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Micro-structure sensors based on ZnO microcrystals with contact-controlled ethanol sensing

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ZnO microcrystals are synthesized through a facile solution method and characterized by field-emission scanning electron microscopy, transmission electron microscopy, selected area electron diffraction and X-ray diffraction. The ethanol sensing properties of these microcrystals are investigated by spin-coating them on a silicon substrate with Pt electrodes to fabricate a micro-structure sensor. The sensitivity is up to 8 when the sensor is exposed to 50 ppm ethanol, and the response time and recovery time are 10 s and 20 s, respectively. A contact-controlled model is established to explain the sensing properties of the microcrystals, which provides another approach to realize high-performance gas sensors.

ZnO, ethanol, micro-structure sensors, semiconducting metal oxides

Gas sensors play an important role in environmental protecting, chemical process controlling and air quality monitoring as well as personal safety[1–5]. Many semiconducting metal oxides have been employed for this application due to their small size, low cost and high compatibility with microelectronic processing[6]. The gas-sensing mechanism of these semiconducting metal oxides mainly involves a change in electrical resistance caused by the adsorption of gas on the sensor surface. Therefore the sensing properties are easily influenced by the micro-structural features, such as the grain size, crystal structure, geometry and connectivity between particles[6].

ZnO is a semiconducting metal oxide which has received a great deal of attention from researchers and industry alike[7–10]. Since the discovery in 1962 that the electrical conductivity of ZnO could be dramatically changed by the presence of reactive gases in the air, there have been tremendous reports on the applications of ZnO as gas sensors[11–18]. Extensive studies have been put on improving the sensing performances based on the ZnO gas sensors, aiming at improving the sensitivity, response/recovery, selectivity, stability and feasibility for practical use[19,20].

In this paper, we present a simple and effective route for the synthesis of ZnO microcrystals with excellent ethanol sensing properties. The micro-structure sensor fabricated from these ZnO microcrystals shows high sensitivity, quick response and recovery to ethanol. The results demonstrate that ZnO microcrystals are very promising materials in fabricating ethanol sensors. Additionally, a contact-controlled model is established based on the nanocrystals, which provides another approach to realize high-performance gas sensors.

1 Experimental

1.1 Preparation and characterization of materials

ZnO microcrystals were synthesized through a facile so-

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lution method under mild conditions. All the chemicals (analytical grade reagents) were purchased from Beijing Chemicals Co. Ltd. and used as received without further purification. The deionized water with a resistivity of 18.0 MΩ/cm was used in all experiments. In a typical synthesis process, 100 mL of an aqueous solution of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and 100 mL of a hexamethylenetetramine ($(CH_2)_6N_4$, HMT) aqueous solution of equal concentration (0.1 $mol{\cdot}L^{-1}$) were mixed together and kept under mild magnetic stirring for 5 min. Then the solution was transferred into a 500 mL flask and heated at 90℃ for 2 h with refluxing. Subsequently, the resulting white products were centrifuged, washed with deionized water and ethanol, and dried at 60℃ in air for further characterization.

Field emission scanning electron microscopy (FESEM) images were performed on a JEOL JEM-6700F microscope operating at 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. X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å).

1.2 Sensor fabrication

Micro-structure sensor was fabricated on a silicon-based substrate with Pt electrodes and a Pt heater. The fabrication of the sensor was achieved according to the following steps: (i) growth SiO_2 (thickness of 3000 Å) on the Si-substrate as insulating layer, (ii) sputtering titanium (thickness of 450 Å) as an adhesive layer, (iii) sputtering platinum (thickness of 1800 Å) as metal electrodes, (iv) mask patterns transfer to the Si wafer by photolithography, (v) etching the two layer metals (Ti and Pt), (vi) removing the photoresist, (vii) finally spin-coating ZnO microcrystals (thickness of 100 μm) on the substrates. The dimension of the sensor area was about 2.0 mm × 0.5 mm, and the sensing film area was about 0.6 mm × 0.5 mm. The width of the signal electrodes and heater was 50 μm, and the distance between the adjacent Pt strips was 25 μm. The cross-section, top-view and optical micrograph of the micro-structure gas sensor are shown in Figure 1(a), (b) and (c), respectively.

