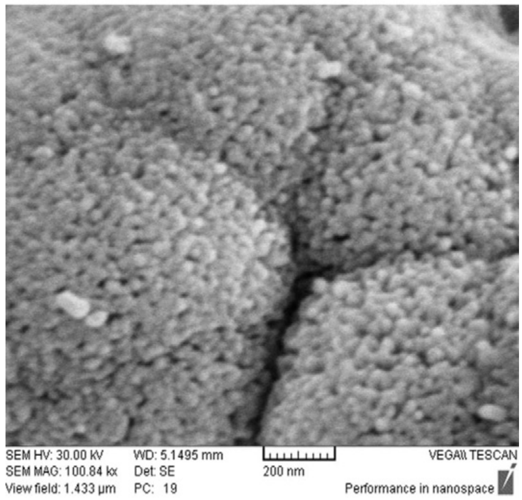

Fig. 3 SEM micrograph of Ce-doped ZnO sintered at 600 °C

The SEM image reveals that the film possesses the grain size of nanometer order and has a nanoporous structure with homogeneous size distribution. It means that such a structure is likely to facilitate the adsorption process of water molecules because of the capillary pore and large surface area.

2.2 Humidity-sensing properties

Fig. 4 shows the humidity sensing properties of undoped and Ce-doped nanoporous samples in terms of impedance variation as a function of relative humidity (RH) by keeping the applied voltage at 1 V and the frequency 100 Hz at a fixed temperature of 25 °C. As can be seen, with increasing RH, the impedance of each sample decreases, indicating that the pure and Ce-doped ZnO samples show humidity sensitivities. However, their decrease rates are quite different. Undoped ZnO shows an obvious change of impedance with respect to the humidity only in ranges higher than 43% RH. Ce-doped ZnO samples show much better sensitivity than that of undoped ZnO on a semilogarithmic scale. The impedance of the Ce-doped nanoporous ZnO sintered at 600 °C decreases by more than four orders of magnitude with increasing RH from 11% to 95%, which has the highest humidity sensing performance among all the samples.