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High performance of 1-D ZnO microwire with curve-side hexagon as ethanol gas sensor

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Abstract ZnO microwires of two different cross-sectional profiles were synthesized by chemical vapor deposition, and their morphologies were characterized by scanning electron microscopy. Their cross-sectional hexagonal profile could be tuned from straight to curved sides, by regulating the ZnO:graphite powder ratio used during synthesis. The ZnO microwires had hexagonal profiles with curved sides at a higher graphite ratio, and hexagonal profiles with straight sides at a lower graphite ratio. The higher graphite ratio was speculated to lower the growth rate from center to hexagonal sides, relative to the corners. The ZnO microwires were fabricated into gas sensors, and their sensing characteristics towards ethanol gas were investigated. The sensor based on a ZnO microwire with curved sides exhibited superior ethanol sensing performance than that based on a microwire with straight sides, which was attributed to the higher surface-to-volume ratio of the curved-side microwire. The sensor based on a ZnO microwire with curved sides was stable, and exhibited rapid response and recovery times. The straight-forward and economical fabrication of the gas sensor at room temperature makes it attractive for practical application.

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1 Introduction

Air pollution from gases such as NO_2, CO, NH_3, and H_2S is an important factor in global warming, climate change, and human illness [1–3]. High-performance gas sensors that accurately detect and monitor such gases are therefore of interest to protect humans from exposure to hazardous agents, and to improve the living environment and prevent environmental disasters. Small, compact, economical gas sensors with low power consumptions have been reported [4–6].

Various sensors based on metal oxide semiconductors, such as ZnO, SnO_2, and TiO_2, have recently been developed [2, 4, 7]. ZnO-based gas sensors can detect various gases and volatile compounds such as ethanol, CO, CO_2, CH_4, H_2, H_2S, NH_3, NO, NO_2, O_2, SO_2, and acetone, as well as humidity. Their sensitivity to different gases depends on their surface state and morphology [3, 5, 6, 8, 9]. Hierarchical micro- and nanostructures have attracted interest, because of their high sensitivity and reliability at room temperature (RT) [10–14]. ZnO microwires have been applied in gas sensors, because of their high chemical and thermal stability, and reasonable sensitivity to different gases [15–19].

Fabricating a sensitive low-power-consumption gas sensor without requiring heating will promote their application. In the current study, ZnO microwires with curved sides (ZnO CMWs) are prepared and applied in an ethanol gas sensor. The hexagonal cross-sectional morphology of the ZnO

CMWs exhibits curved sides, which results from the different ZnO:graphite powder ratio used during synthesis. The ZnO CMW-based sensor can potentially be economically produced on a large scale by chemical vapor deposition (CVD). It can sensitively detect ethanol gas at RT without heating, and is more efficient and sensitive than the sensor based on typical hexagonal ZnO microwires (ZnO HMW).

2 Experiment

2.1 Preparation of ZnO CMWs

ZnO powder, graphite, anhydrous ethanol, anhydrous methanol, acetone, and methylbenzene were of analytical reagent grade (AR), and purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., P. R. China. ZnO microwires were synthesized by CVD at atmospheric pressure. ZnO powder (99.99 %) and graphite powder were mixed in 1:1 or 1:2 molar ratio, which was used as the growth source [20]. The source material was placed 3 cm from the end of a quartz-reacting tube (diameter 3 cm, length 40 cm), which was placed in the center of a horizontal tube furnace. A N_2 flow of 70 standard cubic centimeters per minute (sccm) was introduced into the furnace. The furnace was heated to 550 °C, and 90 sccm oxygen gas was introduced. The temperature at the reactant region was kept at 950 °C for 90 min, under this mixed gas flow. ZnO microwires formed at one end of the quartz tube. The furnace was cooled to RT under a N_2 flow, and the ZnO microwires were then removed from the furnace and characterized by scanning electron microscopy (SEM) (JEOL-6360LV).

2.2 Preparation of ethanol gas sensor

A single ZnO HMW was fixed on a glass board, by spotting its two ends with silver paste and connecting them with metal wires. The fixed ZnO HMW was heated in an oven at 120 °C for 2 h. The ZnO CMW-based sensor was fabricated similarly using a ZnO CMW. A Keithley 4200 semiconductor characterization system was used to check the connection between the ZnO microwire and metal wire, and to investigate the sensitivity of the device to ethanol gas. Tests were conducted at RT under natural lighting, at a bias voltage of 5 V.