1.3 Gas sensing measurement

The as-fabricated sensor was put into several chambers with certain concentration of detecting gas to study the sensing properties. The heater, controlled by a heating voltage (V_H, DC), ensured the operating temperature of the sensor. To measure the electrical signal of the sensing film, a voltage of 6 V was applied to the signal electrode (V_S, DC). The electrical properties of the sensors were measured by a CGS-1 intelligent test system (Beijing Elite Tech. Co., Ltd., China).

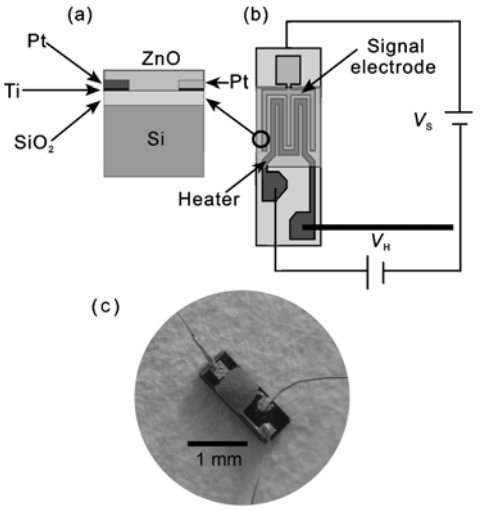

Figure 1 Cross-section (a), top-view (b) and optical micrograph (c) of the micro-structure gas sensor.

The sensitivity of the gas sensors in this paper is defined as $R = R_a/R_g$, where R_a is the baseline resistance of the sensing film in pure air (without access to a target gas) and R_g represents the resistance in a target gas environment. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time in the case of adsorption or the recovery time in the case of desorption.

2 Results and discussion

The morphology of the ZnO microcrystals is characterized by FESEM and TEM as shown in Figure 2. Figure 2(a) shows a typical image of the products, indicating the structured ZnO composed of two hexagonal prisms with the length and diameter of 3.5—5.4 μm and 1.3—1.8 μm, respectively. It can be obviously seen that smaller columns, with lengths of 200—400 nm and diameters of 200—800 nm, grow on the center and edge of end faces of the dumbbells. Further morphology characterization of the ZnO sample is performed on a transmission electron microscope as shown in Figure 2(b), which agrees with the FESEM results. The inset

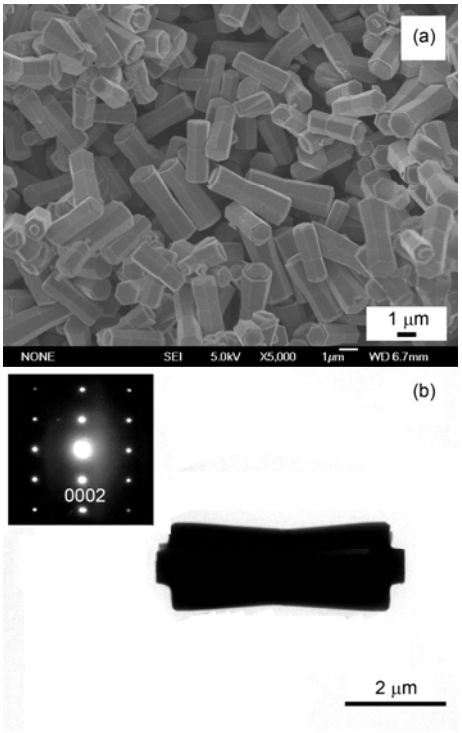

Figure 2 FESEM image (a), TEM image (b) and SAED pattern (inset) of the ZnO microcrystals.

SAED pattern indicates that the dumbbells possess a single-crystal hexagonal structure and grow along the [0001] direction.

