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High-performance ethanol sensing based on an aligned assembly of ZnO nanorods

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ABSTRACT

We report fabrication and characterization of an ethanol sensor using aligned ZnO nanorods. The ZnO nanorods have an average diameter of 50 nm and an average length of 0.5 μm. The sensor response R_a/R_g, where R_a and R_g are the resistance in air and in ethanol vapor, respectively, is about 10 to 1 ppm ethanol, and increases to about 100 as the ethanol concentration is raised to 100 ppm. The mechanism of the highly sensitive ethanol detection is discussed.

1. Introduction

Recently, one-dimensional (1D) nanostructures, such as carbon nanotubes, ZnO, SnO_2, In_2O_3, and TiO_2 nanowires/nanorods have attracted much attention because of their potential applications in fabricating gas sensors. 1D nanostructures have been extensively used as gas sensing materials due to their high surface-to-volume ratios and good chemical and thermal stabilities under the operating conditions [1,2]. In order to illustrate their high-performance sensing characteristics, the sensing mechanisms such as surface-depletion [2], point contact [3], and face contact models [4] have been proposed. However, the sensitivity of the sensors based on the point contact of ZnO nanowires and nanorods is low except the case that the diameter of the nanomaterials is close to or smaller than the space-charge length ($2L_d$) [5]. Although the sensitivity of SnO_2 nanobelts is higher, the length of the nanobelts is up to a few micrometers and only a small fraction of the face contacts really works. In this article, we report fabrication and characterization of an ethanol sensor composed of ZnO nanorods with an aligned and rather closely packed arrangement. When exposed to 1 ppm ethanol the sensor response is ∼10, and as the ethanol concentration is raised to 100 ppm, the sensitivity increases to ∼100.

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2. Experimental

The preparation method of the precursor was simple and outlined as follows. Four chemicals of analytically pure zinc acetate (Zn $(CH_3COO)_2{\cdot}2H_2O$), citric acid ($C_6H_8O_7{\cdot}H_20$), pure distilled water (H_2O) and absolute ethanol (CH_3CH_2OH) were used. For the fabrication of ZnO nanorods with a vertically aligned arrangement, the following experiments were performed. First, a 55 mL solution of citric acid (0.04 M) in ethanol was added slowly to a 15 mL Zn $(CH_3COO)_2$ solution (1 M) in distilled water. After the addition, the obtain suspension (pH ≈ 5.8) was stirred at 80 °C for 10 h to get a precursor. The precursor was calcined in a muffle furnace for 3 h at 400 °C. After calcination, the powder was cooled naturally down to room temperature in air. The morphology of the synthesized ZnO nanorods was characterized by scanning electron microscopy (SEM) [JEOL-JSM-6700F]. The crystal structure of the sample was determined by X-ray diffraction (XRD) using a D5000 X-ray diffractometer (SIEMENS, Germany) with monochromatic Cu Kα (λ = 1.54178 Å) radiation. The surface area of the ZnO nanorods was measured based on the principle of N_2 sorption with a Brunauer–Emmett–Teller (BET) surface analyzer (SA3100, Coulter, USA).

3. Results and discussion

A typical powder XRD pattern of the product is shown in Fig. 1. The diffraction peaks can be indexed as those from the known wurtzite-structured (hexagonal) ZnO (a = 3.249 Å, c = 5.026 Å, space

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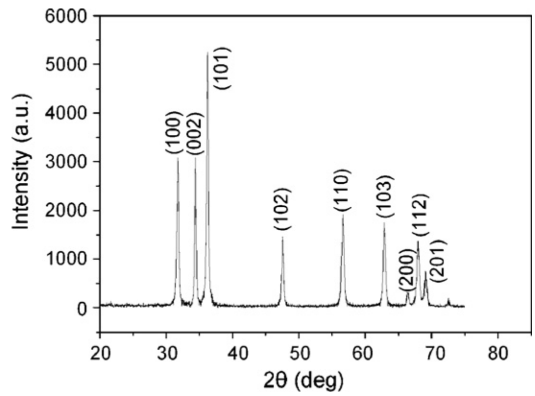

