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Ethanol sensor based on ZnO and Au-doped ZnO nanowires

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Abstract

ZnO nanowires and Au-doped ZnO nanowires were prepared by oxidation reaction. The oxidation was performed by heating zinc powder and a mixture of zinc and 1 wt% gold powder which was pressed into a tube shape at 600 °C for 24 h. The ethanol sensors based on ZnO nanowires were simply fabricated by applying silver electrode at each end of the tube and inserting a coil heater into the tube. The ethanol sensing properties of ZnO nanowires were observed from the resistance change under ethanol vapor atmosphere. By considering the sensitivity and response time, the optimum operating temperature of the ethanol sensor was found to be 240 °C. Also, it was found that the sensitivity of the sensor based on Au-doped ZnO nanowires exhibits higher value than that of the sensor based on undoped ZnO nanowires.

Keywords: A. Powder: solid state reaction; C. Electrical properties; D. ZnO; E. Sensors

1. Introduction

Zinc oxide (ZnO) is one of the metal oxide wide-band gap semiconductors that are commonly used for gas sensor applications [1–13]. Recently, nanostructures of oxide semiconductors have received great interest due to their very large surface-to-volume ratios. Usually, the gas sensing properties of oxide semiconductors strongly depend on the surface of these materials. Thus, gas sensors based on nanostructures are expected to be able to detect sensing gas molecules at lower concentration and exhibit better sensing properties than gas sensors based on bulk material or thin films [4,6,7]. ZnO nanostructure gas sensors have been widely investigated and are reported to show increases of sensitivity and the reductions of response time [1,4,8,12].

In addition, metal doping such as Au, Pt or Pd, etc. in oxide semiconductors is a typical method used to enhance sensing properties. The metal dopant acts as a catalyst to modify surface reactions of metal oxide semiconductors toward sensing gases. Several studies have been reported on the enhancement of sensitivity and stability of sensors using doping with metal catalysts [14–18]. For example, Wang et al. [14] have investigated Pd-doped ZnO nanotetrapods as an ammonia sensor and found that the sensitivity, response time and stability of Pd-doped ZnO sensor have been enhanced. Also, Tien et al. [17] have investigated Pt-coated ZnO nanorods and thin films for hydrogen sensing at room temperature. It was found that the nanorods showed higher responses to hydrogen than these of thin films.

Typically, the gas sensors based on ZnO nanostructures can be fabricated by various growth techniques [19,20]. One interesting technique is an oxidation reaction technique which is simple and low cost [13]. The main idea of this technique is based on an oxidation reaction at high temperature.

This work examined the ethanol sensing properties of the sensors based on the ZnO nanowires and the Au-doped ZnO nanowires which were fabricated by the oxidation reaction technique. The ethanol sensing properties of ZnO nanowires and Au-doped ZnO nanowires were compared.

2. Experimental procedure

The ZnO nanowires and the Au-doped ZnO nanowires were prepared by oxidation reaction. The oxidation was performed by heating zinc powder (purity 99.9%) and a mixture of zinc powder and 1 wt% gold powder. Prior to heating process, all mixed powders were pressed into a tube shape with a diameter

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about 3 mm and the pressed powders were covered with an alumina crucible to sinter in a horizontal furnace under air atmosphere at temperature 600 °C for 24 h. The ZnO nanowires and the Au-doped ZnO nanowires were characterized using field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS) to examine morphology and composition, respectively. The ethanol vapor sensors based on the ZnO nanowires and the Au-doped ZnO nanowires were simply fabricated by applying silver electrode at each end of the tube and inserting a coil heater into the tube. The ethanol sensing properties of ZnO nanowires were observed from the resistance change under ethanol vapor atmosphere, for ethanol concentrations of 100, 500, 1,000 and 2,000 ppm, and at operating temperatures of 180–280 °C. The response and recovery characteristics were monitored and recorded via an interfaced personal computer.

3. Results and discussion

The color of the tube of zinc powder and the mixture of zinc and gold powder changes from grey to white after sintered at temperature of 600 °C for 24 h. The general morphology of the resultant ZnO nanowires and Au-doped ZnO nanowires revealed by FE-SEM is shown in Fig. 1. The ZnO nanowires on the tube surface were observed as shown in Fig. 1(a and b) with magnifications of 3,000 and 10,000, respectively. The nanowires have diameters between 60 and 180 nm and lengths of about 5–10 μm. However, the morphology of the Au-doped ZnO nanowires as shown in Fig. 1(c and d) has a similar surface morphology to undoped ZnO. This suggests that the addition of 1 wt% Au dopant has no effect on the morphology of ZnO nanowire.

