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CuO nanowire gas sensors for air quality control in automotive cabin

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ABSTRACT

CuO nanowires (NWs) were grown by the thermal oxidation of Cu foil at 400 °C and gas sensors were fabricated by the deposition of a solution containing the CuO NWs. At 300–370 °C, the sensor resistance increased upon exposure to 30–100 ppm CO. This has been explained by the gas sensing characteristics of the p-type oxide semiconductor. In contrast, the sensor showed two opposite NO_2 sensing behaviors; the resistance decreased upon exposure to 30–100 ppm NO_2, but increased upon contact with ≤5 ppm NO_2. The increase in resistance upon contact with both reducing CO and a low concentration of oxidizing NO_2 gases provides a simple and novel sensing algorithm for air quality control in automotive cabins.

1. Introduction

Semiconductor gas sensors show a resistance change upon exposure to toxic and dangerous gases [1,2]. One-dimensional (1D) nanowires (NWs) with high surface area/volume ratio and less agglomerated configuration are advantageous to accomplish high gas sensitivity and rapid response speed [3]. So far, research has concentrated on improving the gas sensing performance of n-type semiconductor NWs, such as SnO_2 [4–9], ZnO [10–12], and In_2O_3 [13,14]. The corresponding gas sensing mechanisms are now well established.

By contrast, CuO NW gas sensors with p-type semiconducting behavior have scarcely been investigated, although a few studies have reported the gas sensing characteristics of CuO nanopowders [15,16], nanoribbons [17], and nanorods [18]. Many physico-chemical routes to prepare Cu_2O or CuO 1D nanostructures have been explored. Some examples include a polyol method [19], seed-mediated solution growth [20], a hydrothermal reaction [21], anodization [22], electrospinning [23], and thermal oxidation [24–30].

The CuO NWs prepared by thermal oxidation exhibit higher crystallinity and longer aspect ratios compared to those prepared via solution-based routes. Thus, in this study, the CuO NWs were grown by the thermal oxidation of Cu foil. Subsequently, the CO and NO_2 sensing characteristics of the CuO NWs were studied. Interesting results were found for the NO_2 sensing aspect. That is, the sensor resistance increased at high NO_2 concentrations (30–100 ppm) but decreased with decreasing NO_2 concentration down to ≤5 ppm. The main aim of the study was to suggest a new type of gas sensor for air quality control in automotive cabins. The sensor should undergo the same direction of resistance change upon exposure to both CO and low concentrations of NO_2.

2. Experimental

Pieces (10 mm × 10 mm × 0.25 mm) of commercial Cu foil (purity: 99.98%, Sigma–Aldrich Co., Ltd.) were washed in ethanol for 5 min by ultrasonic treatment, rinsed using deionized water, and then allowed to dry in air at 25 °C. The specimens were placed on an alumina substrate and heated to the desired thermal oxidation temperature (400–700 °C). The samples were held at the chosen temperature for 1–12 h. The heating rate was fixed at 50 °C/min.

The gas sensors were fabricated using CuO NWs that had been prepared by heat treatment at 400 °C for 12 h. The CuO NWs were separated from the Cu foil by 5 s of ultrasonic treatment of 5 sheets of the oxidized Cu foil contained within a solvent mixture (2 ml distilled water + 1 ml isopropyl alcohol). After removing the Cu foils, a droplet (40 μl) of the solution containing the CuO NWs was dropped onto the surface of an alumina substrate using a micro-pipette and then dried at 120 °C using a hot plate. This procedure was repeated 20 times. The alumina substrate had two Au electrodes (on its top surface) and a micro-heater (on its bottom surface).

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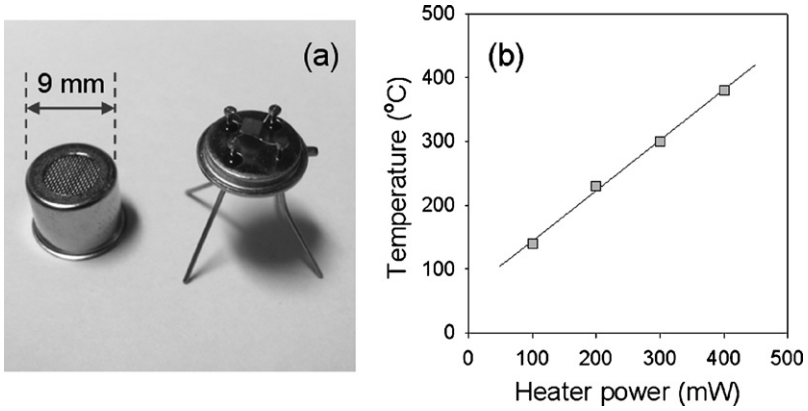

Fig. 1. (a) Sensor structure and (b) sensing temperature as a function of heater power.

