Research Article

Acetone Gas Sensing Properties of a Multiple-Networked Fe_2O_3 -Functionalized CuO Nanorod Sensor

Sunghoon Park,¹ Hyejoon Kheel,¹ Gun-Joo Sun,¹ Taegyung Ko,¹
Wan In Lee,² and Chongmu Lee¹

¹Department of Materials Science and Engineering, Inha University, Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea

²Department of Chemistry, Inha University, Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea

Correspondence should be addressed to Chongmu Lee; cmlee@inha.ac.kr

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Fe_2O_3 -decorated CuO nanorods were prepared by Cu thermal oxidation followed by Fe_2O_3 decoration via a solvothermal route. The acetone gas sensing properties of multiple-networked pristine and Fe_2O_3 -decorated CuO nanorod sensors were examined. The optimal operating temperature of the sensors was found to be 240°C. The pristine and Fe_2O_3 -decorated CuO nanorod sensors showed responses of 586 and 1,090%, respectively, to 1,000 ppm of acetone at 240°C. The Fe_2O_3 -decorated CuO nanorod sensor also showed faster response and recovery than the latter sensor. The acetone gas sensing mechanism of the Fe_2O_3 -decorated CuO nanorod sensor is discussed in detail. The origin of the enhanced sensing performance of the multiple-networked Fe_2O_3 -decorated CuO nanorod sensor to acetone gas was explained by modulation of the potential barrier at the Fe_2O_3 -CuO interface, highly catalytic activity of Fe_2O_3 for acetone oxidation, and the creation of active adsorption sites by Fe_2O_3 nanoparticles.

1. Introduction

Cupric oxide (CuO) is a p-type semiconductor with a bandgap of 1.2–1.9 eV [1, 2]. Gas sensors based on CuO 1D nanostructures have attracted considerable attention because of their excellent sensitivity and selectivity in detecting a range of gases: humidity, HCOH, $\text{C}_2\text{H}_5\text{OH}$, NO_2 , H_2S , and CO [3]. A range of techniques such as wet chemical methods, room-temperature liquid-solid growth, low-temperature solid-phase processes, anodic aluminum oxide template-assisted electrodeposition, liquid-liquid methods, and catalyzed synthesis have been used to synthesize 1D CuO nanostructures [4], but these methods have difficulty in controlling the diameters and composition of nanowires and are unsuitable for mass production. In recent years, Cu thermal oxidation technique has been widely used for the synthesis of CuO 1D nanostructures [5].

On the other hand, enhancing their sensing performance and detection limit further still remains a challenge. Several techniques such as metal catalyst doping [6, 7], oxide nanoparticle-decoration, core-shell structure formation [8, 9], and

UV irradiation [10, 11] have been developed to improve the sensitivity, stability, and response speed of the 1D nanostructure-based sensors further. This paper reports the synthesis of $\alpha\text{-Fe}_2\text{O}_3$ -decorated CuO nanorods by a two-step process involving thermal oxidation and solvothermal methods and their enhanced acetone gas performance. The origin of the enhanced acetone gas sensing properties of the Fe_2O_3 -decorated CuO nanorod sensor is also discussed.

2. Experiments

The Fe_2O_3 -decorated CuO nanorods were synthesized by a two-step process involving direct heating of Cu sheets in air and Fe_2O_3 decoration via a solvothermal route. First, the CuO nanorods were synthesized in a quartz tube furnace by the thermal oxidation of a copper sheet at 500°C in air without a metal catalyst or supplying of any other gas. The thermal oxidation process was carried out for 1 h and the furnace was cooled to room temperature. Subsequently, the CuO nanorods were decorated with Fe_2O_3 nanoparticles by a

FIGURE 1: (a) XRD patterns of pristine and Fe_2O_3 nanoparticle-decorated CuO nanorods. (b) SEM image of Fe_2O_3 nanoparticle-decorated CuO nanorods. Inset, enlarged SEM image of a typical Fe_2O_3 nanoparticle-decorated CuO nanorod.

