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Ethanol sensing properties of CuO nanowires prepared by an oxidation reaction

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Abstract

The ethanol sensing properties of CuO nanowires prepared by oxidation reaction of copper plate have been examined. The characterization of CuO nanowires by FE-SEM, EDS, and TEM revealed diameters of 100–400 nm and a monoclinic structure with a growth direction along ⟨1 1 0⟩ direction. The ethanol sensing characteristics of CuO nanowires were studied at ethanol concentrations of 100–1000 ppm and working temperatures of 200–280 °C. An increase of resistance was observed under an ethanol vapor atmosphere due to the p-type semi-conducting property of CuO. It was found that the sensitivity, the response and the recovery time depended on the working temperatures and also ethanol concentration. The sensor exhibited the optimum sensitivity of 1.5 to ethanol vapor concentration of 1000 ppm at the working temperature of 240 °C with a response and recovery time of 110 and 120 s, respectively.

Keywords: B. Electron microscopy; E. Sensors

1. Introduction

Copper oxide (CuO) is a metal-oxide semiconductor with a narrow band gap of 1.2 eV and is one of the few metal-oxide semiconductors that exhibit p-type conductivity. Also, it is an important building block of most high-temperature superconductors. Recently, nanostructures of semiconductors have caught attention due to the unique property of having a huge surface-to-volume ratio which is expected to enhance the performance of the devices based on semiconductor nanostructures.

CuO nanostructures can be synthesized by various growth techniques such as thermal evaporation, thermal decomposition, sol–gel, and oxidation reaction [1–8]. An oxidation reaction technique is one of the more practical and simple ways of synthesis [8]. CuO can be used for a wide range of applications such as photoconductive, photothermal, catalysis and gas sensor [9–13]. For gas sensor application, it is interesting to investigate the effect of CuO nanostructure, which has a huge surface-to-volume ratio, on gas sensing properties. Thus, in this work, the ethanol sensing properties of CuO nanowires prepared by oxidation reaction are examined. The ethanol sensing properties were studied for various ethanol concentrations and working temperatures.

2. Experimental method

The commercial grade copper plate with thickness of 0.1 mm was cut and cleaned by alcohol in an ultrasonic bath for 2 min and dried at room temperature. The copper plate was loaded into a center of a tube furnace at 600 °C at normal atmosphere for oxidation reaction. The oxidation reaction [8] follows in Eqs. (1) and (2).

$$4Cu + O_2 \rightarrow 2Cu_2O \tag{1}$$

$$2Cu_2O + O_2 \rightarrow 4CuO \tag{2}$$

After oxidation reaction for 6 h, the copper plate was taken out of the furnace and immediately cooled down in air. The colour of the copper plate changed to black after oxidation reaction. It has been reported that the colour of CuO, Cu_2O and Cu are black, red and copper, respectively [8]. Therefore, the black product that

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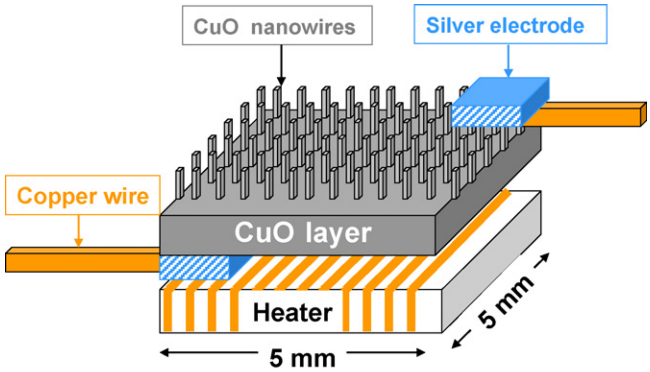

Fig. 1. Schematic diagram of a sensor fabricated from CuO nanowires and a layer of CuO.

