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Detection of ethanol gas using In_2O_3 nanoparticle-decorated ZnS nanowires

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ABSTRACT

An In_2O_3 nanoparticle-decorated ZnS nanowire gas sensor was fabricated by following a three-step process. The ZnS nanowires were fabricated by the vapor-liquid-solid mechanism using ZnS powder as a precursor. The In_2O_3 nanoparticles were fabricated by a hydrothermal mechanism. The In_2O_3 nanoparticles were spin coated on the surface of the ZnS nanowires, and the resulting sample was annealed for 1 h at 500 °C in vacuum. The ethanol gas sensing response of these nanowires was 2.9 times higher than that of pristine ZnS nanowires when these sensors were exposed to 500 ppm ethanol. The selectivity of the resulting sensor to ethanol gas among the other volatile organic compounds gases also improved by the decoration of ZnS nanowires with In_2O_3 nanoparticles. Furthermore, since ZnS and In_2O_3 are known as effective ethanol gas sensing materials, their combination creates a synergistic effect for ethanol gas sensing, selectivity, and sensitivity. In this study, we synthesized a hybrid structure containing In_2O_3 nanoparticles and ZnS nanowires to fabricate a high-response ethanol gas sensor. We also investigated the ethanol gas sensing mechanism of the resulting sensor.

1. Introduction

Recently, lots of smart devices are developed and applied in human life and in industry such as wireless telecommunication devices [1–4], and sensors [5,6]. Chemical gas sensor is one of the most important smart device which makes human life affluent. And detection of ethanol gas is an important in breath analyzers, wine makers, food, and medical diagnosis industries [7–10]. Ethanol gas is different from other chemical gases and is not very dangerous even at high concentrations. It can be sensed easily owing to its unique smell. Although the detection of this gas at ppb scale is not required, accurate detection is still important [11,12]. Ethanol gas sensors are commonly used to detect drunken driving [13]. They are also used in brewing high-quality liquor [14]. Even though the detection of ethanol gas is not difficult unlike the other chemical gases such as NO_2, hydrogen, and benzene, the fabrication of fast and accurate ethanol gas sensors is important.

Owing to their unique properties, lots of types of devices are developed using nanomaterials [15–17]. And among them, chemiresistive-type gas sensors based on one-dimensional (1D) nanomaterials such as nanowires, nanorods, and nanotubes have been studied during several decades of years [18]. 1D nanomaterials have extremely large surface area, high surface to volume ratio, and linear morphology. The resistance of 1D nanomaterials changes drastically upon exposure to chemical gases, thus they can be detected by measuring the change in the resistance of 1D nanomaterials. Likely to ZnO [19–23], ZnS nanomaterials are the most famous ethanol gas sensitive materials. Gas sensors with high and fast response toward ethanol detection can be fabricated using ZnS nanomaterials. Different kinds of ZnS-based nanomaterials have been used to fabricate high-quality ethanol gas sensors [24]. Xiao et al. reported the ethanol sensing properties of hollow-type ZnS microspheres [25]. The sensor based on ZnS microspheres provided a quick ethanol sensing response as compared to the other micro and nanosphere sensors. However, it showed a low sensing selectivity and sensitivity. Wang et al. fabricated a gas sensor based on ZnS nanowires for detecting ethanol and acetone [26]. This sensor showed high sensing response and fast response time. However, its ethanol selectivity was not as good as that of the sensor fabricated by Xiao et al. This sensor showed a higher sensing response toward acetone than that toward ethanol. Many nanostructured hybrids have been studied for gas senor applications owing to their enhanced sensing properties [27–30]. Sensors based on nanostructured hybrids show their improved sensing selectivity, sensitivity, and operating temperature. Several methods such as fabrication of core/shell structures and decoration with noble metals and com-

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pound semiconductor nanomaterials are widely used to improve the sensing properties of gas sensors. By combining the gas sensing properties of two different materials, a gas sensor with high sensitivity and selectivity can be fabricated. In_2O_3 is well known to have high sensitivity toward ethanol gas [31]. In this research, an In_2O_3 nanoparticle-decorated ZnS nanowire gas sensor was fabricated, and its ethanol sensing response and selectivity were evaluated. We also discussed the gas sensing mechanism of this hybrid sensor.

2. Experimental procedure

The In_2O_3 nanoparticle-decorated ZnS nanowires were fabricated by following a three-step process. First, the ZnS nanowires were synthesized by the vapor-liquid-solid (VLS) process. A 3 nm thin film of Au was deposited on the Si substrate as a catalyst by the direct current (DC) magnetron sputtering. To deposit this thin film, a current of 10 mA was applied to the sputtering gun for 1 min. After depositing the Au catalyst, the substrate was placed in the horizontal tube furnace having two temperature zones. The Si substrate was located at one side of the temperature zone. An alumina crucible containing 1 g of ZnS powder as a precursor was placed at the other temperature side of the furnace. The two temperature zones were set at different temperatures. The furnace was sealed tightly and evacuated to 1 mTorr. The temperature zone containing the Si substrate was heated up to 650 °C over a period of 1 h, and the temperature zone containing ZnS powder was heated up to 850 °C over a period of 1 h. When both the temperature zones reached the set temperature, 50 sccm of N_2 gas was supplied to the furnace. The pressure of the chamber was fixed at 1 Torr during this period. After 1 h, when the synthesis of the ZnS nanowires was complete, the gas supply was cut off and the chamber was cooled down to the room temperature. In the meantime, the In_2O_3 nanoparticles were synthesized by the hydrothermal method. First, 29.2 mg of indium(III) acetate powder was mixed with DI water to make a 10 mM solution. This solution was mixed with 10 mL of 10 mM NaOH solution and stirred using a magnetic stirrer for 30 min. This solution was then transferred to an autoclave, and the autoclave was sealed tightly. The autoclave was kept in an oven and was heated to 150 °C for 10 h. After heating, the autoclave was cooled down to the room temperature. A white powder was observed at the bottom of the autoclave. Spin coating and annealing processes were carried out to synthesize the In_2O_3 nanoparticle-decorated ZnS nanowires. Then, 1 mL of In_2O_3 nanopowder solution was dropped on the ZnS nanowire template and spin coated at 3000 rpm for 30 s. This template was dried using a 150 °C hot plate. This process was repeated five times to decorate enough amount of the In_2O_3 nanoparticles on the ZnS nanowires. The template was then mounted to a horizontal tube furnace, and the furnace was sealed tightly. The furnace was heated to 500 °C at a pressure of 1 mTorr for 1 h. After 1 h, the furnace was cooled down to the room temperature.