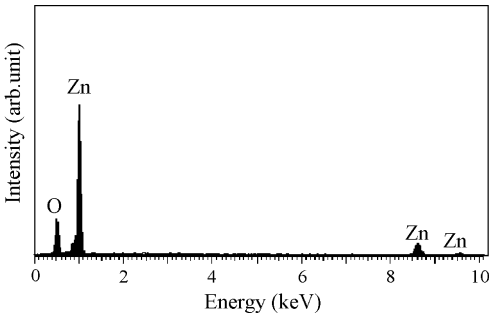

Fig. 2. EDS spectrum of Au-doped ZnO nanowires.

Fig. 2 shows EDS spectrum of the Au-doped ZnO nanowires. The peaks of the pattern correspond to Zn and O elements and the quantitative analysis of the EDS spectrum indicates that the atomic composition ratios of Zn:O is close to 1:1. The Au signal at around 2.1 keV which corresponds to M_α energy level could not be observed in the EDS spectrum. This maybe due to the doping concentration of 1 wt% is less than the detection limit of the EDS system.

The response and recovery curves of the ethanol sensors based on ZnO and Au-doped ZnO nanowires are shown in Fig. 3(a and b), respectively. The sensors were tested to ethanol concentration of 1,000 ppm at different operating temperatures of 220–280 °C. Clearly, the sensing characteristics of sensors depend on the operating temperatures. Also, it can be seen that the resistance of the sensors decrease under ethanol atmosphere. This can be explained by the adsorption of gas on the surface of ZnO [4,21,22]. In air atmosphere, oxygen molecules are adsorbed onto the surface of the ZnO sensor at high operating temperature to form O_2^- or O^{2-} ions by attracting electrons from the conduction band of the ZnO. Under ethanol atmosphere, the ethanol gas reacts with oxygen ion molecule on

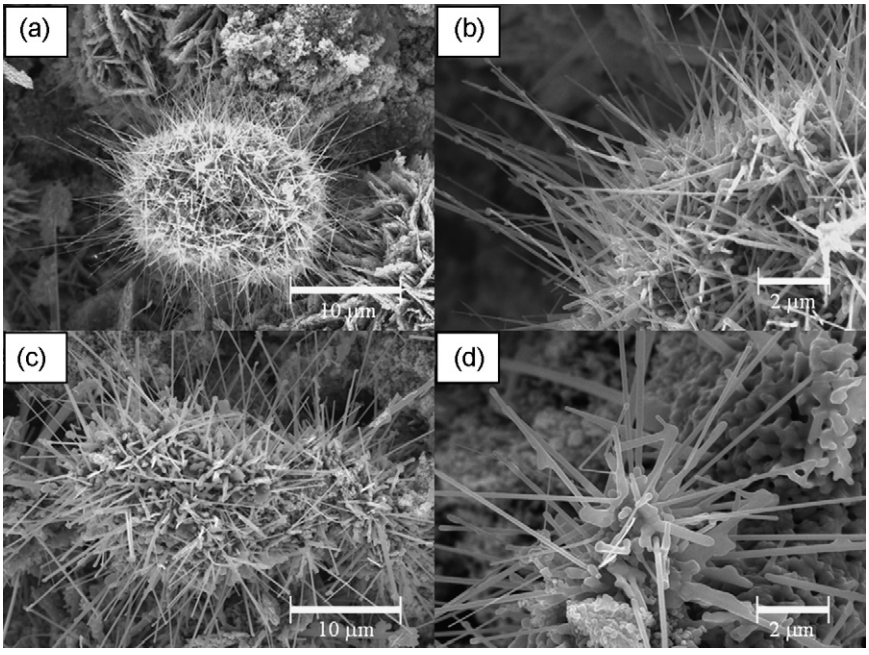

Fig. 1. FE-SEM image (a), (b) of ZnO nanowires and (c), (d) of Au-doped ZnO nanowires, which low and high magnification of 3000× and 10,000×, respectively.

