CuO Thin Film/ZnO Nanorods Heterojunction Diode Structure for Efficient Detection of NO Gas

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***Abstract*—We report on the efficient detection of NO gas by an oxide semiconductor p-n heterojunction diode structure with n-type ZnO nanorods embedded in p-type CuO thin film, which was fabricated on an indium tin oxide-coated glass substrate by combining a hydrothermal synthesis method and a sputtering deposition method. The transport behavior and NO gas sensing properties of the hybrid CuO thin film/ZnO nanorods heterostructure were characterized. The oxide heterojunction structure exhibited a definite rectifying diode-like behavior at various temperatures ranging from room temperature to 250 ºC. When the oxide p-n heterojunction diode structure was exposed to the acceptor gas NO in dry air, a significant decrease in the forward diode current was observed. The NO gas sensing response of the CuO thin film/ZnO nanorods heterostructure at 2 V was found to show a value as high as ~1,000% for the NO concentration of 10 ppm at a comparatively low operating temperature of 150 ºC and increase linearly with increasing NO gas concentration in the range of 2-14 ppm. The experimental results indicate that this type of oxide heterostructure can be effectively used in various gas sensing applications thanks to its simple fabrication procedure and potential performance.**

Keywords-oxide heterostructure; gas sensor; p-n junction; zinc oxide, copper oxide.

I. INTRODUCTION

Recent great concern about anthropogenic environmental pollution and accidental leakages of toxic or explosive gases has led to an urgent demand for relevant gas sensors for detecting harmful gases in air. A nitric oxide or nitrogen monoxide (NO) gas sensor is much required because NO gas is closely connected with human life. Because of recent intensive studies of NO gas sensors, several types of NO gas sensors have been proposed. The most practical and effective are of the oxide semiconductor type, which utilizes oxide semiconductors including ZnO and CuO as the gas sensing element [1]. However, most oxide semiconductor-based gas sensors require operation at relatively high temperatures and have lowly sensitive responses. Recent developments in the synthesis of ZnO and CuO nanostructures with controllable size and shape have provided a good opportunity to improve gas sensing performance thanks to their large surface-to-volume ratio. In particular, a significant enhancement in the gas sensing properties of gas sensors based on ZnO nanorods has been reported [2]. Meanwhile, oxide semiconductor p–n heterojunction structures have been regarded as a key technology in many electronic and optoelectronic devices including gas sensors [3].

In this study, we report on the fabrication and characterization of an oxide semiconductor heterojunction diode structure with n-type ZnO nanorods embedded in p-type CuO thin film for sensing of NO gas. Section II provides the fabrication procedure for the CuO thin film/ZnO nanorods heterojunction structure. Section III offers a concise sketch of the experimental results for the CuO/ZnO heterojunction gas sensor element. Finally, a brief summary of this study is given in Section IV.

II. FABRICATION PROCEDURE

ZnO nanorods were grown on a glass substrate coated with an indium tin oxide (ITO) electrode via a seed-mediated hydrothermal technique with the use of a ZnO nanoparticle seed layer with a thickness of 10 nm, which was formed by thermally oxidizing a sputtered Zn metal film. Aligned ZnO nanorods were prepared by dipping the ZnO-coated substrate into an aqueous solution which consisted of 50 mM $Zn(NO_3)_2 \cdot 6H_2O$ and 50 mM $C_6H_{12}N_4$ in distilled water, and then keeping the prepared mixture under continuous magnetic stirring at 95 °C for 6 h. The substrate covered with ZnO nanorods was rinsed with deionized water and dried under a high-purity nitrogen gas flow. To fabricate an oxide p–n junction heterostructure, Cu metal film was deposited onto the array of ZnO nanorods for 20 min at RT by using a rf magnetron sputtering system with power of 50 W and then thermally oxidized in dry air at 600 °C for 1 h, yielding the oxide heterostructure with n-type ZnO nanorods embedded in p-type CuO thin film.

III. RESULTS

The crystalline phases and morphologies of CuO thin film/ZnO nanorods heterostructures fabricated on the ITO-coated glass substrate were characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. A typical SEM image for the cross-sectional morphology of the oxide heterostructure is presented in Figure 1. It is clearly seen that the surface of the distinct ITO layer is covered by vertically aligned ZnO nanorods with a length of approximately 500 nm and an average diameter of approximately 40 nm. Also, an apparently blurred interface between ZnO nanorods and CuO thin film is observed with a thickness of approximately 300 nm, revealing the formation of a structure in which the ZnO nanorods are embedded in the CuO thin film. XRD was used to verify the formation of CuO and ZnO crystalline phases, showing the diffraction peaks which simply correspond to either monoclinic tenorite CuO or hexagonal wurtzite ZnO phase without any other second phase peaks being detected, as shown in Figure 2.

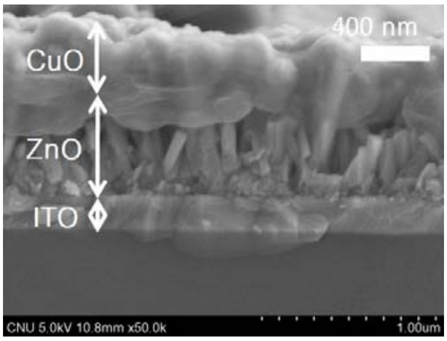

Figure 1. Cross-sectional SEM image of the CuO thin film/ZnO nanorods heterostructure fabricated on an ITO-coated glass substrate.

