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Short communication

Vertical ZnO nanorod array as an effective hydrogen gas sensor

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Abstract

We report a vertical ZnO nanorod array as a highly sensitive hydrogen gas sensor. The vertical ZnO nanorod array on an Nb/Si substrate was fabricated using an anodized aluminum oxide nanotemplate and an atomic layer deposition method. The vertical ZnO nanorod array hydrogen gas sensor exhibited a high sensitivity for hydrogen in a wide concentration range.

Keywords: Semiconductor; Vertical nanorod array; ZnO atomic layer deposition; Gas sensor

1. Introduction

One-dimensional semiconductor nanorods have been widely studied for applications in nanoscale electronic devices such as nanorod field-effect transistors (FET) and nanorod sensors because semiconductor nanorods have various merits as an active layer such as a high mobility and a high surface/volume ratio [1–5]. Even in the early stages of nanorod-based device development, semiconductor nanorods, mostly fabricated by self-assembled nanorod growth techniques such as vapor–liquid–solid (VLS) methods with metal catalysts or vapor phase epitaxy (VPE), demonstrated the extensive possibilities of nanoscale electronic devices [1–5]. Synthesis of nanorods, however, requires multiple processes such as dispersion of nanorods with precise position control and electron beam lithography patterning for nanoscale electronics applications [6–9]. Thereby, a template-based nanorod synthesis is desirable because a nanotemplate can be prepared at low-cost using conventional photolithography [10–12].

In recent studies, a nanotemplate for the formation of nanodots or nanorod arrays is prepared using template-based fabrications such as diblock copolymers, polycarbonates and anodic aluminum oxides (AAO). Here, nanodot or nanorod arrays can be controlled by adjusting a pore diameter or depth and a pore-to-pore distance in the nanotemplate [13–18]. For example, an AAO nanotemplate can be used to form a thermally stable Al_2O_3 layer [12,21]. Pore-to-pore distance and pore diameter or depth in an AAO nanotemplate can be controlled by adjusting anodization conditions [12,21]. Neither diblock copolymers nor polycarbonate nanotemplates can be used to form a thermally stable Al_2O_3 layer because of their thermal instability [15,17–20]. In a previous study, an AAO nanotemplate was fabricated using Al sheets or Al thin films on desired substrates [12]. For the Al sheet, the AAO nanotemplate must be implanted on the substrate to vertical stand nanorods as a nanorod FET or nanorod sensor [12]. For the Al thin film, an AAO nanotemplate without implantation can be used as a nanorod gas sensor [22–24].

Fuel cells, where electrical currents are generated by chemical reaction between hydrogen and oxygen, have attracted attention as promising next generation power sources [25]. One crucial task for realizing wide-spread use of fuel cells is the safe handling of hydrogen gas because of the risk of explosion [26]. Thus, proper design of both a hydrogen container and a hydrogen sensor are important issues [26,27].

In this study, we fabricated a vertical ZnO nanorod array as an effective hydrogen sensor using an AAO nanotemplate on an Nb/Si substrate. The array was prepared by depositing a ZnO layer with a photolithography-based atomic layer deposition (ALD) method onto an AAO nanotemplate.

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2. Experimental

To fabricate an AAO nanotemplate, Al film and Nb films were thermally evaporated on a Si substrate. The thicknesses of the Al and the Nb were about 1600 nm and 30 nm, respectively. We used a four-step anodization and the chemical etching method to improve pore uniformity of the AAO nanotemplate [22]. All the anodization processes were carried out in a 0.3 M oxalic acid solution with an anodization voltage of 40 V at a temperature of 15 °C where the anodization speed was 1 nm/s. As for the chemical etching, the AAO nanotemplate was etched in a 0.1 M phosphoric acid solution at 30 °C for 30 min. In the AAO nanotemplate, pore diameter and pore depth were about 60 nm and 600 nm, respectively. Thereby, the depth-to-diameter ratio of pores in the AAO nanotemplate was about 10.

