ISSN 2288-8403(Online)

한국표면공학회지
J. Surf. Sci. Eng.
Vol.56, No.4, 2023.
https://doi.org/10.5695/JSSE.2023.56.4.219

〈Research Article〉

Vertically aligned cupric oxide nanorods for nitrogen monoxide gas detection

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(Received 11 June, 2023 ; revised 22 August, 2023 ; accepted 23 August, 2023)

Abstract

Utilizing low-dimensional structures of oxide semiconductors is a promising approach to fabricate relevant gas sensors by means of potential enhancement in surface-to-volume ratios of their sensing materials. In this work, vertically aligned cupric oxide (CuO) nanorods are successfully synthesized on a transparent glass substrate via seed-mediated hydrothermal synthesis method with the use of a CuO nanoparticle seed layer, which is formed by thermally oxidizing a sputtered Cu metal film. Structural and optical characterization by x-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy reveals the successful preparation of the CuO nanorods array of the single monoclinic tenorite crystalline phase. From gas sensing measurements for the nitrogen monoxide (NO) gas, the vertically aligned CuO nanorod array is observed to have a highly responsive sensitivity to NO gas at relatively low concentrations and operating temperatures, especially showing a high maximum sensitivity to NO at 200 ℃ and a low NO detection limit of 2 ppm in dry air. These results along with a facile fabrication process demonstrate that the CuO nanorods synthesized on a transparent glass substrate are very promising for low-cost and high-performance NO gas sensors.

Keywords : Cupric oxide; Oxide semiconductor; Nanorod; NO gas sensor; Hydrothermal synthesis.

1. Introduction

In the field of solid-state gas sensors, recent decades have seen an increasing interest in oxide semiconductor gas sensors due to their unique applications, including automotive and environmental applications [1]. Specifically, recent atmospheric contamination and industrial pollution have led to a requirement for relevant gas sensors that can effectively detect various harmful air pollutants, including nitric oxide or nitrogen monoxide (NO) gas. NO gas is responsible for the generation of photochemical smog and toxic nitrogen-dioxide (NO_2) greenhouse gas. In the cases of oxide semiconductor gas sensors, the operating principle is based on the phenomenon that the electrical conductivity G or resistivity R of an oxide semiconductor varies with the composition and concentration of the gas atmosphere surrounding it [2]. In the field of oxide semiconductor gas sensors, the gas sensing properties of n-type oxide semiconductors such as ZnO, SnO_2 and In_2O_3 have been extensively investigated [3], but a few studies on the gas sensing properties of p-type

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oxide semiconductors have been reported [4]. In general, *n*-type oxide semiconductor gas sensors are known to require relatively high operating temperatures and have rather low sensitivities [5]. A variety of studies have revealed certain enhancements in the gas sensing properties of gas sensors by using oxide nanostructures in the forms of nanocrystals, nanowires and nanorods, which possess large surface-to-volume and large length-to-diameter ratios [6-8]. The present work focuses on the synthesis and characterization of vertically aligned *p*-type CuO nanorods for NO gas detection.

It is known that the cupric oxide (CuO), which is a kind of *p*-type oxide semiconductor with a bandgap of ~1.5 eV [9], can be applied in various fields including heterojunction components, catalysts and photoelectrodes for photoelectrochemical application [10-12]. Among CuO-based nanostructures including nanoparticles, nanowires, nanosheets, etc., reports on CuO nanorod gas sensors are somewhat rare, and their sensing mechanism remains unclear [13]. While various synthesis techniques of CuO nanorods, such as a precipitation method, an arc-discharge process, an oxidation of a Cu substrate, thermal decomposition of copper-based complexes, and hydrothermal synthesis have been reported [14], a recent observation of good response behaviors in hydrothermally synthesized CuO nanorods by Yang et al. [7] suggests a feasible application of CuO nanorods as gas sensing elements.

In the present paper, we report on the characterization of vertically aligned *p*-type CuO nanorods array synthesized on a transparent glass substrate via seed-mediated hydrothermal synthesis method with the use of a CuO nanoparticle seed layer in order to serve as the sensing material for the NO gas detection. This work demonstrates a promising potential of the hydrothermally synthesized CuO nanorods array as a gas-sensing element for an effective NO detection.