solvothermal method. 50 mM Fe_2O_3 precursor solution was prepared by dissolving iron chloride (FeCl_3) in 50 mM NaOH solution. 10 mL of the mixed solution was then ultrasonicated for 5 min to form a uniform solution and then rotated using a centrifuge at 5,000 rpm for 5 min to precipitate the Fe_2O_3 powders. The precipitated powders were collected by removing the liquid leaving the powders behind. The collected powders were rinsed in a 1:1 solution of isopropyl alcohol and distilled water to remove the impurities. The rinsing process was repeated five times. Subsequently, the Fe_2O_3 precursor solution was dropped onto the CuO nanorods on a substrate and the substrate was rotated at 2,000 rpm for 30 s for Fe_2O_3 decoration. After the spin-coating process, the Fe_2O_3 -decorated CuO nanorod sample was dried at 150°C for 1 min. This process was repeated for three times and then Fe_2O_3 -decorated CuO nanorod sample was annealed in air at 500°C for 1 h.

The structure and morphology of the collected nanorod samples were examined by glancing angle X-ray diffraction (XRD, Philips X'pert MRD) with Cu- K_α radiation ($\lambda = 0.1541$ nm) and scanning electron microscopy (SEM, Hitachi S-4200, 10 kV). The as-synthesized pristine and CuO nanoparticle-decorated Fe_2O_3 nanorods (50 mg) were dispersed ultrasonically in acetone. Suspensions of nanorods in acetone were spread over oxidized Si substrates with interdigitated Pt electrodes. A flow-through technique was used to measure the gas sensing properties in a tube furnace with a resistance heater. The pristine or Fe_2O_3 nanoparticle-decorated CuO nanorods were inserted in the chamber. Acetone gas diluted with dry synthetic air was injected into the quartz tube at a flow rate of $200\text{ cm}^3/\text{min}$ at room temperature. The electrical measurements were taken at 200°C under 40% RH by a voltamperometric method. The electrical

resistance of gas sensors was determined by measuring the electric current using a Keithley SourceMeter 2612 with a source voltage of 1 V. The detailed procedures for the sensing tests are described elsewhere [12].

3. Results and Discussion

3.1. Structure of the Fe_2O_3 Nanoparticle-Decorated CuO Nanorods. Figure 1(a) shows the XRD patterns of the pristine and Fe_2O_3 nanoparticle-decorated CuO nanorods. XRD showed that the pristine CuO nanorod sample comprises CuO and Cu_2O phases and that the Cu_2O phase was predominant over the CuO phase. The tall Cu reflection peak is not from the synthesized CuO nanorods but from the copper sheet used as a substrate for the synthesis of CuO nanorods. The Fe_2O_3 nanoparticle-decorated CuO nanorods were found to be a combination of crystalline Fe_2O_3 and CuO. The smaller reflection peaks for Fe_2O_3 compared to those for Cu_2O might be due to the smaller volume of Fe_2O_3 nanoparticles compared to that of the CuO nanorods. Figure 1(b) presents a SEM image of the Fe_2O_3 nanoparticle-decorated CuO nanorods synthesized in this study. The CuO nanorods were 20–60 nm in diameter and 5–10 μm in length. The diameter of the Fe_2O_3 nanoparticles ranged from 5 to 30 nm.