ZnO thin films were uniformly deposited on the AAO nanotemplate using an ALD method with diethyl zinc (DEZ) as a precursor and H_2O as a reactant gas at a temperature of 200 °C, resulting in ZnO nanorod arrays formed by filling pores of the AAO nanotemplate [28]. A ZnO film thickness of 600 nm was measured by means of an ellipsometer. The AAO nanotemplate was chemically etched by a chromic/phosphoric acid solution to expose the surface of the ZnO nanorod array to ambient gas. A gold electrode was thermally deposited on top of the ZnO thin film with the combination of photolithography and lift-off techniques and was annealed at 400 °C for 30 min. For hydrogen gas sensing measurements, hydrogen gas mixed with argon gas was used in a quartz tube at room temperature, where the total gas flow rate was about 2 L/min. The sensitivity of the gas sensor was monitored by measuring resistance with a Keithley 4200 as a function of time, and the hydrogen concentration range was 1–500 ppm.

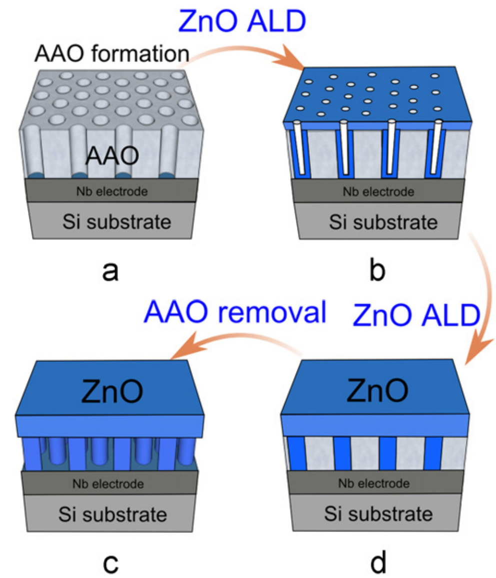

Fig. 1. Schematic diagram showing the fabrication of a vertical ZnO nanorod array using an AAO nanotemplate and ZnO ALD.

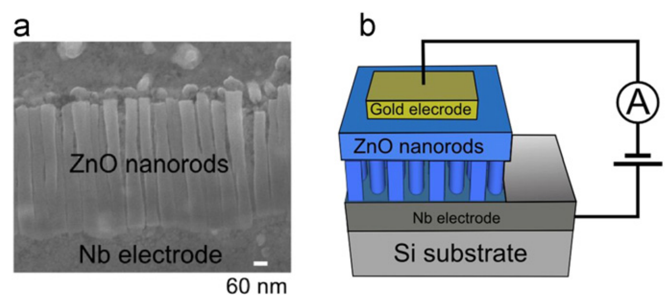

Fig. 2. (a) SEM images of the vertical ZnO nanorod array on the Nb electrode. The diameter and the length of the ZnO nanorods were about 60 and 600 nm, respectively and (b) schematic of the vertical ZnO nanorod gas sensor.

3. Results and discussion

Fig. 1 shows schematic drawings of the fabrication processes for the gas sensor consisting of a vertical ZnO nanorod array [22]. First, an AAO nanotemplate was prepared on an Nb/Si substrate, as shown in Fig. 1(a). We used the AAO nanotemplate having a pore diameter and a pore depth of about 60 nm and 600 nm, respectively. Pores of the AAO template were overfilled with ZnO nanorods to cover the surface of the AAO nanotemplate using an ALD method (Fig. 1(b) and (c)). Then, the AAO nanotemplate was chemically etched, as shown in Fig. 1(d).