To test the sensing of the device, a 1-L sealed glass chamber containing a small hole was made, through which the probe could be inserted into and extracted. The experimental setup is shown in Fig. 1. Sensing performance (S) was determined by the sensors current change upon exposure to ethanol gas, according to:

$$S = \left(\left(I_{air} - I_{gas}\right)/I_{air}\right) \times 100\,\%,$$

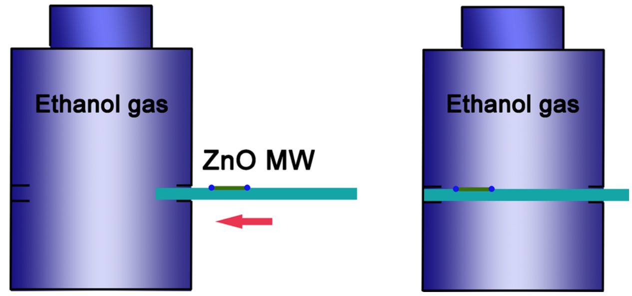

Fig. 1 Schematic diagram of measurement setup

where I_{air} and I_{gas} are the current measured in air and steady-state current measured in ethanol gas at the same bias voltage, respectively. The recovery time (τ) is defined as the time required for the sensor to reach 90 % of the minimum current change after exposure to a given gas. A certain amount of liquid ethanol was injected into the sealed chamber, using a syringe with a minimum scale of 0.01 mL. The corresponding ethanol gas concentration was calculated by the ratio of the mass of injected ethanol (mg) to the chamber volume (L).

3 Results and discussion

3.1 Structure and morphology

Figure 2a–d shows SEM images of the two ZnO microwires. Figure 2a shows a high magnification SEM image of a ZnO HMW, with a hexagonal structure, smooth surface, and diameter of ~30 μm. Figure 2b shows that its cross-section was that of a straight-sided hexagon, similar to previous reports [18]. Figure 2c shows a high magnification SEM image of a ZnO CMW, which was also hexagonal but with curved sides differing from the ZnO HMW and previous reports. The average diameter of the ZnO CMW was also ~30 μm. Figure 2d shows that its cross-section was curved. The ZnO CMWs could only be obtained by CVD using a source powder containing the 1:2 ZnO:graphite powder ratio. Qiu et al. [20], Leprince-Wang et al. [21], and d'Abbadie et al. [22] reported that rapid nucleation leads to the nonlinear growth of ZnO nuclei. ZnO microwires reportedly rapidly nucleate, in the presence of high graphite concentrations [23]. We estimated that the ZnO nuclei were subjected to nonlinear growth at high graphite powder ratio. The higher graphite ratio may have resulted in a lower growth rate from center to each side relative to each corner, yielding hexagonal microwires with curved sides. A more detailed understanding of the mechanism requires further study.