The gas sensor was contained within a quartz tube for the high-temperature ambient atmosphere gas sensing measurements. Prior to the gas sensor measurements, the sensor within the quartz tube was heat treated at 600 °C for 2 h in order to remove any organic content. The temperature of the furnace was kept at 400 °C and the gas concentration was controlled by changing the mixing ratio of the parent gases (100 ppm CO, 5 ppm NO_2, and 100 ppm NO_2, all in air balance) and dry synthetic air. A flow-through technique with a constant flow rate of 500 cc/min was used. The gas response ($S = R_g/R_a$) was measured at 400 °C by comparing the resistance of the sensor in the target gases (R_g) and that in the high-purity air (R_a). The dc 2 probe resistance of the sensor was measured using an electrometer interfaced with a computer.

In order to measure the gas sensing characteristics of the sensor at a room temperature ambient atmosphere, the sensor element was packaged with a stainless steel mesh cap (Fig. 1(a)). The sensor temperature was controlled by modulating the power of the micro-heater underneath the alumina substrate. The temperature of the gas sensor at various heater powers was measured using an IR temperature sensor (Rayomatic 14814-2, Euroton IRtec Co., Ltd.). Varying the heater power between 100 and 400 mW resulted in the sensor temperature varying from 140 to 370 °C (Fig. 1(b)). Prior to the measurements, the sensor was heated at a power of 400 mW for 6 h to remove any organic content. The sensor was again contained within a quartz tube, this time held at room temperature. The same flow-through technique (as mentioned previously) was used during these gas sensing measurements.

The gas sensor packaged within the stainless steel cap was placed 50 cm from the tail pipe of a gasoline vehicle (SM5, Samsung Motors Co., Ltd., Korea) or a diesel sports utility vehicle (TUCSON, Hyundai Motors Co., Ltd., Korea). The detectability of the automotive pollutant gases was checked by measuring the sensor resistance by controlling the rpm of the engine under a no load condition. For reference, the NO_2 concentration behind the tail pipe of the diesel vehicle was also measured using a commercial multi-gas sensor (PGM-2000, RAE Systems, Inc., USA).

3. Results and discussion

3.1. Preparation of CuO nanowires

The images of the surfaces of the Cu foils oxidized at 400–700 °C for 1 h are shown in Fig. 2. Oxidation at 400 °C yielded the greatest

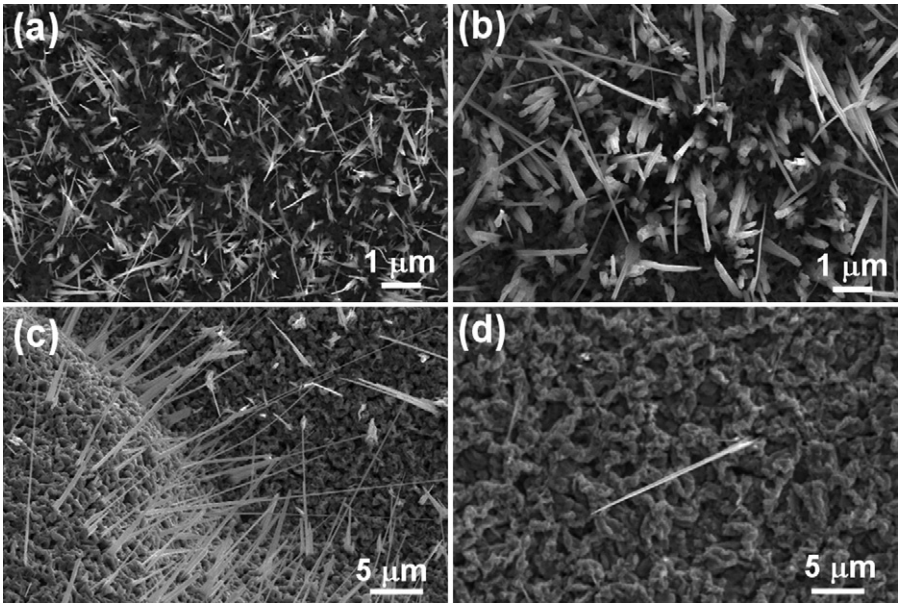

Fig. 2. Top-view SEM images of the CuO nanowires grown at: (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C, for 1 h by thermal oxidation.