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Extended Abstract

H_2S Sensing Properties of a Diode-Type Device Using ZnO Nanorods Coupled with CuO Nanocrystals †

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1. Introduction

Hydrogen sulfide (H_2S) is known as a colorless, flammable and highly toxic gas with strong odor. Therefore, to avoid the risk of its leakage, continuous monitoring of H_2S is extremely important. Semiconductor gas sensor is promising for such applications because of its high sensitivity, selectivity, fast response, and good stability. It has been reported in many papers that CuO/SnO_2 sensor shows a high sensitivity to H_2S since the pioneering work by Tamaki et al. [1]. It is believed that sulfidation of CuO with H_2S degrades the PN junction between CuO and SnO_2, resulting in a significant change in electrical resistance. However, the detailed mechanism remains unclear yet. In this study, we fabricated a PN junction film using p-type CuO nanocrystals and n-type ZnO nanorod films to make a sensor device and studied its diode properties under H_2S atmosphere to reveal the sensing mechanism. It was expected that the combination of nanorods and nanocrystals increases the area of junction interfaces, leading to a pronounced change in electrical properties upon gas reaction.

2. Experimental

ZnO nanorods (NRs) were grown on an ITO-coated glass substrate by a seeding method [2]. As seeds, ZnO nanocrystals (NCs) were synthesized by a hot-soap method, in which zinc acetylacetone and 1,2-hexadecanediol were dissolved in oleylamine and heated at 220 °C for 90 min. The synthesized ZnO NCs were deposited on an ITO-coated glass and annealed in air at 350 °C for 30 min to remove surface capping agents. The ZnO NC film was dipped in an aqueous solution containing $Zn(NO_3)_2$ and hexamethylenetetramine (HMT), and then heated at 95 °C for 5 h to synthesize ZnO NRs.

Cu_2O nanocrystals (NCs) were also synthesized by a hot-soap method using oleylamine as a high-boiling-point solvent. Typically, Cu (II) acetylacetonate and 1,8-octanediol were added to oleylamine in a three-necked flask. The temperature was raised to 160 °C under an Ar flow and kept at 160 °C for 60 min. The surface ligands, olylamine, were replaced with 3-mercaptopropyl acid by dispersing NCs in a solution containing water, methanol, and NaOH with pH 12. The ligand exchange reaction was carried out for 30 min.

The Cu_2O NCs were deposited onto the ZnO nanorod film by drop casting and annealed in air at 250 °C for 30 min. Gold electrodes with 100 nm thickness were deposited on the film by thermal evaporation to fabricate a sensor device. IV curves of the device were measured at 50 to 200 °C in air and air containing H2S with a Keithly 2400 source meter.

3. Results and Discussion

Figure1 shows a representative SEM image of ZnO NRs deposited on ITO. ZnO NRs grew perpendicular to the substrate to form a porous film. The diameter and the length of the NRs were estimated to be ca. 100 and 700 mm, respectively. Figure 2 shows a TEM image of CuO / Cu_2O NCs. The size of the NCs is 8 to 10 nm with a narrow size distribution. XRD results revealed that Cu_2O was converted into CuO after ligand exchange with an alkaline solution.

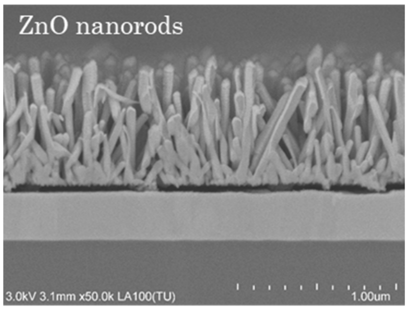

Figure 1. SEM image of ZnO nanorods deposited on an ITO substrate.

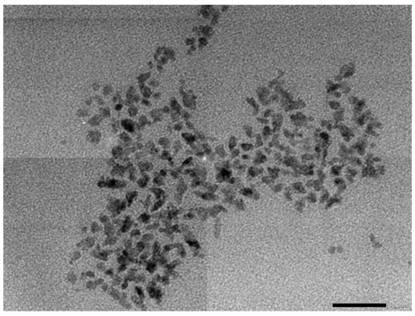

Figure 2. TEM image of CuO nanocrystals synthesized by a hot-soap method. The scale bar is 50 nm.

Figure 3 shows IV curves of the device, in which CuO NCs were deposited onto ZnO NRs, in air and air containing 8 ppm H_2S at 150 °C. The device exhibited a clear rectification behavior in air at 150 °C, indicating that PN junctions were formed between CuO NCs and ZnO NRs. However, such a clear rectification behavior was lost under H_2S atmosphere. The current in the forward and reverse directions significantly reduced after exposure to H_2S. We have recently confirmed that CuO NCs-based sensors respond to H_2S by an increase in electrical resistance due to reaction of adsorbed oxygen with H_2S, representing a typical behavior of p-type semiconductors [3]. Thus, the observed increase in resistance for the present device is possibly due to surface reaction of adsorbed oxygen with H_2S and the resulting annihilation of holes. The rectification of the current recovered by reintroduction of air, which possibly increased the electron concentration in CuO. On the other hand, at higher temperature, the device showed a simple ohmic behavior (no figure), suggesting that complete conversion of CuO into CuS occurred. Thus, the sensing mechanism should be dependent on temperature. The above results demonstrate the feasibility of nanorod/nanocrystal-based PN-junction devices in constructing gas sensors. Currently, a more detailed mechanism is under investigation.

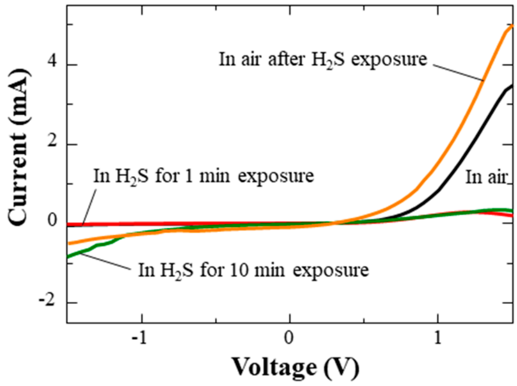

Figure 3. IV curves of the CuO NCs/ZnO NRs device in air and air containing 8 ppm H_2S at 150 °C.

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Conflicts of Interest: The authors declare no conflict of interest.

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