Fig. 1. An XRD pattern of ZnO nanorods.

group: $P6_3mc$ (186)) and are in agreement with the JCPDS card of ZnO (JCPDS 36-1451). No characteristic peaks of impurities, such as $Zn(CH_3COO)_2 \cdot 2H_2O$ and other precursor compounds, are observed. Then the results show that the product is single phase hexagonal ZnO. Fig. 2a is a low-magnification SEM image of the ZnO nanorods, showing the uniformity of the microstructure. Fig. 2b is a high-magnification SEM image of the ZnO nanorods. It is obvious that the product consists of a large quantity of straight and smooth nanorods. The average diameter of the nanorods was about 50 nm, and their average length was about 0.5 μm. It is also seen that most of the nanorods are highly oriented.

The N_2 adsorption/desorption isotherms of the ZnO product are shown in Fig. 3, which displays the nitrogen sorption of type IV isotherm with a hysteresis loop of H_1 type. The specific surface area was 8.667 m^2/g, indicating that the ZnO nanorods have a fairly small surface to volume ratio.

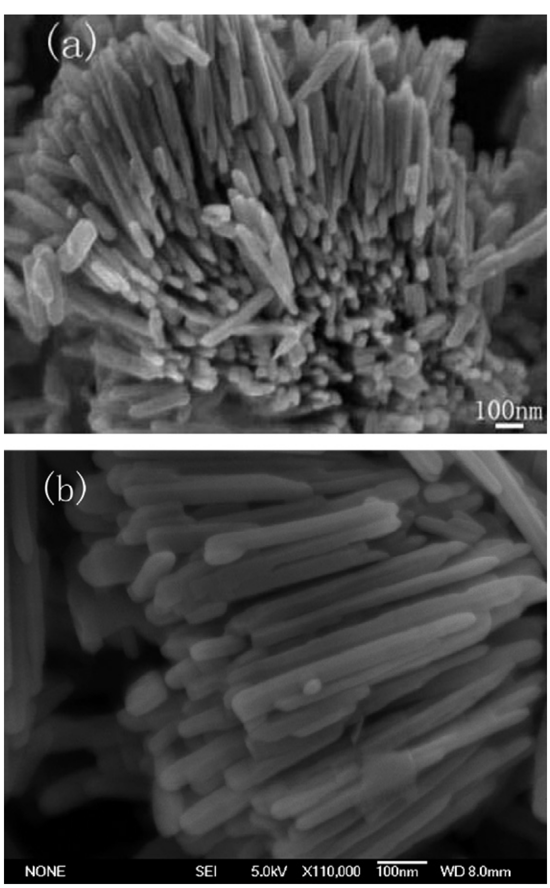

Fig. 2. (a) Low- and (b) high-magnification SEM images of ZnO nanorods.

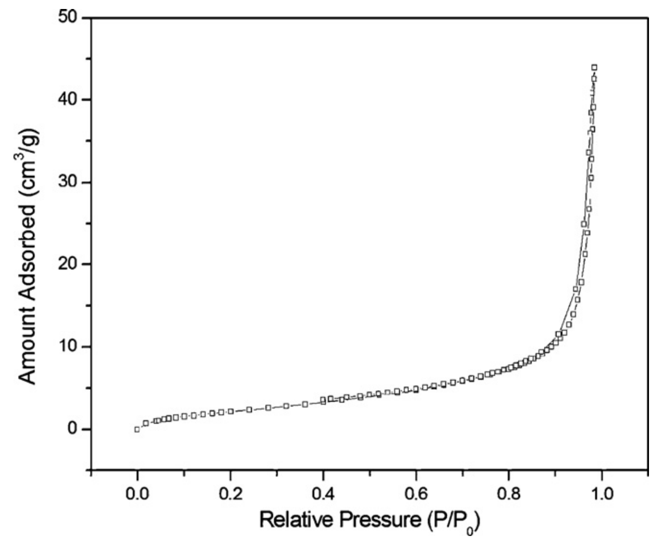

Fig. 3. N_2 adsorption/desorption isotherms of ZnO nanorods.