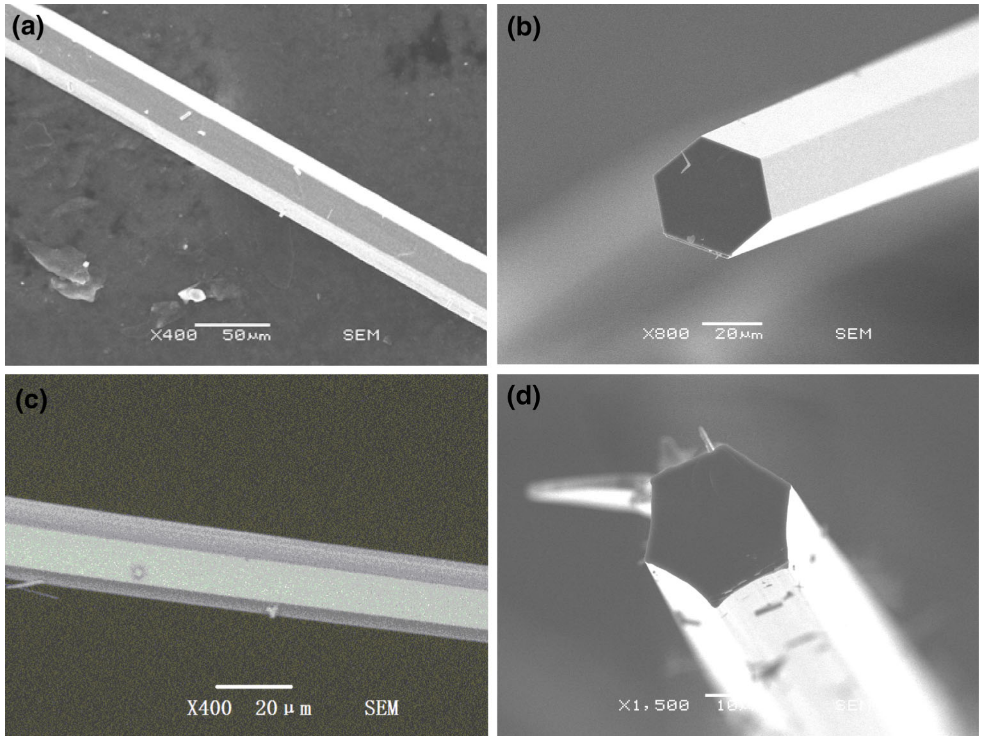

Fig. 2 High-magnification SEM images of a **a** ZnO HMW and **b** its cross-section, and a **c** ZnO CMW and **d** its cross-section

3.2 Ethanol gas sensing performance

Figure 3 shows the responses of sensors based on a ZnO CMW and ZnO HMW to ethanol gas. The current rapidly decreased when each sensor was exposed to ethanol gas. The current largely returned to its initial value upon exposure to air. Stability is an important property for sensors. The responses of the two sensors indicated their good stability and reproducibility over repetitive tests. The sensor based on the ZnO CMW exhibited a higher current in air and lower current in ethanol gas, than those for the ZnO HMW-based sensor at the same ethanol concentration.

Figure 4 shows the responses of the two sensors to different concentrations of ethanol gas. Sensitivity is another important property of sensors. Both sensors exhibited differing sensitivities to different ethanol gas concentrations. Sensitivity was tested in ethanol gas concentrations of 40, 80, 120, and 200 ppm. Figure 5a shows that the sensor based on the ZnO CMW exhibited higher sensitivity than that based on the ZnO HMW. The recovery time of the former sensor was lower than that of the later at the same concentration, as shown in Fig. 5b. These results indicated that the ZnO CMW-based sensor was superior. At low ethanol gas concentration (40 ppm), its response and recovery time were

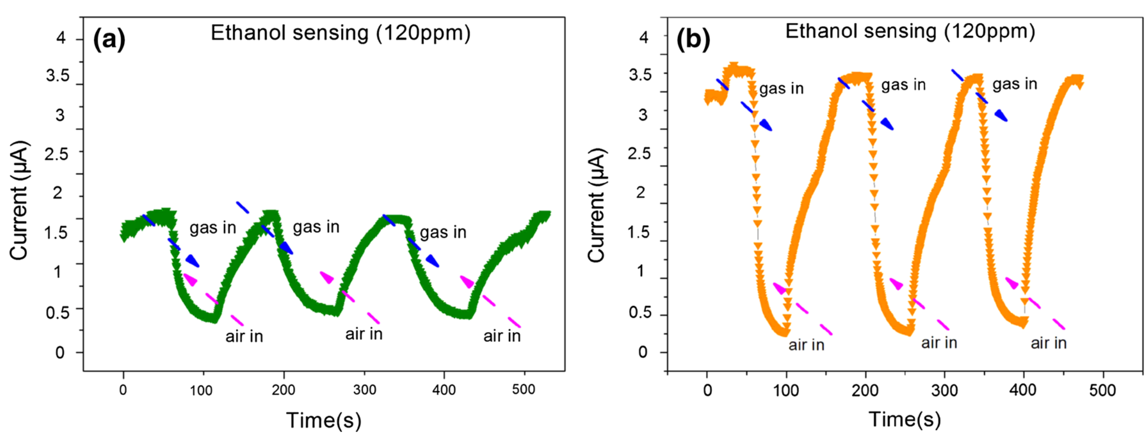

Fig. 3 Three response-recovery cycles to 120 ppm ethanol gas for sensors based on a **a** ZnO HMW and **b** ZnO CMW