3.2. Sensing Performance of the Pristine and Fe_2O_3 Nanoparticle-Decorated CuO Nanorod Gas Sensors. Figures 2(a) and 2(b) present the acetone gas response transients of the pristine and Fe_2O_3 nanoparticle-decorated CuO nanorod gas sensors, respectively. The resistance showed good reversibility and reproducibility during the introduction and exhaust cycles of acetone gas. Both sensors responded to

FIGURE 2: Gas response transients of the (a) pristine and (b) Fe_2O_3 nanoparticle-decorated CuO nanorod gas sensors.

acetone gas slowly and recovered instantaneously. Figure 3(a) shows the responses of the two sensors to acetone gas as a function of acetone concentration. The response was defined as $(R_g/R_a) \times 100$ for acetone gas, where R_g and R_a are the electrical resistances of sensors in acetone gas and air, respectively. The responses of both samples to acetone gas tended to become stronger with increasing acetone gas concentration, but the Fe_2O_3 nanoparticle-decorated CuO nanorod sensor showed a higher increasing rate. The Fe_2O_3 nanoparticle-decorated CuO nanorod sensor exhibited almost twofold stronger response than the pristine CuO counterpart in an acetone concentration range of 50–1,000 ppm. Figures 3(b) and 3(c) present the response and recovery times of the pristine and Fe_2O_3 nanoparticle-decorated CuO nanorod gas sensors, respectively. The response and recovery times were defined as the times to reach 90% resistance change upon exposure to acetone and air, respectively. The Fe_2O_3 nanoparticle-decorated CuO nanorod sensor showed shorter response and recovery times than the pristine CuO counterpart at the same acetone concentration. The response and recovery times of the Fe_2O_3 nanoparticle-decorated CuO nanorod sensor at 1,000 ppm acetone were 64 s and 80 s, respectively. In contrast, the response and recovery times of the pristine CuO nanorod sensor at 1,000 ppm acetone were 149 s and 133 s, respectively.

The responses of the pristine CuO and Fe_2O_3 nanoparticle-decorated CuO nanorod sensors to 1,000 ppm of acetone gas as a function of operating temperature are shown in Figure 4. Both sensors showed the strongest response at 240°C , suggesting that the optimal operating temperature for the two sensors is 240°C . Based on these results, all other sensing tests in this study were carried out at 240°C . At low temperatures, upon exposure to oxygen, because of the inactive ionosorption of oxygen due to rare active adsorption sites at the CuO and Fe_2O_3 surfaces, inactive oxidation of acetone gas occurs, resulting in poor response. As the operating temperature increases, adsorption

of oxygen and acetone molecules by the sensor surface and acetone oxidation becomes more active, leading to enhanced response to acetone gas. However, further increases in temperature than 240°C will result in an increase in charge-carrier concentration and, thereby, a decrease in Debye length, leading to poor response again. Moreover, desorption of many of the species in the surface region might occur at temperatures higher than 240°C [13].

3.3. Sensing Mechanism of the Fe_2O_3 Nanoparticle-Decorated CuO Nanorod Gas Sensors. In the case of the pristine CuO nanorod gas sensor, upon exposure to air, the oxygen molecules in the atmosphere are adsorbed by the CuO nanorod surfaces and the adsorbed oxygen molecules are ionized to O_2^- , O^- , or O^{2-} depending on the sensor operating temperature and at the operating temperature of 240°C , O^- is formed [14] by releasing holes to the valence band of CuO as follows:

This reaction causes an increase in carrier concentration and formation of an accumulation layer, resulting in an increase in resistance. In this case, the accumulation plays a role of a conduction channel.

When the CuO nanorod surfaces are exposed to acetone gas, the width of the accumulation layer near the surface is decreased by the following reactions between CH_3COCH_3 and $\text{O}^-(\text{ad})$, resulting in an increase in resistance [2]:

Reactions (2) and (4) capture holes from the valence band of CuO, forming a depletion layer, leading to an increase in

FIGURE 3: (a) Responses, (b) response times, and (c) recovery times of the pristine and Fe₂O₃ nanoparticle-decorated CuO nanorod gas sensors as a function of the acetone concentration.

resistance. In this case, the entire nanorod except the depletion layer in its surface region acts as a conducting channel. Current flows along the axis of the nanorod. In other words, modulation of the accumulation and depletion layer width and thereby modulation of the conduction channel width occur in the sensor accompanying the adsorption of air and acetone gas. As a result of the change in conduction channel width the resistance changes and thereby the response of the sensor to acetone changes.