was separated out from the copper plate after being taken from the furnace was CuO from appeared colour. The CuO was investigated by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F) for morphology, energy dispersive spectroscopy (EDS) for chemical composition, and transmission electron microscopy (TEM, JEOL JEM-2010 operating at 200 kV) for the crystal structure. The black product, CuO, was separated from the copper plate for fabrication of ethanol sensor as shown in the schematic diagram, Fig. 1. It should be noted that the black plate (black product) substance was composed of CuO layered with CuO nanowires. The black plate was cut into a square shape with dimensions of 5 mm × 5 mm before silver paint was applied at the diagonal corners of the black square to be silver electrodes, sized 1 mm × 1 mm. A heater for the ethanol sensor was made from a nickel-chromium coil and wound around an alumina plate, resistance 80 Ω, and placed beneath the CuO plate. Finally, copper wires were attached to the silver electrodes for resistance measurement to complete the ethanol sensor. The sensing properties were studied by observing the change of resistance in air and in ethanol ambiences of ethanol concentration of 100, 200, 500 and 1000 ppm, respectively, and at working temperatures of 200–280 °C. The response and the recovery characteristics were monitored and recorded via an interfaced personal computer.

3. Result and discussion

3.1. FE-SEM and TEM analysis

Fig. 2(a) and (b) shows FE-SEM top and cross-section view images, respectively of CuO plate (black product) separated

