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High-performance NO_2 gas sensor based on ZnO nanorod grown by ultrasonic irradiation

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ABSTRACT

A facile and fast sonochemical route for the fabrication of a resistive-type ZnO gas sensor has been demonstrated. Vertically aligned ZnO nanorod arrays were grown on a Pt-electrode patterned alumina substrate under ambient conditions. The average diameter and length of the ZnO nanorods were 50 and 500 nm, respectively. Sonochemically grown ZnO nanorod gas sensor was highly sensitive to NO_2 gas with a very low detection limit of 10 ppb at 250 °C; further, its response and recovery time were short. Considering the advantageous properties of this sonochemical technique, we believe that it can be used to fabricate high-performance gas sensors.

1. Introduction

Nitrogen dioxide (NO_2) gas is a common air pollutant produced during combustion in automotive engines, industrial factories, and power plants. Health and safety guidelines suggest that humans should not be exposed to 3 ppm or less NO_2 gas for periods longer than 8 h because of its toxicity; the effects of an exposure to NO_2 include olfactory paralysis and deterioration in health [1–3]. Therefore, the development of a stable NO_2 gas sensor that can detect extremely low concentrations of NO_2 with high sensitivity is highly desirable. Such a sensor can be used for environmental monitoring. It can also be used in an early warning system that detects the presence of NO_2 before the critical concentration of NO_2 is reached. These advantages have propelled considerable research activities related to the development of sensors that can detect extremely low concentrations of NO_2. Metal-oxide semiconductors such as SnO_2, TiO_2, and ZnO have high sensitivity, good chemical stability and are easy to operate; therefore, these semiconductors have been extensively studied to determine their suitability for use as NO_2 gas sensors [4–6].

Thus far, ZnO gas sensors based on various forms – thin-films, heterojunctions, nanoscale particles, and one-dimensional (1D) nanomaterials – have been proposed. Resistive-type gas sensors based on 1D nanostructured materials have recently been attracting considerable attention due to their high surface-to-volume ratio [7]. Although 1D ZnO nanostructures can be synthesized by various methods, sensors utilizing these nanostructures have a few drawbacks. For example, vapor-phase reaction approaches [8–10] require severe environmental condition such as high temperature and a complicated heating system. Such high temperatures are not suitable for on-chip circuit integration. Unlike the vapor-phase synthesis method, the hydrothermal synthesis method can produce 1D ZnO nanostructured materials at low temperatures (below 200 °C). The reaction time required for the growth of 1D ZnO nanostructured materials, however, is relatively long (usually several hours) [11–13].

Recently, we presented a simple and fast sonochemical route to vertically aligned ZnO nanorods on various substrates without a catalyst under ambient conditions [14]. However, the application of this sonochemical route to a resistive-type gas sensor was not investigated.

In this paper, we report sonochemical growth of high-density ZnO nanorod arrays on patterned electrodes for applications to a

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resistive-type gas sensor. High-performance sensing properties of the sonochemically grown ZnO nanorods to NO_2 gas will also be discussed.

2. Experimental

2.1. Preparation of ZnO nanorod sensors

Fig. 1(a) shows the sensor substrate; it has interdigitated comb-like Pt electrodes on the front side and a resistive heater on the back. Pt electrode was deposited with 100 nm thickness by DC sputtering method at the front side of alumina substrate. The resistive heater was screen printed using the Pt paste at the back side of alumina substrate (heater resistance is 10 Ω). The area of the sensor substrate was 8 mm × 10 mm. Zn thin-film was deposited on the sensor substrate using RF sputtering technique. Deposition of Zn layer was achieved at a pressure of 5 mTorr and RF power of 100 W for 2 min. After Zn thin-film (40 nm) deposition on the interdigitated Pt electrodes as shown in Fig. 1(b), the sensor substrate was immersed in a mixed aqueous solution of 0.01 M $Zn(NO_3)_2{\cdot}6H_2O$ and 0.01 M $(CH_2)_6N_4$ (hexamethylenetetramine, HMT). Ultrasonic waves (frequency: 20 kHz) were introduced in the solution at an intensity of 39.5 W/cm^2 for 1 h under ambient conditions. A schematic illustration of the sonochemical growth of vertically aligned ZnO nanorod arrays on the substrate is shown in Fig. 1(c).

2.2. Characterization of ZnO nanorods

The morphology and size distribution of as-prepared ZnO nanostructures were observed by field emission scanning electron microscope (FE-SEM, Hitachi S-4200). The crystallinity and crystal structure were investigated by transmission electron microscope (TEM, JEOL JEM-2010).