2. Experimental Details

The vertically aligned CuO nanorods array was prepared on a glass substrate via a seed mediated hydrothermal technique with the use of a CuO nanoparticle seed layer formed via a two-step method [15]. To form the CuO seed layer, Cu metal film was first deposited on the glass substrate from a pure Cu metal target by a radio-frequency (rf) magnetron sputtering method with the sputtering power of 30 W in an Ar atmosphere of 5 mTorr for 2 min. The substrate temperature was kept at room temperature (RT) and the substrate-to-target distance was set to be 12 cm. The as-sputtered Cu film was then thermally oxidized in dry air at 400 ℃ for 1 hour by using a rapid thermal annealing system to form CuO nanoparticles, which acted as nucleation sites for synthesizing CuO nanorods. Subsequently, the vertically aligned CuO nanorods were synthesized by dipping the CuO-deposited substrate into a solution which consisted of 20 mM $Cu(NO_3)_2 \cdot 3H_2O$ and 40 mM $C_6H_{12}N_4$ in distilled water, and then by heating it at 90 ℃ for 3 hour in an oven. Finally, the substrate covered with CuO nanorods was carefully cleaned with deionized (DI) water and dried under a high-purity nitrogen gas flow.

The crystalline phases of the prepared CuO nanorods were characterized by X-ray diffraction (XRD) using Kα radiation along with Raman spectroscopy, and then its microstructures were analyzed by scanning electron microscopy (SEM). The optical properties of the CuO nanorods were examined by UV-vis-NIR spectrometer. The electrical and NO gas sensing properties of the CuO nanorods were measured via two conductive electrodes by a multi-

meter assembled in a computer-controlled gas sensing characterization system using flow-through method [16]. The fabricated gas sensing element was placed in a sealed chamber having one inlet and one outlet with electrical feedthrough. Carrier gas (dry air) and target gas (NO) were loaded into the measurement chamber through the inlet port while the gases automatically came out through the outlet port due to the difference in pressure between the interior and exterior of the chamber. Before performing each measurement of gas sensing properties, the formation of an Ohmic contact between the CuO active layer and electrodes was confirmed by the current-voltage (I–V) measurements, in which the applied voltage was varied from -3 to +3 V. For the gas sensing measurements, the applied dc voltage was fixed at 2 V and the change in current with time was recorded. The concentration of the target NO gas in dry air was controlled by adjusting the flow rate of the NO gas using separate mass flow controllers. The operating temperature was controlled using a small isolated hot plate integrated in the measurement chamber.

3. Results and Discussion

We present typical scanning electron microscopy (SEM) images for the top-view and cross-sectional morphologies of the hydrothermally synthesized CuO nanorods array on a glass substrate in Figure 1(a) and 1(b), respectively. It is clearly seen from Figure 1(a) and 1(b) that the CuO nanorods with an average diameter of ~45 nm and an average length of ~375 nm are vertically grown.

X-ray diffraction (XRD) was used to verify the formation of CuO single crystalline phase. As presented in Figure 2(a), a typical XRD pattern of the synthesized CuO nanorods array shows the diffraction peaks simply corresponding to the monoclinic tenorite CuO crystalline phase (JCPDS card. No. 80-1268) without any other second phases being detected, indicating the successful

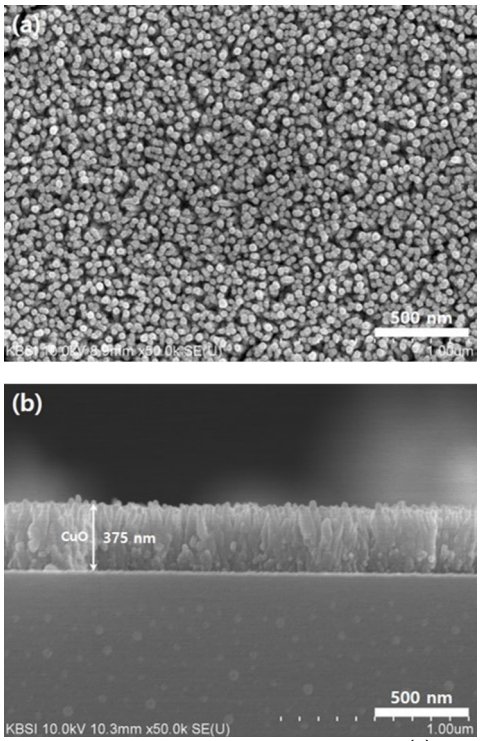

Fig. 1. Typical SEM images showing (a) top view and (b) cross-sectional view of the hydrothermally synthesized CuO nanorods array on a glass substrate.

