Sensors and Actuators B 133 (2008) 638–643

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Properties of humidity sensing ZnO nanorods-base sensor fabricated by screen-printing

Qi Qi[a], Tong Zhang[a,b,*], Qingjiang Yu[c], Rui Wang[a], Yi Zeng[a], Li Liu[a], Haibin Yang[c]

[a] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, PR China
[b] Key Laboratory of Low Dimensional Materials & Application Technology, Ministry of Education, Xiangtan 411105, PR China
[c] National Laboratory of Superhard Materials, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 29 December 2007
Received in revised form 25 March 2008
Accepted 31 March 2008
Available online 8 April 2008

Keywords:
Humidity sensitivity
Flower-like ZnO nanorods
Complex impedance plots
Sensor

ABSTRACT

The humidity sensitive characteristics of a sensor fabricated from flower-like ZnO nanorods by screen-printing on a ceramic substrate with Ag–Pd interdigital electrodes have been investigated. The sensor shows high humidity sensitivity, rapid response and recovery, small hysteresis, and good stability. It is found that the impedance of the sensor decreases by about five orders of magnitude with increasing relative humidity (RH) from 11 to 95%. The response and recovery time of the sensor is about 5 and 10 s, respectively. These results indicate that the flower-like ZnO nanorods can be used in fabricating high-performance humidity sensors.

1. Introduction

Fabrication of sensitive chemical sensors has gained special focus driven by their diverse applications in air-quality detection, inflammable-gas inspection, environmental monitoring, health-care, defense and security, and so on [1–5]. Recently, inspired by the advantages of high surface-to-volume ratios, fabrication of nanomaterial electronic devices and exploration of their properties are of current interest [6–18]. Hitherto, different types of sensors based on three-dimensional (3D), two-dimensional (2D), one-dimensional (1D), and zero-dimensional (0D) architectures have been successfully obtained [10–18]. Among those nanostructures, 1D sensors, based on ceramic structures (SnO_2 [19], TiO_2 [20], ZnO [14–18], In_2O_3 [21], and WO_3 [22]), have attracted much focus owing to their high surface area and low dimensionality, which could facilitate fast mass transfer of the analyte molecules to and from the interaction region as well as require charge carriers to transverse the barriers introduced by molecular recognition along the 1D nanostructures [23]. Although many successes have been obtained, most of those papers focus on the gas sensors (e.g. CO, O_2, and C_2H_5OH) [10–18], and few papers on humidity sensors have been explored. Additionally, the fabrication of sensitive and stable humidity sensors with rapid response and recovery is still in great demand.

In this paper, we report a highly sensitive humidity sensor with rapid response and recovery, which is based on the flower-like ZnO nanorods. ZnO has been chosen in our experiment for its versatile properties in optoelectronic devices, sensors, lasers, transducers, and photovoltaic devices [24,25]. Additionally, ZnO nanostructures are believed to be nontoxic, bio-safe, and possibly biocompatible, and have been used in many applications in our daily life. We believe that our method not only provides a new avenue for fabricating highly effective humidity sensors, but also offers a powerful platform to understand and design desirable humidity sensors.

2. Experimental

2.1. Preparation and characterization of materials

Flower-like ZnO nanorods were synthesized by a simple wet chemical method [26]. All chemicals (analytical grade reagents) were purchased from Beijing Chemicals Co. Ltd. and used as received without further purification. Deionized water with a resistivity of 18.0 $M\Omega\,cm^{-1}$ was used in all experiments. In a typical synthesis process, 100 mL of an aqueous solution of zinc nitrate and 100 mL of a hexamethylenetetramine (HMT) aqueous solution of equal concentration (0.05 M) were mixed together and kept under mild magnetic stirring for 5 min. Then the solution was transferred

---

* Corresponding author at: State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, PR China. Tel.: +86 431 85168385; fax: +86 431 85168270.
E-mail address: zhangtong@jlu.edu.cn (T. Zhang).

0925-4005/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2008.03.035

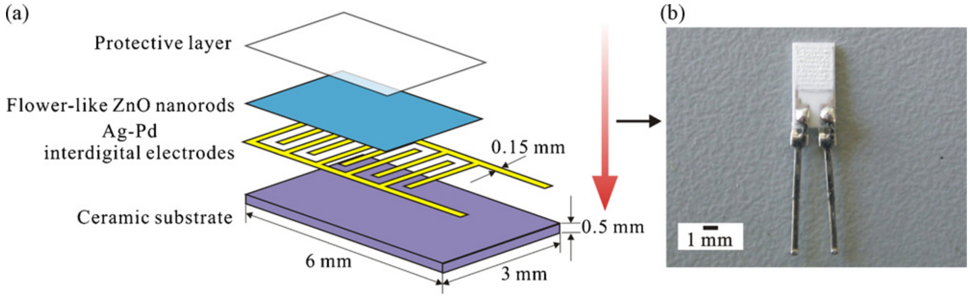

Fig. 1. (a) Scheme of the sensor structure and (b) top-view optical micrograph of the sensor.

into a 500-mL flask and heated at 90 °C for 3 h with refluxing. Subsequently, the resulting white products were centrifuged, washed with deionized water and ethanol and dried at 60 °C in air for further characterization.