To investigate the ethanol sensing properties of the ZnO nanorods with a vertically aligned arrangement, a sensor was fabricated by a method similar to that described in previous papers [3,6]. During the measurement each sensor was connected in series with a standard resistor of 47 kΩ under a bias of 5 V (dc), and the voltage across the standard resistor was measured at a temperature of 300 °C and a relative humidity of ~50% (at 22 °C) to evaluate the resistance of the sensors. The sensor response (S) is defined as the ratio of the sensor resistance in air (R_a) to that in ethanol vapor (R_g), $S = R_a/R_g$.

The response versus time curves at different ethanol concentrations are shown in Fig. 4a. At each concentration, five cycles of measurement are given and the response in the later cycle decreases slightly compared with the preceding cycles. This is due to the leakage of ethanol, which occurs when the sensor is taken out from the test chamber, so the data in the first cycles are taken to represent the correct response. When exposed to 1 ppm ethanol, the sensor response is ~10. With increasing ethanol concentration, the response increases significantly. For ethanol vapor at levels of 1, 5, 10, 30, 50, and 100 ppm, the responses are about 10, 12, 16, 36, 60 and 100, respectively.

The sensor response versus ethanol concentration is shown in Fig. 4b. The sensor exhibits a nearly linear response to ethanol in the range of 1–50 ppm. Such favorable characteristics indicate that the present sensor is very suitable for the detection of ethanol vapor at low levels.

ZnO nanorod gas sensors respond to the change of the carrier concentration, which is usually induced by oxygen adsorption on the surface of the sensing materials [2]. The oxygen vacancy (V_O) in ZnO nanorods acts as an electron donor to provide electrons to the conduction band of ZnO and makes the ZnO nanorods be an n-type semiconductor [7]. When exposed to air, the surface of the ZnO nanorods will adsorb some oxygen molecules. The adsorbed oxygen will capture electrons from the conduction band of the ZnO nanorods to become oxygen ions (O^-, O^{2-}, or O_2^-), and O^- is believed to be dominant [8]. Consequently, depletion layers are formed in the surface area of the ZnO nanorods with an aligned arrangement, causing the carrier concentration to decrease, so that the resistance of ZnO nanorods in ambient air is higher than that

Table 1
Contrast of ethanol sensors based on 1D mental oxide nanostructures

Material	Size (nm)	Concentration (ppm)	Testing temperatures (°C)	Response	Ref.
ZnO nanowires	25 ± 5	100	300	32	[2]
ZnO nanorods	150	100	300	14.6	[3]
SnO_2 nanobelts	200 × 30	250	400	41.6	[4]
ZnO nanorods aligned	50	100	300	100	This work

in vacuum. When the ZnO nanorods are exposed to ethanol, the ethanol molecules will react with the adsorbed O^-, releasing the trapped electrons back to the conduction band, and then the carrier concentration of ZnO will increase. Accordingly, the resistance of the sensor decreases.

The response to ethanol of our sensor is much higher than those reported by other authors [2,3,6] (Table 1). To understand the high sensor response of our sensor, we speculate that the resistance (R) of the vertically aligned assembly of ZnO nanorods is mainly due to the bulk resistance of the nanorods (R_N) and the contact resistance (R_c), i.e. $R = R_N + R_c$. We first consider the surface depletion width is about several nanometers for ZnO in air. Because the diameter of each rod is as much as the depletion width, the surface depletion greatly affects the density of the carrier electrons in the rods. According to the neck resistance in the neck-grain boundary control model [9], we deduce the following resistance equation for the aligned assembly of ZnO nanorods:

$$R_N = \frac{L}{n\pi e[\mu_b n_b r_o{}^2 + n_d \mu_d (r_m{}^2 - r_o{}^2)]}$$

In this equation, e is the charge of electron, n is the number of ZnO nanorods, m_b is the electron mobility in the neutral layer, m_d is the electron mobility in the depleted layer, n_b is the free-electron density in the nanorods, n_d is the free-electron density in the depleted layer, r_o is the width of depletion layer, r_m is the radius of nanorods, and L is the length of nanorods. If we assume a ZnO nanorod as a resistance, the resistance of the ZnO nanorod assembly is the parallel resistance of a mass of single ZnO nanorod resistances. The total resistance is lower than the single ZnO nanorod resistance. The ZnO nanorod assembly has a structure of arrayed surface-depletion layers. The arrayed surface-depletion would be stronger than the common surface-depletion.