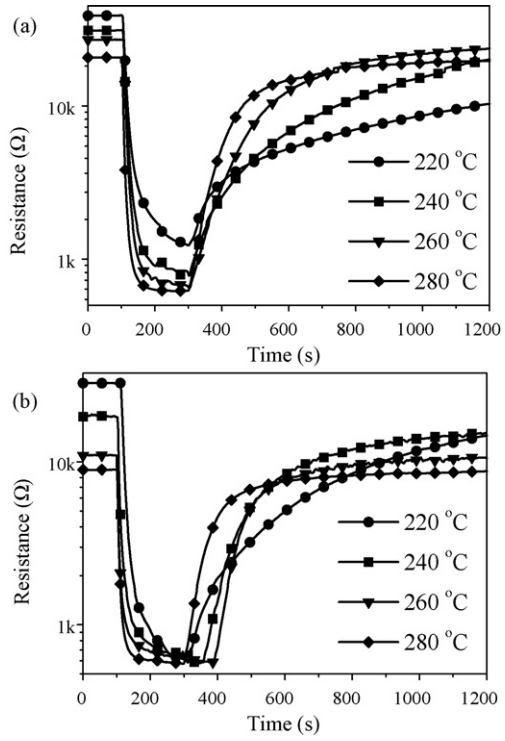

Fig. 3. (a and b) Response and recovery characteristics of ZnO nanowires sensors and Au-doped ZnO nanowires sensors, respectively, upon exposure to ethanol concentration of 1,000 ppm at difference operating temperature.

the surface and gives back electrons into the conduction band lowering the resistance of ZnO sensors. It should be noted that the resistance of Au-doped ZnO is slightly less than ZnO which could be explained by doping effect.

The sensitivity of the sensor in this work is defined as R_a/R_g where R_a is the electrical resistance of sensor in air and R_g is the electrical resistance of sensor in ethanol–air mixed gas. The sensitivity of ZnO-nanowire sensors and Au-doped ZnO-nanowire sensors as a function of operating temperature and as a function of ethanol vapor concentration is plotted in Figs. 4 and 5, respectively. It can be seen that the sensitivity of both ZnO-nanowire and Au-doped ZnO-nanowire sensors depends on the operating temperature at each ethanol concentration. Furthermore, the response time of both ZnO-nanowire and Au-doped

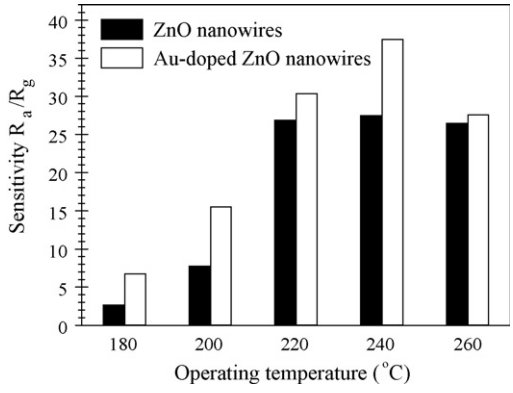

Fig. 4. Show the sensitivity of the ethanol vapor sensor of ZnO nanowires compare with Au-doped ZnO nanowires with ethanol vapor concentration of 1000 ppm.

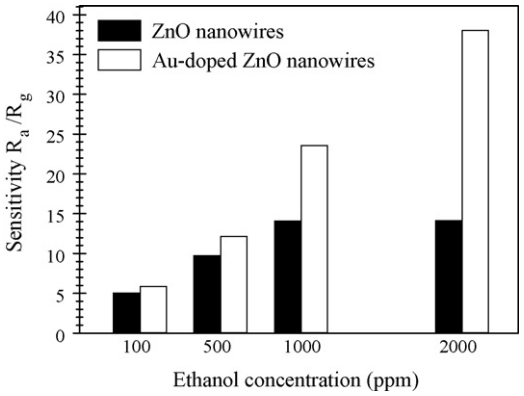

Fig. 5. Show the sensitivity of the ethanol vapor sensor of ZnO nanowires compare with Au-doped ZnO nanowires difference ethanol vapor concentration at operating temperature 240 °C.

ZnO-nanowire sensors is in the order of seconds. It turns out that the optimum operating temperature is at 240 °C with the highest sensitivity of 27 for ZnO-nanowire sensors and 37 for Au-doped ZnO-nanowire sensors. The highest sensitivity at an elevated temperature may be due to the enhanced reaction between the ethanol and the adsorbed oxygen at an optimum temperature. Also, it was found that the sensitivity of Au-doped ZnO-nanowire sensors is higher than undoped ZnO-nanowire sensors at entire operating temperature and ethanol concentration. This suggests that the sensors based on Au-doped ZnO nanowires have enhanced performance for use as ethanol sensors.

4. Conclusions

ZnO and Au-doped ZnO nanowires were prepared by an oxidation reaction, and by pressing into a tube shape at 600 °C for 24 h. Gas sensor based on the ZnO and Au-doped ZnO nanowires were then fabricated. By considering the sensitivity and response time, the optimum operating temperature of the ethanol sensor was found to be 240 °C. It was found that the sensitivity of the sensor based on Au-doped ZnO nanowires exhibits higher values than that of the sensor based on undoped ZnO nanowires. This suggests that the Au-doping on ZnO nanowires has enhanced the performance of the ethanol sensor.

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