The pristine and In_2O_3 nanoparticle-decorated ZnS nanowire templates were immersed into 5 mL of acetone and were ultrasonicated for 1 min to make nanowire colloidal solutions. These solutions were dropped on an interdigital electrode (IDE) patterned chip and dried naturally at room temperature. The space between the electrodes was fixed to be 30 μm, and the two electrodes were connected by the interconnected nanowires channel. The IDE chip was mounted to the sensing equipment made in-house to examine its ethanol gas sensing property. The resistance and response and recovery times were measured when the variation in the resistance of the sensors reached 90% of the equilibrium value. The sensing responses were defined as R_a/R_g where R_a and R_g represent the resistance when the sensors were exposed to air and the target gases, respectively. The structure of the sensing equipment used in this experiment is described elsewhere [32]. The synthesized samples were characterized by X-ray diffraction (XRD, Philips X'pert MRD Pro) using Cu Kα radiation (0.15406 nm), scanning electron microscopy (SEM, Hitachi S-4200SE), and field emission-transmission electron microscopy (FE-TEM, Jeol 2100F).

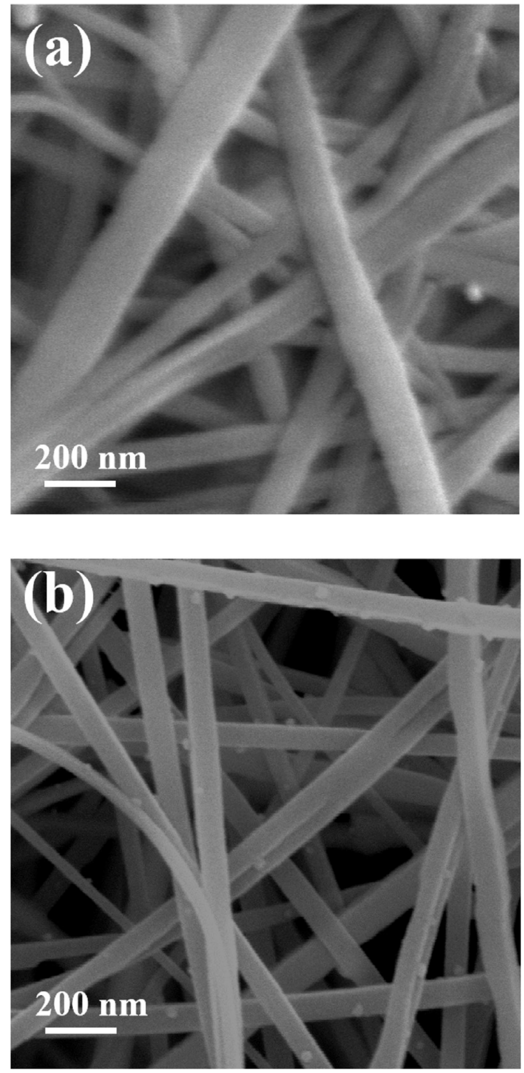

Fig. 1. SEM images of (a) pristine and (b) In_2O_3 nanoparticle-decorated ZnS nanowires.

3. Results and discussion

Fig. 1 shows the SEM images of the (a) pristine and (b) In_2O_3 nanoparticle-decorated ZnS nanowires. These images reveal that the nanowires have diameters of approximately 100 nm and lengths of tens of micrometers, respectively. The diameter of the nanoparticles decorated on the surface of the nanowires is in the range of 2–5 nm. Fig. 2 shows the XRD patterns of the (a) pristine and (b) In_2O_3 nanoparticle-decorated ZnS nanowires. Both patterns show (100), (002), (101), (102), (110), (103), (112), (203), and (221) peaks which assign ZnS (JCPDS No. 89-2942). Fig. 2(b) reveals additional peaks such as (222), (400), and (622) which assign In_2O_3 (JCPDS No. 88-2160). Since the amount of In_2O_3 was much lower than that of ZnS, the peak intensity of In_2O_3 was relatively low compared to that of ZnS. Fig. 3(a)–(c) shows the low and high-magnification TEM images, and the corresponding selected area electron diffraction (SAED) patterns of the In_2O_3 nanoparticle-decorated ZnS nanowires. Low TEM image of this hybrid structured nanowire is shown in Fig. 3(a). Through this image, it can be