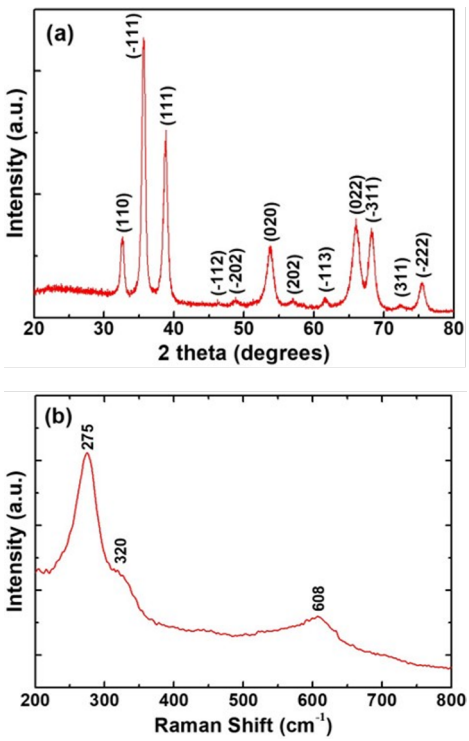

Fig. 2. (a) Typical X-ray diffraction pattern. (b) Raman spectrum of hydrothermally synthesized CuO nanorods array on a glass substrate.

preparation of the crystalline CuO nanorods of the single tenorite phase.

The formation of the tenorite CuO crystalline phase can be further confirmed by the Raman spectroscopy analysis. Figure 2(b) shows the Raman spectrum of the hydrothermally synthesized CuO nanorods array on a glass substrate at room temperature (RT). In the observed spectrum at RT, three distinct lines at 275, 320, and 608 cm^{-1} can be ascribed to the characteristic phonon frequencies of the tenorite CuO crystalline phase [17]. Consequently, both the observed XRD and Raman spectroscopy results further demonstrate the successful preparation of the CuO nanorods of the single tenorite phase.

Figure 3 shows the UV-vis-NIR absorbance spectrum of the hydrothermally synthesized CuO nanorods array on a glass substrate at RT. It is clearly seen from the observed spectrum at RT that the CuO nanorods array has an absorption edge at about 900 nm owing to the small optical bandgap energy of CuO around 1.5 eV [9]. In general, Tauc plot, which is obtained from the UV-vis-NIR spectrum, is used to determine the bandgap energy of semiconductor based on the following equation [18]:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where α is the absorption coefficient which can be obtained from UV-vis-NIR spectrum, $h\nu$ is the energy of photon, A is a constant, E_g is the optical bandgap energy, and exponent n is dependent on the nature of the optical transition. It is known that n is 2 for direct transition and n is 1/2 for indirect transition [18]. As can be seen in the inset of Figure 3, a straight line is obtained when $(\alpha h\nu)^2$ is plotted against photon energy $(h\nu)$, indicating that the absorption is owing to a direct transition for CuO. The bandgap energy of the hydrothermally synthesized CuO nanorods array, which can be obtained from the intercept on the abscissa, is estimated to be about 1.47 eV. This estimated value is found to be slightly smaller than the known standard value of 1.5 eV for the bulk CuO [9]. Among other things, the observed slight decrease in the optical bandgap energy can be primarily attributed to a lower dimensionality of CuO nanorod than that of bulk CuO. And also, as we have seen [12], the absorption edge of the CuO nanorods array is expected to shift to a longer wavelength than the bulk CuO, possibly resulting in an enhancement of the light absorbance.

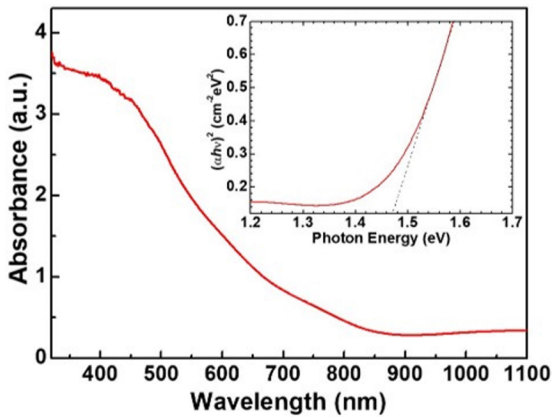

Fig. 3. Optical absorption spectrum of the hydrothermally synthesized CuO nanorods on a glass substrate. The inset shows the Tauc plot for the prepared CuO nanorods.

The NO gas sensing properties of the CuO nanorods array gas sensor were measured for various NO gas concentration and operating temperatures. The formation of an Ohmic contact between the CuO nanorods array and electrodes was confirmed by observing a linear I-V characteristic of the sensor, as shown in Figure 4.