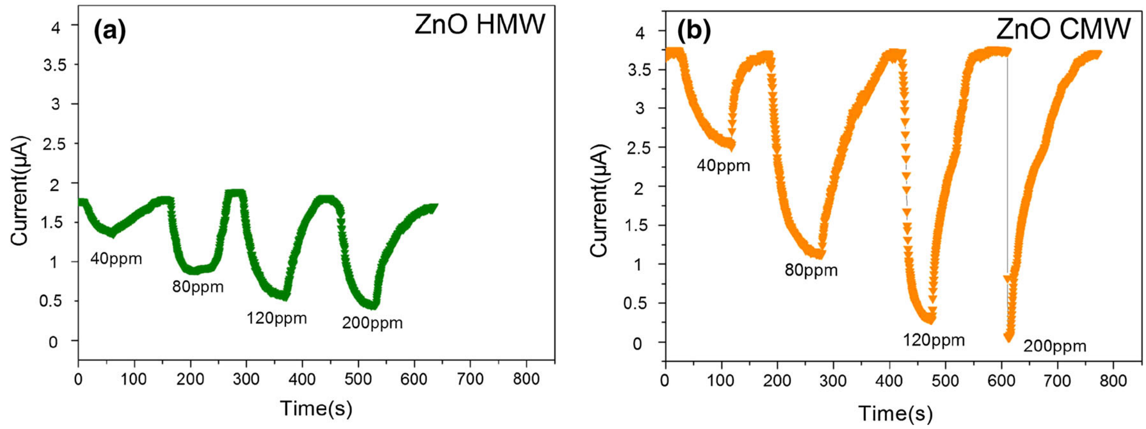

Fig. 4 Responses to different concentrations of ethanol gas by sensors based on a **a** ZnO HMW and **b** ZnO CMW

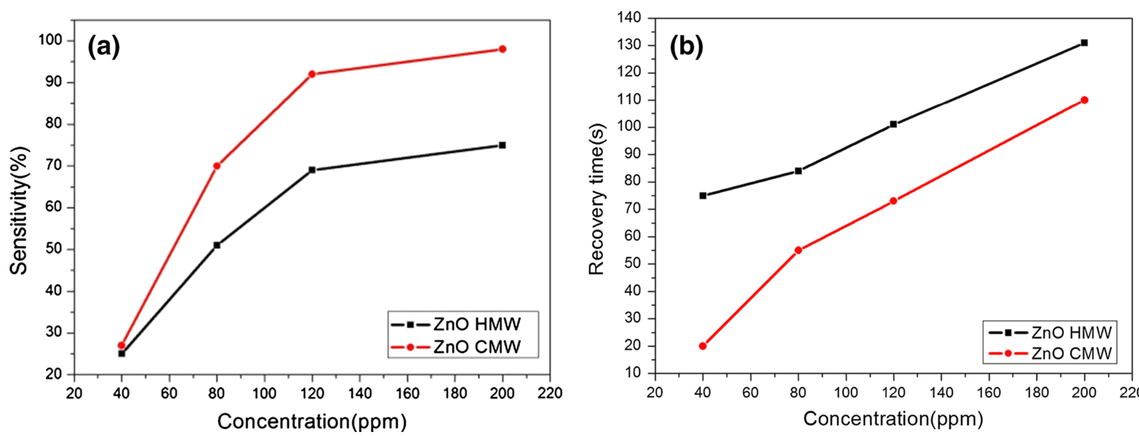

Fig. 5 **a** Sensitivity and **b** recovery time at various ethanol gas concentrations at RT for sensors based on the ZnO CMW and ZnO HMW

~60 and 20 s, respectively. At high concentration (200 ppm), its response and recovery times were ≤2 and ~110 s, respectively. The current sensor was compared to those reported by Li et al. [18] and Xu et al. [21], which also operated at RT. The current sensor was superior, both in response and recovery time and in simplicity of fabrication.

3.3 Ethanol gas sensing mechanism

Ethanol vapor was introduced into the test chamber, and interacted with adsorbed O_2 on the sensor surface. The growth of ZnO crystallites reportedly follows the mechanism [24–26]:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow \quad (1)$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (2)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (3)$$

During response (recovery), the chemisorption (desorption) of $Zn(OH)_2$ on the microwire surface captures (releases) many photon-generated carriers, causing a decrease (increase) in current. A large rapid change in current indicates favorable sensing behavior. The synthesis conditions of the two current ZnO microwire samples were the same, except the differing ZnO:graphite powder ratio. The sensing mechanism of semiconductor gas sensors is controlled by their surface at RT. The ZnO CMWs with curved sides had a higher surface-to-volume ratio than the straight-sided ZnO HMWs, so the ZnO CMW-based sensor exhibited better sensing properties.

4 Conclusions

ZnO microwires with different cross-sectional profiles were synthesized by CVD. The ZnO:graphite ratio of the source material greatly affected the ZnO microwire morphology. The sensor based on the ZnO microwire with curved sides exhibited superior ethanol gas response to that based on the straight-sided microwire, with higher sensitivity, faster response and recovery times and good repeatability. This resulted from the larger surface-to-volume ratio of the curved-side microwire. This study provides a straight-forward method for fabricating an ethanol gas sensor at RT.

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