2.3. Measurement of gas sensing properties

For measurement of gas sensing properties, the home-made gas dilution system was utilized. The total gas flow rate of the diluted NO_2 gas by dry air is 1000 ml/min. The ZnO nanorod array sensor was inserted between the pin connectors in the chamber. The diluted NO_2 gas was injected to the test chamber. The gas sensing properties were examined in a chamber (1000 ml). The electrical response of the sensor was measured with an automatic analysis system, controlled by personal computer.

3. Results and discussion

Fig. 2(a) and (b) show the top and side views of the FE-SEM images of the ZnO nanorod arrays grown sonochemically on the front of the substrate. The average diameter and length of the ZnO nanorod arrays are approximately 50 and 500 nm, respectively. The SEM images clearly show that the ZnO nanorods were vertically well-aligned over the surface of the sensor substrate with a high density of ~1.5×10^{10}/cm^2. From the TEM images and the corresponding electron diffraction pattern in Fig. 2(c)–(e), it can be observed that the ZnO nanorods are highly crystalline with a lattice spacing of about 0.26 nm. This lattice spacing corresponds to the interlayer spacing of the (0 0 0 2) planes in the ZnO crystal. ZnO nanorods grew preferentially due to the higher crystal growth rate along the [0 0 0 1] direction [15]. The detailed growth mechanism of ZnO nanorod arrays due to ultrasonic irradiation has been published elsewhere [14].

It is worthwhile to mention that the proposed approach for the practical fabrication of a resistive-type ZnO gas sensor has several merits. This method does not require severe conditions such as high temperature and high vacuum. In addition, the process is simple, and the time required for the fabrication of sensor arrays is very short. For low-level sensing measurement, the concentration of the NO_2 gas was regulated by the relative concentration between dry air and the injected NO_2 gas.

In the present study, response is defined as follows:

$$\text{response}\ (\%) = \frac{(R_g - R_a)}{R_a} \times 100 \quad (1)$$

where R_a and R_g are the electric resistance in air and in NO_2 gas, respectively.

Fig. 3 shows the effect of operating temperature on response with 100 ppb NO_2. Temperature dependence on the sensing properties could result from change of the adsorption and desorption rates of the oxygen ions on the metal-oxide surface [16]. It is well known that oxygen molecules adsorbed on the surface of ZnO to form O_2^-, O^-, and O^{2-} ions from the conduction band of ZnO depending on temperature in air atmosphere. The stable oxygen ions are O_2^- below 100 °C, O^- between 100 and 300 °C, and O^{2-} above 300 °C

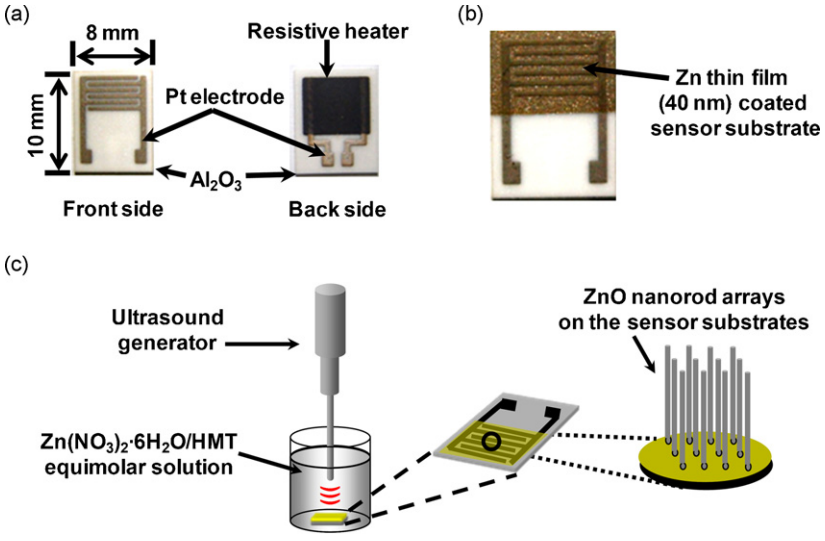

Fig. 1. (a) Photograph of sensor substrate including interdigitated comb-like Pt electrodes and a resistive heater. (b) Zn thin-film sputtered sensor substrate. (c) A schematic illustration for the sonochemical growth of vertically aligned ZnO nanorod arrays on a sensor substrate.