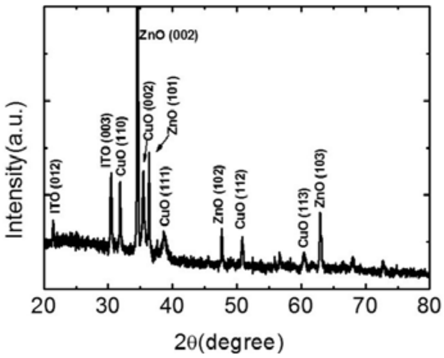

Figure 2. Typical X-ray diffraction pattern of the CuO thin film/ZnO nanorods heterostructure fabricated on an ITO-coated glass substrate.

The formation of p–n heterojunction diode structure can be confirmed by the *I–V* characteristic curves as presented in Figure 3, the inset of which shows a schematic circuit of the oxide heterostructure. Here, for electrical measurements, two square silver contacts with an area of 1×1 cm^2 were formed on CuO and ITO surfaces. All of the *I–V* characteristic curves observed in dry air at several temperatures exhibit a well-defined rectifying diode-like behavior, revealing a typical semiconductor p–n junction. With increasing the temperature, the turn-on voltage of the p-n heterojunction diode gradually decreases while its forward current distinctly increases, as expected for semiconducting materials.

In order to see the potential for gas sensing, the CuO thin film/ZnO nanorods heterostructure was exposed to NO gas in dry air. During the electrical measurements, the NO gas concentration in dry air was varied from 2 ppm to 14 ppm. Figure 4(a) illustrates the effect of NO gas concentration in dry air on the *I–V* characteristics of the oxide heterostructure at an operating temperature of 150 °C. It is clearly seen that the oxide p–n junction heterostructure exhibits a diode-like nature in the examined NO concentration range. The forward current of the oxide heterojunction diode is found to decrease significantly with the increase in NO gas concentration. Now the gas sensing response S of a p–n heterojunction structure can be estimated using the formula $S = \Delta I/I_g = (I_a - I_g)/I_g$ where I_a and I_g are the forward currents at a specific forward voltage (e.g., 2 V) in dry air and upon exposure to NO gas in dry air, respectively.

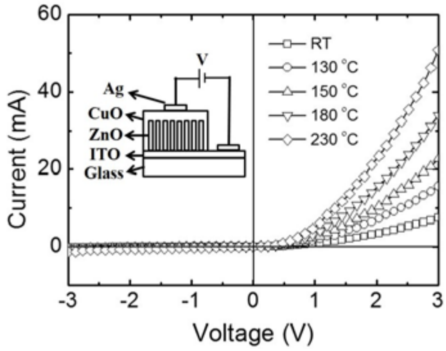

Figure 3. Current–voltage (*I–V*) characteristic curves of the CuO thin film/ZnO nanorods heterostructure in dry air at several temperatures. The inset shows a schematic circuit of the oxide p-n heterojunction device.

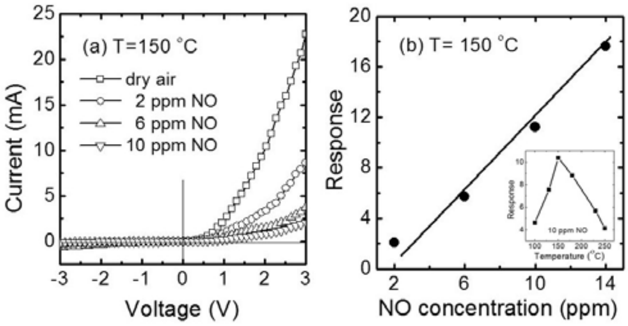

Figure 4. (a) Current–voltage (*I–V*) characteristic curves of the CuO thin film/ZnO nanorods heterojunction diode structure for several NO gas concentration in dry air at 150 °C. (b) Variation of the sensitivity as a function of the NO gas concentration in dry air.

Figure 4(b) illustrates the variation of the NO gas sensing response of the oxide heterojunction diode operating at 150 °C as a function of the NO concentration in dry air for a forward bias of 2 V, revealing a good linear relationship between gas sensing response and NO concentration. Now the observed value of the response of the CuO/ZnO hetero-junction NO gas sensor was estimated to be as high as ~1,000% for 10 ppm NO concentration at 150 °C, which is several times higher than the values observed for conventional CuO film NO gas sensors. The NO gas sensing response of the oxide heterojunction was also found to depend on the operating temperature and reach a maximum value at 150 °C, as shown in the inset of Figure 4(b).

IV. CONCLUSION

In summary, we fabricated an oxide p–n heterojunction diode structure with n-type ZnO nanorods embedded in p-type CuO thin film for efficient sensing of NO gas. The CuO thin film/ZnO nanorods heterojunction structure showed a good rectifying behavior and a significant decrease in the forward diode current upon exposure to NO gas in dry air. The NO gas sensing response of the oxide diode structure at 2 V was found to show a value as high as ~1,000% for 10 ppm NO concentration at 150 °C. This work suggests that this type of oxide heterojunction diode structure could be effectively used in various gas-sensing applications thanks to its simple fabrication procedure and good performance.

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