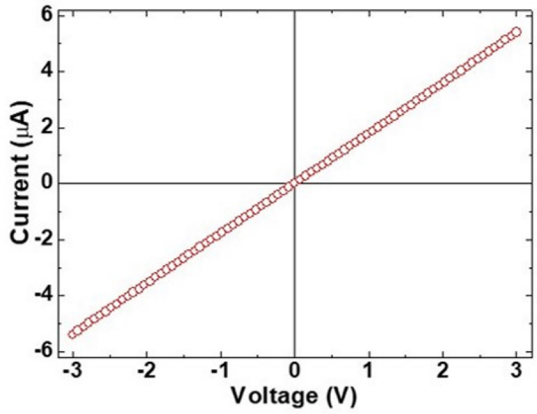

Fig. 4. A representative I-V characteristic curve of the CuO nanorod gas sensor at room temperature.

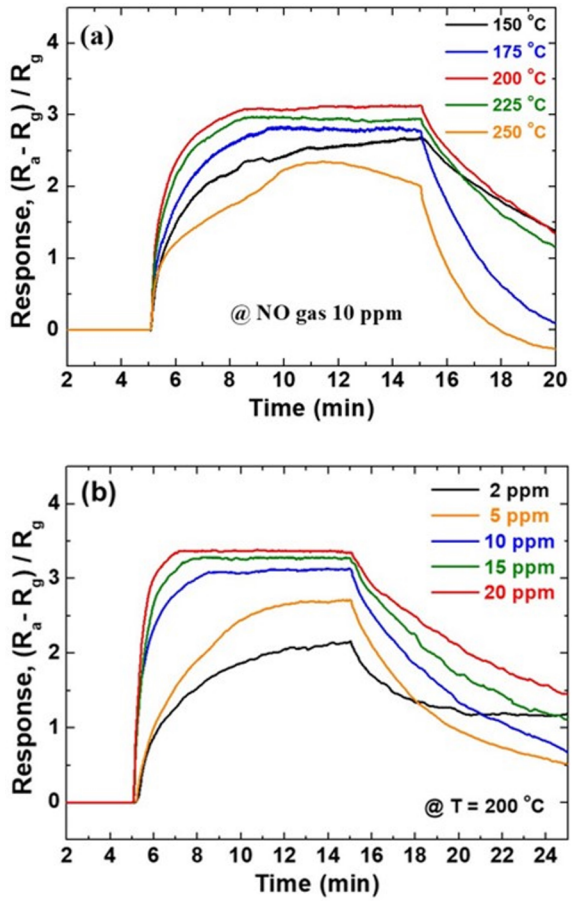

Fig. 5. Typical transient response curves of the CuO nanorod gas sensor (a) for a NO concentration of 10 ppm in dry air at various operating temperatures and (b) for several NO concentration in dry air at the operating temperature of 200 ℃.

In Figure 5(a), we present the gas sensing response curves of the CuO nanorods array gas sensor for a NO gas concentration of 10 ppm in dry air at various operating temperatures of 150, 175, 200, 225, and 250 ℃. Here, in the case of a *p*-type oxide semiconductor such as CuO upon exposure to an oxidizing gas such as NO, the sensor response was calculated by using the ratio of the change in conductance upon exposure to the oxidizing target gas in dry air ($\Delta G = G_g - G_a$) to the conductance in dry air (G_a) because the conductance of a *p*-type oxide semiconductor gas sensor increases when the sensor is exposed to an oxidizing gas : $S = \Delta G/G_a = (R_a - R_g) /R_g$, where R_a and R_g is the electrical resistance in dry air and upon exposure to the target gas in dry air, respectively [19]. At each temperature, as can be seen in Figure 5(a), the response of the sensor initially increases somewhat abruptly and then stabilize into a saturated state when it is exposed to the oxidizing NO gas, and it decreases gradually when the NO gas flow is closed. It is clearly seen that the response characteristics of the CuO gas sensor depend on the operating temperature. It is also found that the resistance measured after exposure to NO does not recover to the initial level. Such behavior can be explained by the presence of adsorbed gas molecules, which were not removed from the surface of the CuO nanorods. Furthermore, in Figure 5(b), we present the gas-sensing response curves the CuO nanorods array gas sensor operating at a temperature of 200 ℃ for various NO concentration in dry air. The observed NO gas sensing response evidently exhibits a distinct variation and increases with increasing NO concentration in dry air.

Given that CuO is a *p*-type semiconductor, the NO gas sensing mechanism in the CuO-based gas sensors can be explained in terms of the following surface reaction [20]: $2NO \rightarrow N_2 + 2O^- + 2h^+$, where O^- is a typical oxygen species adsorbed on the CuO surface. This reaction takes electrons from the valence band of CuO, thus generate holes. Consequently, the carrier or hole concentration in the surface region of the CuO nanorod will increase, and the depletion region will shrink, which results in an increase of the conductance, *i.e.*, a decrease of the resistance as observed.