We next consider the contacts between vertically aligned nanorods. The contact resistance of the ZnO nanorods is controlled by the interrod barriers at the contacts. The barriers control the transport of electrons between the rods through the following equation [10]:

$$R_c = R_o \exp\left\{-\frac{e\Delta V_b}{k_B T}\right\}$$

ΔV_b is the change of the barrier potential defined as the potential in air minus that in ethanol, R_o is a factor including the resistance in air and other parameters, e is the charge of electron, k_B is the Boltzmann's constant, and T is the absolute temperature. Accordingly, the sensor response results partly from the barrier modulation at the contacts by ethanol vapor.

Lastly, we consider pores. Between the nanorods there are a lot of pores through which gas can percolate inside. We think that the response of the present material is better than others due to these pores which are absent in other cases. We measured the responses to different gases like H_2, CO, N_2 and CO_2 and found that the responses to the different gases were much lower than to ethanol; the response values were 1.31, 1.47, 0 and 0 to 10 ppm of H_2, CO, N_2 and CO_2 at 300 °C. This result shows that the adsorption of oxygen is responsible for the high resistance of the ZnO nanorods and substantiates that the structure of aligned arrangement is responsible for the highly efficient detection of ethanol.

Furthermore, the large surface area of the ZnO nanorods with an aligned arrangement provides more positions to adsorb oxygen molecules. A larger quantity of (V_O) induces higher adsorption sites for oxygen without lowering the expansion level of depletion layer for as-grown ZnO samples, which results in a further increase of the gas sensitivity of ZnO nanorods.

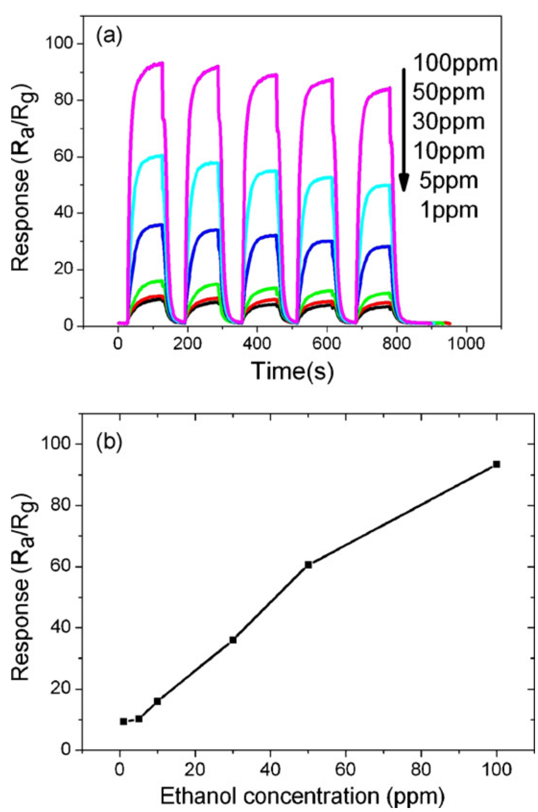

Fig. 4. (a) Sensitivity response vs. time for ethanol concentrations of 1–100 ppm at a work temperature of 300 °C. (b) Sensor response vs. ethanol concentration.

4. Conclusions

In summary, a high-performance ethanol sensor has been realized by using aligned ZnO nanorods. The sensor response is as high as 10 to 1 ppm ethanol. The high response is explained in terms of the arrayed surface depletion layers and the entire surface contact between the aligned nanorods. Our results demonstrate that an aligned assembly of ZnO nanorods is a very promising material for fabricating gas sensors.

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