X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL JEM-6700F microscope operating at 3 and 5 kV. Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were obtained on a JEOL JEM-2000EX microscope with an accelerating voltage of 200 kV. Raman-scattering spectrum was measured by an HR-800 LabRam confocal Raman microscope with a backscattering configuration made by JY company in France, excited by the 514.5 nm line of an argon-ion laser at room temperature (25 °C).

2.2. *Fabrication and measurement of sensors*

The flower-like ZnO nanorods powders were ground and mixed with deionized water in a weight ratio of 100:25 to form a paste. The paste was screen-printed on a ceramic substrate (6 mm × 3 mm, 0.5-mm thick) with five pairs of Ag–Pd interdigital electrodes (electrodes width and distance: 0.15 mm) to form a film with a thickness of about 10 μm, and then the film was dried in air at 60 °C for 5 h. In order to improve the sensor antipollution, we made a 0.1 g of an ethyl cellulose solution in ethyl ester acetate (4 mL), which was coated on the surface of the sensitive film as a protective layer [27]. Finally, the humidity sensor was obtained after aging at 95% relative humidity (RH) with a voltage of 1 V, 100 Hz for 24 h. Fig. 1 shows the structure and optical micrograph of the sensor.

The characteristic curves of humidity sensitivity were measured on a ZL-5 model LCR analyzer (Shanghai, China). The voltage applied in our studies was ac 1 V, and the frequency varied from 40 Hz to 100 kHz. The sensor was successively put into several chambers with different RH levels at a temperature of 25 °C. The RH range of 11–95% was obtained using saturated salt solutions as the humidity generation sources [27]. The six different saturated salt solutions were LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3, and their corresponding RH values were 11, 33, 54, 75, 85, and 95% RH, respectively.

3. Results and discussion

The structure of the flower-like ZnO nanorods has been characterized by XRD as shown in Fig. 2. All the diffraction peaks can be indexed as hexagonal ZnO with lattice constants $a = 3.249$ Å and $c = 5.206$ Å, which are consistent with the values in the standard card (JCPDS 36-1451). No diffraction peaks from any other impurities are detected.

Fig. 3(a) and (b) shows the FE-SEM images of the as-prepared products at different magnifications. Fig. 3(a) shows the low-resolution image of the sample, indicating the flower structure composed of closely packed nanorods with lengths of 1.5–3 μm and diameters of 200–400 nm. The high-resolution image in Fig. 3(b) clearly reveals that the obtained ZnO exhibits well-defined flower-like morphology and each of the rods has one end outside and another end binds to other rods. Further morphology characterization of the ZnO sample was performed on a transmission electron microscope (TEM) as shown in Fig. 3(c), which agrees with the FE-SEM results. To further determine the accurate structure of the product, the TEM–selected area electron diffraction pattern of the product was recorded as shown in Fig. 3(d). From the SAED, all the detectable dots are perfectly indexed to the same position as those from hexagonal wurtzite ZnO structure, which grows along the [0 0 0 1] direction [28].

Raman spectroscopy is also carried out to study the vibrational properties of the flower-like ZnO nanorods. Fig. 4 shows the room-temperature Raman spectrum of the ZnO nanorods. All observed spectral peaks can be assigned to a wurtzite ZnO structure according to the literature values [29]. The peak at 437 cm^{-1} is attributed to the ZnO nonpolar optical phonon E_2(high) mode. The peak at 409 cm^{-1} corresponds to the E_1(TO) mode, but it is not obvious. As the characteristic peak of hexagonal wurtzite ZnO, the E_2(high) at 437 cm^{-1} is very intense and has a full width at half-maximum of 12 cm^{-1}. The asymmetrical and line-broadening characteristics mask E_1(TO) on the left-hand side of E_2(high). The peak at 579 cm^{-1} is attributed to the E_1(LO) mode, which is caused by the defects such as oxygen vacancy, zinc interstitial, or their complexes [30]. In addition, the peak at 378 cm^{-1} corresponds to the A_1(TO) mode. Besides these "classical" Raman modes, the Raman spectrum also shows other modes with frequencies of 333, 541, 661, and 1147 cm^{-1}. These

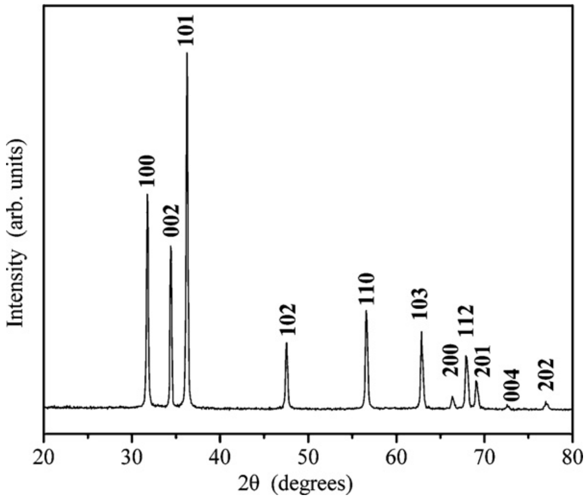

Fig. 2. XRD pattern of the flower-like ZnO nanorods.