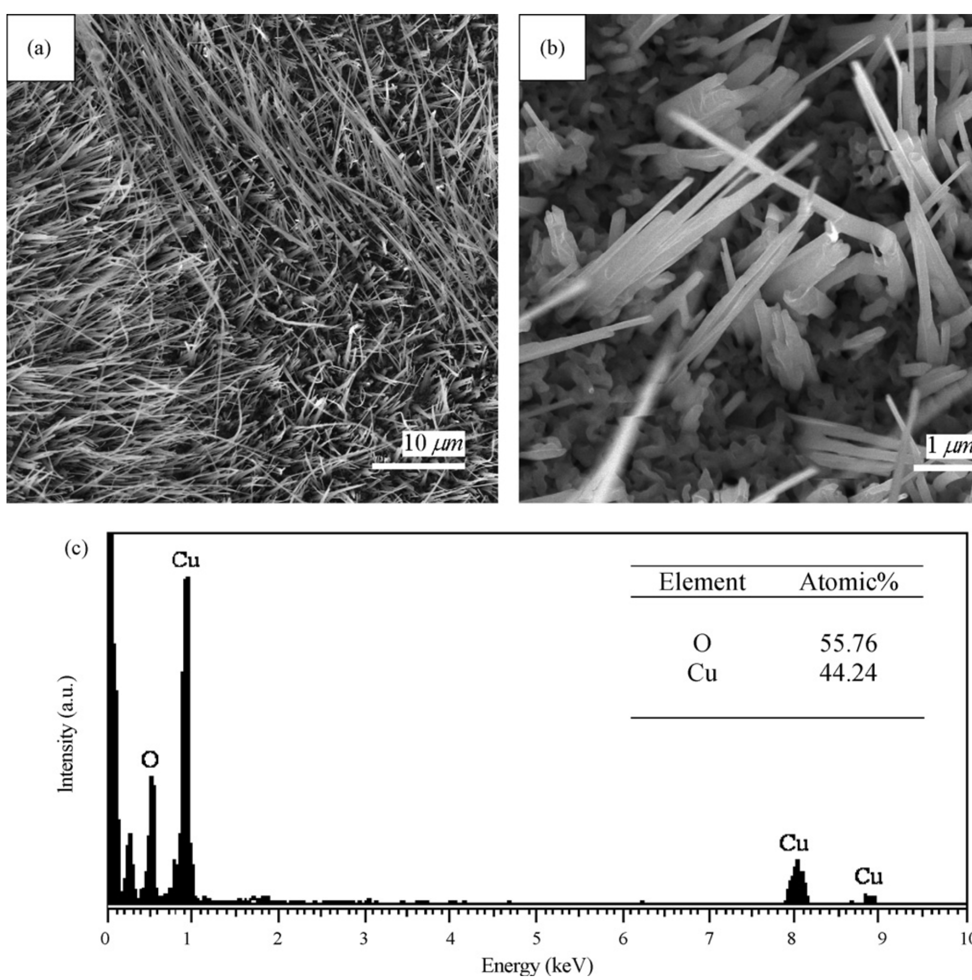

Fig. 2. (a) and (b) show FE-SEM images of top view and cross-section view, respectively, of the CuO plate (black product) separated out from the copper plate after oxidation reaction (c) EDS spectrum of the CuO plate.

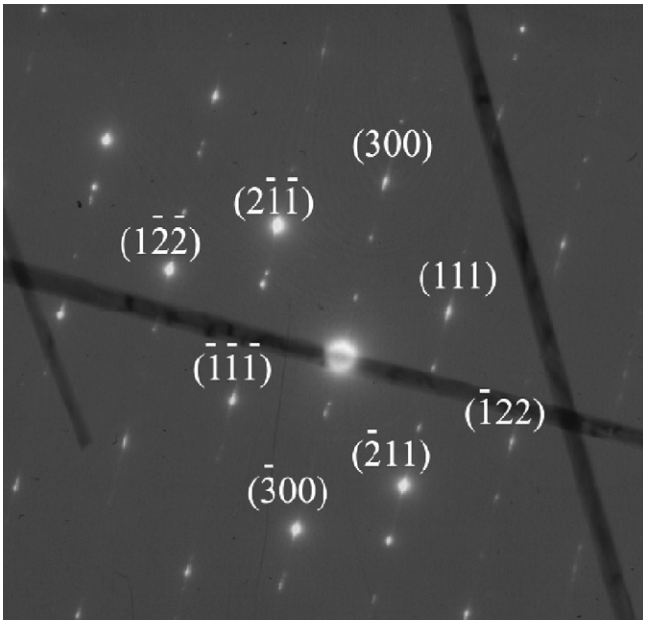

Fig. 3. A bright-field TEM image superimposed with the corresponding SADP of the CuO nanowires.

from the copper plate after oxidation reaction. The nanowires having a diameter of 100–400 nm and the length of around several micrometers were observed. The result of EDS shown in Fig. 2(c) confirms that the black product is CuO layered with CuO nanowire.

A bright-field TEM image of the CuO nanowires is shown in Fig. 3 superimposed with the corresponding SADP. Three wire-like structures with diameter about 100 nm can be observed. The SADP shows a spot pattern indicating the single-crystalline property of the CuO nanowire with monoclinic structure. Also, the spots show line-streaking along [3 0 0] corresponding to the shape factor of the nanowires on the reciprocal lattice node. Trace analysis results suggest that CuO has the growth direction along ⟨1 1 0⟩ direction.

Table 1
The ethanol sensing properties of CuO nanowires at an ethanol concentration of 1000 ppm, and a working temperature of 200–280 °C

Working temperature (°C)	Steady resistance (R_g, Ω)	Ethanol ambient resistance (R_a, Ω)	Sensitivity
200	5314	7749	1.4
220	4290	6302	1.5
240	3232	4690	1.5
260	2610	2925	1.1
280	2229	2428	1.1

3.2. Gas sensing properties

Fig. 4 shows the response and the recovery curves of ethanol sensors based on CuO nanowires being exposed to an ethanol concentration of 1000 ppm and working temperatures of 200–280°C. At the beginning, the measured resistance was steady in an ambient atmosphere. But when ethanol vapor was injected into the chamber, an increase of resistance was observed; and when ethanol vapor was removed, a decrease of resistance was observed. The increase of resistance under in ethanol vapor atmosphere is due to the p-type conductivity of CuO. It can be clearly seen from Fig. 4 that the characteristic of the sensor depends on the working temperature. It should be noted that the lower resistance of CuO nanowires at higher working temperatures is due to the common, semiconductor property of CuO.