The sensitivity of the gas sensor is usually defined as the maximum response upon exposure to the target gas. Figure 6(a) shows the sensitivity of the CuO nanorods array gas sensor as a function of the operating temperature upon exposure to 10-ppm NO in dry air. In general, the sensitivity of the gas sensor is affected by the operating temperature because of the strong influence of temperature on the adsorption-desorption of gases on the surface of the gas sensing

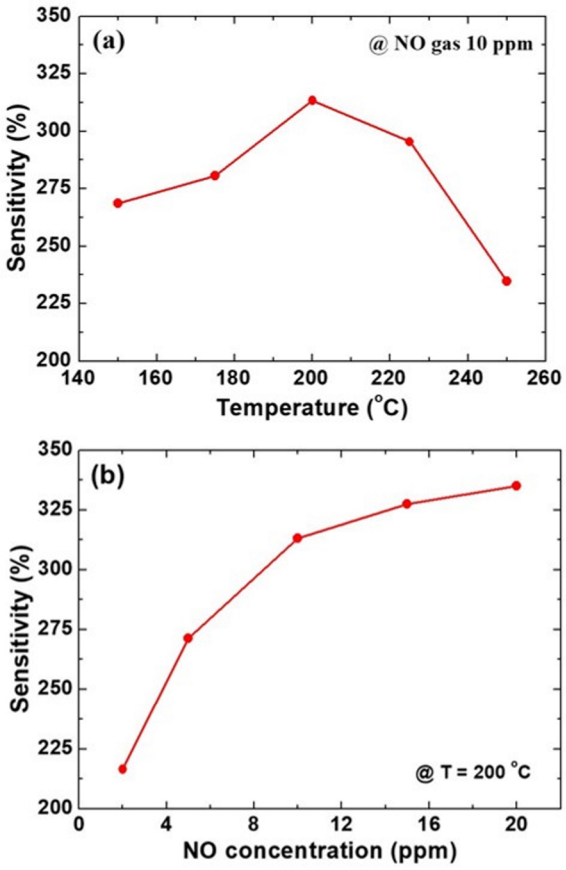

Fig. 6. (a) Sensor sensitivity versus operating temperature of the CuO nanorod sensor when exposing to 10 ppm NO in dry air. (b) Variation of the sensitivity as a function of NO gas concentration for the CuO nanorod sensor operated at 200 ℃.

material. Figure 6(a) clearly illustrates that the sensitivity of the CuO nanorods array gas sensor upon exposure to 10-ppm NO in dry air reaches a maximum value of 3.13, *i.e.*, ~310% at an operating temperature of 200 ℃, which is several times higher than those of conventional CuO thin film NO gas sensors [21]. The observed enhancement in the sensitivity is most likely attributable to the higher surface-to-volume ratio associated with the vertically aligned CuO nanorods and the resultant increase of the interaction strength between the target NO gas and the sensing CuO layer. Additionally, the variation of the sensitivity as a function of the NO concentration for the CuO nanorods array gas sensor operating at the optimal temperature of 200 ℃ is shown in Fig. 6(b). It is clearly seen from Fig. 6(b) that the NO gas sensitivity of the CuO nanorod array gas sensor increases steadily with increasing NO concentration in the low concentration region below 20 ppm. However, the NO gas sensitivity is expected to be saturated in the higher NO gas concentration region more than 20 ppm, indicating the resolution of the NO gas detection will be poor in the higher NO gas concentration region and should be improved.

4. Conclusion

In summary, the vertically oriented CuO nanorods array to serve as the sensing material for the NO gas detection has been successfully synthesized on a transparent glass substrate via seed-mediated hydrothermal synthesis method with the use of a CuO nanoparticle seed layer, which is formed by thermally oxidizing a sputtered Cu metal film. The XRD, SEM, and Raman analyses reveal that the synthesized CuO nanorods have a monoclinic tenorite crystal structure with an average diameter of ~45 nm and an average length of ~375 nm. It is noted here that the sensitivity value of the CuO nanorods array upon exposure to 10-ppm NO gas was observed to be as high as ~310% at 200 ℃, which is much greater than that of CuO thin film NO gas sensor. The observed enhancement of the NO gas sensing performance is ascribed to an increase in the area of possible surface reaction resulting from the vertically aligned nanorod structure. These results, along with the simple synthesis route, demonstrate the promising feasibility of fabricating low-cost, high-performance CuO-based gas sensors.

Acknowledgement

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF)

funded by the Ministry of Education (NRF-2017R1D1A3B04030425).

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