The structure of the as-prepared ZnO was characterized by XRD as shown in Figure 3. All the diffraction peaks can be indexed as hexagonal ZnO with lattice constants of 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.

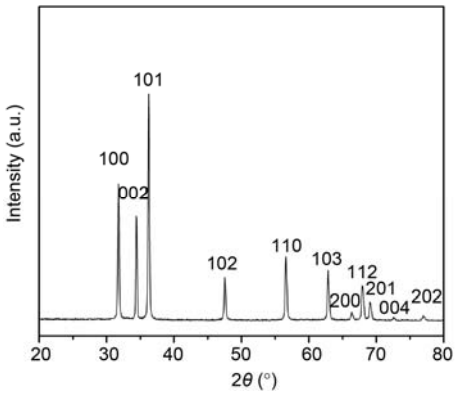

Figure 3 XRD pattern of the ZnO microcrystals.

Gas sensing experiments are performed at different operating temperatures to find the optimum operating condition. Figure 4 shows the relationship between the operating temperature and the sensitivity to 50 ppm ethanol. The sensitivity increases and reaches its maximum at 260℃, and then decreased rapidly with the increasing temperature. This behavior is mainly because of the influence of operating temperature on the activation of absorbed oxygen species on the surface of ZnO film[6]. At a relatively low temperature the activation of absorbed oxygen species is low and the sensor response is consequently very small. If the temperature increases too much, the progressive desorption of the previously adsorbed oxygen species occurs and the sensor signal decreases. Accordingly, 260℃ is believed to be the optimum operating temperature for the detection of ethanol, which is applied in all the investigations hereinafter.

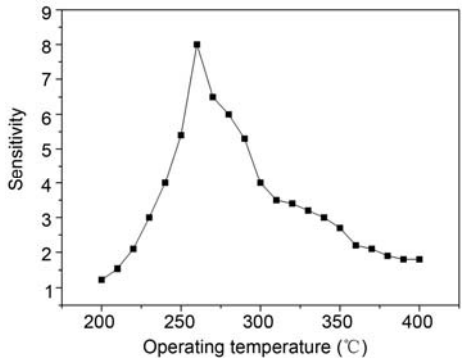

Figure 4 The sensor sensitivity to 50 ppm ethanol at different operating temperatures.

The response and recovery characteristics of the sensor to 50 ppm ethanol at 260℃ are shown in Figure 5. The sensor exhibits quick response and recovery to ethanol, and the electrical signal increases abruptly in 10 s when the sensor is exposed to ethanol. About 10 s later, the sensor is placed in air ambient again, and the electrical signal decreases to the original value in 20 s. Thus the response and recovery time are 10 s and 20 s, respectively.

Figure 6 shows the sensitivity of the sensor versus ethanol concentration at 260℃, and the insert is the calibration curve in the range of 1—300 ppm. The sensitivity rapidly increases by increasing the ethanol concentration below 300 ppm. Above 300 ppm, the sensitivity slowly increases by increasing the ethanol concentration, which indicates that the sensor becomes more or less saturated. Finally the sensor reaches saturation at about 3000 ppm. In fact, the sensitivity of the semicon-

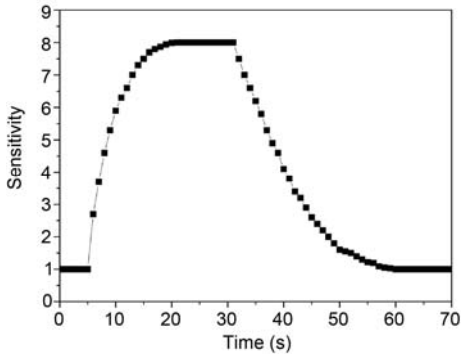

Figure 5 Response and recovery characteristics of the ZnO microcrystal sensor to 50 ppm ethanol at 260℃.