The sensitivity, S_g, of the sensor is defined as R_g/R_a where, R_g is the electrical resistance of a sensor in ethanol-air mixed gases; and R_a is the electrical resistance of sensor in air. The sensitivity obtained for the CuO nanowire sensor at different working temperatures at the ethanol concentration of 1000 ppm is listed in Table 1. The highest sensitivity was obtained at the working temperature of 240 °C, suggesting this was the optimum working temperature. In addition, the response time and the recovery time also depended on the working temperature, in the range of 30–235 s and 60–245 s, respectively.

Fig. 5 shows the response and the recovery curves of ethanol sensors based on CuO nanowires when exposed to an ethanol

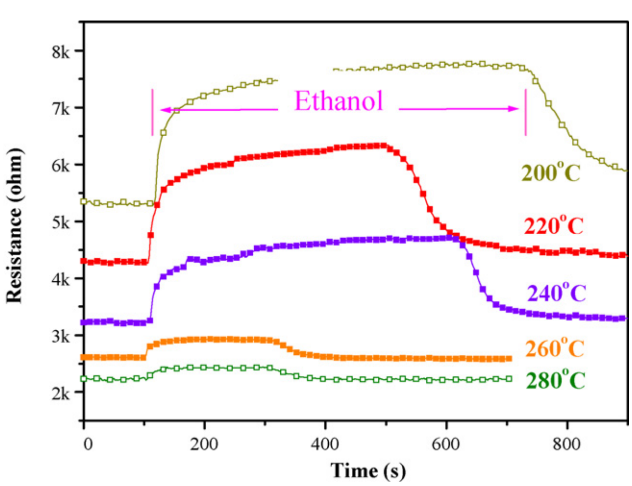

Fig. 4. The response and recovery curves of the CuO nanowires sensor at an ethanol concentration of 1000 ppm, working temperature of 200–280 °C.

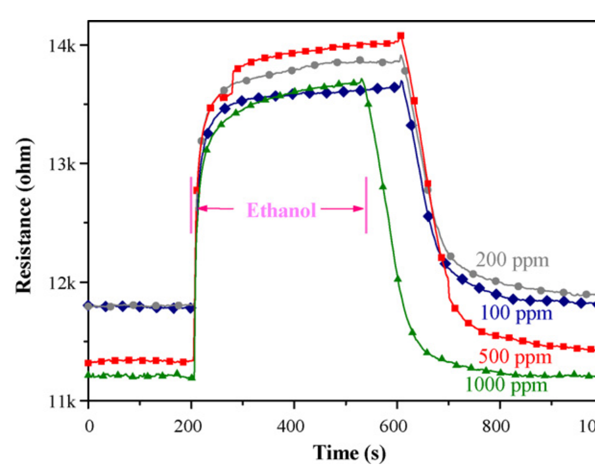

Fig. 5. The response and the recovery curves of the CuO nanowires sensor at ethanol concentration of 100–1000 ppm and working temperature of 240 °C.

concentration of 100–1000 ppm at the working temperature of 240 °C. It was found that the sensitivity only slightly depended on the ethanol concentration.

4. Conclusion

The ethanol sensors based on CuO nanowires were successfully fabricated. The CuO nanowires were prepared by an oxidation reaction of copper plate. From FE-SEM, EDS and TEM characterization, CuO nanowires exhibited diameters of 100–400 nm having a monoclinic structure with a growth along $\langle 1\ 1\ 0 \rangle$ direction. Moreover, the CuO nanowire sensor responded to ethanol vapor, exhibiting the optimum sensitivity of 1.5 to an ethanol vapor concentration of 1000 ppm with a working temperature of 240 °C, the response time of 110 s, and recovery time of 120 s. The CuO nanowires could be explored for gas sensor application.

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