On the other hand, at the Fe₂O₃-CuO p-n junction, upon exposure to air, a depletion layer with a width of W_{D1} and an accumulation layer with a width of W_{A1} form on the Fe₂O₃ and CuO sides, respectively. In contrast, upon exposure to acetone gas, thin depletion layers form on both sides of Fe₂O₃ and CuO and the total width of the depletion layer is W_{D2} . If we compare the conduction channel width in a Fe₂O₃-decorated CuO nanorod with that in a pristine

CuO nanorod, the difference is quite small. Therefore, the enhanced sensing performance of the decorated sensor might not be mainly attributed to the difference in conduction channel width between the pristine and Fe₂O₃-decorated CuO nanorod sensor, even though the depletion layer formed on the Fe₂O₃ side in the Fe₂O₃ nanoparticle-decorated CuO nanorod sensor in air is slightly thicker than that in the pristine CuO nanorod sensor due to the existence of the accumulation layer on the CuO side.

The enhanced sensing properties of the decorated CuO nanorod sensor might be mainly due to the following several factors: (1) modulation of the potential barrier height at the CuO-Fe₂O₃ interface, (2) the high catalytic activity of Fe₂O₃ for the oxidation of acetone, and (3) creation of more active adsorption sites by Fe₂O₃ nanoparticles. First, one of the important differences between the pristine and Fe₂O₃ nanoparticle-decorated CuO nanorod sensor is the

FIGURE 4: Responses of pristine and Fe₂O₃ nanoparticle-decorated CuO nanorod gas sensors to 1000 ppm of acetone as a function of operation temperature.

FIGURE 5: Schematic diagrams showing the depletion layer and potential barrier forming at the Fe₂O₃-CuO junction upon exposure to air and acetone gas and energy band diagrams of the Fe₂O₃-CuO system in air and acetone gas.

existence of p-n heterojunctions in the latter. A potential barrier develops at the p-CuO/n-Fe₂O₃ interface due to built-in potential (Figure 5) [15, 16]. Modulation of the potential barrier height also occurs during the adsorption and desorption of acetone gas. (Desorption of acetone gas corresponds to adsorption of air.) The potential barrier height at the p-n junction changes from V_1 (in air) to V_2 (in acetone gas) as shown in Figure 5. Second, the high catalytic property of Fe₂O₃ on the oxidation of organic species has been reported recently by several research groups [17–19]. Functionalization of Fe₂O₃ nanoparticles on the CuO nanorods creates crystallographic defects at the Fe₂O₃-CuO interface due to the lattice mismatch between the two materials, which provides preferential adsorption site for acetone and oxygen molecules [20]. The sensing performance of the Fe₂O₃ nanoparticle-decorated CuO nanorod sensor is believed to be enhanced by a combination of the above three factors.

4. Conclusions

Fe₂O₃-decorated CuO nanorods were synthesized by a two-step process involving thermal oxidation and solvothermal methods. The response and sensing speed have been significantly improved by decorating the nanorods with Fe₂O₃ nanoparticles. The operating temperature of the pristine and Fe₂O₃-decorated CuO nanorods was found to be 240°C. The underlying mechanism for the enhanced sensing performance of the multiple-networked Fe₂O₃-decorated CuO nanorod sensor to acetone gas was explained by modulation of the potential barrier at the Fe₂O₃-CuO interface, highly catalytic activity of Fe₂O₃ for acetone oxidation, and the creation of active adsorption sites by Fe₂O₃ nanoparticles. We believe that these results will make a meaningful contribution to the development of an acetone gas sensor with high performance by showing significantly enhanced acetone sensing performance of multiple-networked Fe₂O₃-decorated CuO nanorods.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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