Fig. 2(a) shows scanning electron microcopy (SEM) images of a vertical ZnO nanorod array on an Nb electrode, where the diameter and length of the ZnO nanorods were about 60 and 600 nm, respectively, and the pore-to-pore distance was about 100 nm. The thickness of the ZnO layer on top was estimated to be about 30 nm. Fig. 2(b) shows a schematic drawing of a gas sensor in the measurement setup. Here, a $50 \times 50\ \mu m^2$ top gold electrode and the Nb thin film on a Si substrate are used as drain and source electrodes, respectively. Note that the surface-to-volume ratio of the gas sensor was estimated to be about $16.3\ \mu m^{-1}$.

The sensitivity of the gas sensor, as defined by R_{AIR}/R_{GAS}, was assessed, where R_{AIR} and R_{GAS} are the resistances in ambient gas without and with hydrogen gas, respectively. Fig. 3(a) shows the response and recovery for hydrogen gas with various concentrations in a vertical ZnO nanorod array gas sensor as a function of time at room temperature. Fig. 3(b) shows the sensitivity as a function of hydrogen gas concentration. For example, sensitivity was about 21 and 162 at a hydrogen concentration of 5 and 500 ppm, respectively, with a response time shorter than 30 s. When hydrogen gas was exposed to the surface of the ZnO nanorod, the resistance of the ZnO nanorod became smaller because the oxygen adsorbed at the surface of the ZnO nanorods was removed by the reaction of the hydrogen gas. Thereby, the hydrogen gas could be detected [30].

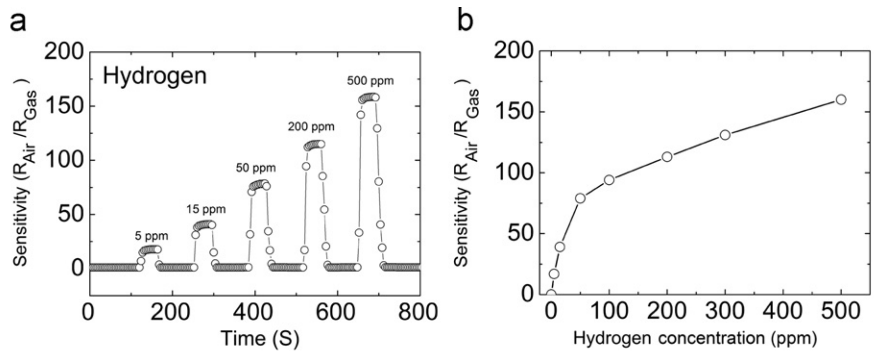

Fig. 3. (a) Response and recovery curves of the vertical ZnO nanorod gas sensor for hydrogen gas at room temperature and (b) sensitivity curve as a function of hydrogen gas concentration.

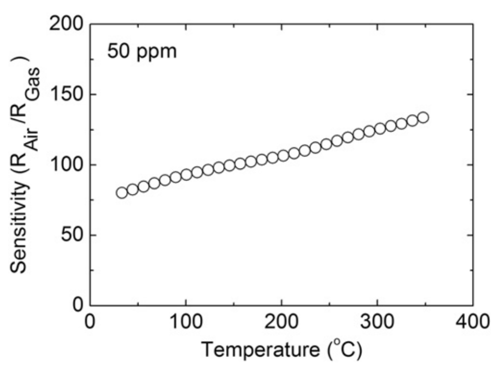

Fig. 4. Sensitivity curve as a function of sensing temperature for a hydrogen gas concentration of 50 ppm.

Fig. 4 shows the sensitivity of the gas sensor as a function of temperature for a hydrogen gas concentration of 50 ppm. Here, the sensitivity increased with increasing temperature due to the temperature dependence of the reaction between hydrogen and oxygen [1,21]. Sensitivity of the gas sensor was comparable to or higher than that in previous reports [27,29–33].

4. Conclusion

A vertical ZnO nanorod array was fabricated on an Nb electrode using an AAO nanotemplate and an atomic layer deposition method. The hydrogen gas sensor exhibited high sensitivity for hydrogen concentration in a wide range at temperatures up to 350 °C.

Acknowledgments

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