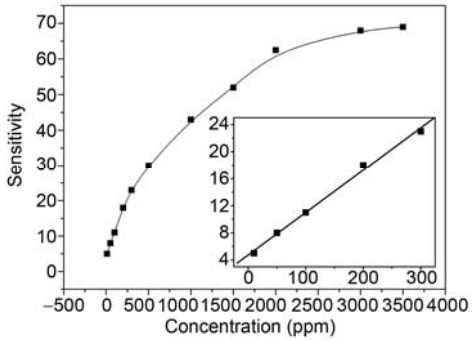

Figure 6 The sensitivity of the ZnO microcrystal sensor vs. ethanol concentration. The insert is the calibration curve in the range of 1−300 ppm.

ducting oxide gas sensor can usually be empirically represented as $S_g=AP_g^{\beta}$, where P_g is the target gas partial pressure, which is in direct proportion to its concentration, and the sensitivity is characterized by the prefactor A and exponent β. β may have some rational fraction value (usually 1 or 1/2), depending on the charge of the surface species and the stoichiometry of the elementary reactions on the surface[21–25]. As shown in Figure 6, when the ethanol concentration is in the range of 1−300 ppm, β is found to be 1, which confirms that the ZnO microcrystals can be used as a promising material for gas sensors.

Figure 7 shows the sensitivity of ZnO microcrystal sensor to 100 ppm different gases at 260℃. The results imply that the sensor is less sensitive to NH_3, and totally insensitive to H_2, CH_4, CO, C_2H_2 and Cl_2. Thus the sensor exhibits prominently and highly selective, and can be put into various practical applications.

A possible qualitative mechanism to explain the gas sensing properties of ZnO microcrystal sensor is proposed hereafter[26]. Normally, the O_2 molecules, which

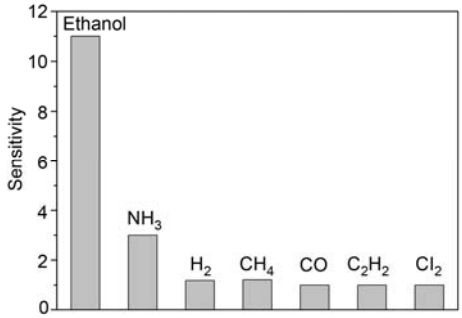

Figure 7 The sensitivity of ZnO microcrystal sensor to 100 ppm different gases.

are chemisorbed and dissociated on the surface of semiconductor oxides, can generate oxygen species. These oxygen species lead to a decrease in the conductance of the sensing layer, resulting in a high resistance of the sensor. When the sensor is exposed to a reducing gas such as ethanol, the reducing gas may react with the adsorbed oxygen molecule and increase the conductance of the sensing film, thereby the sensor response can be easily found by comparing the resistance of the sensing layer in air and the target gas. The present sensor has the advantages of high sensitivity, quick response and recovery. In order to illustrate its high-performance sensing characteristics, a contact-controlled sensing is proposed based on the morphology of ZnO microcrystals. We think that many contacts are formed among the ZnO microcrystals, leading to the formation of many junctions in the sensing film. The surface depletion width is about several nanometers for ZnO in air[24]. Because the diameter of ZnO microcrystals is much larger than the depletion width, surface depletion does not greatly affect the density and mobility of the electrons in the microcrystals but does significantly modify the potential barrier of the contacts between the microcrystals. Comparing with many semiconductor metal oxide sensors, more effective contacts will form and most of them in the sensing film contribute to the sensing, thus the modulation in carrier concentration of the contacts between ZnO microcrystals becomes lager and a higher sensitivity can be realized.

3 Conclusions

ZnO microcrystals have been synthesized through a facile solution method and characterized by FESEM, TEM and XRD. The micro-structure sensor fabricated from

these ZnO microcrystals exhibits high sensitivity and quick response-recovery to ethanol at 260℃. A contact-controlled model is established to explain the sensing properties of our microcrystals. Our results demonstrate the potential application of ZnO microcrystals for fabricating high-performance gas sensors.

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