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Fabrication of H_2 Gas Sensor Based on ZnO Nanarod Arrays by a Sonochemical Method

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We report a simple method for fabricating ZnO gas sensors *via* a sonochemical route and their H_2 gas sensing properties. Vertically aligned ZnO nanorod arrays as a sensing material were synthesized on a Pt-electrode patterned alumina substrate under ambient conditions. The advantage of the proposed method is a high speed of processing. The gas sensor based on ZnO nanorod arrays with large specific surface area showed a high response to H_2 and a detection limit of 70 ppm at 250 °C. Also, their response and recovery time were relatively short and a complete regeneration was observed. A mechanism for sensing H_2 gas on the surface of ZnO nanorods is proposed.

Key Words : Sonochemistry, ZnO gas sensors, Nanorod arrays

Introduction

Gas sensors based on semiconductor metal oxides have attracted great attention due to their unique advantages, such as low cost, easy fabrication, high response, and good compatibility with micro-fabrication.[1-3] Zinc oxide (ZnO) gas sensors based on various forms such as thin-films, heterojunctions, nanoscale particles, and one-dimensional (1D) nanomaterials have been studied.[3-5] 1D nanostructured material-based gas sensors have attracted considerable attention due to their high surface-to-volume ratio.[6] Although 1D ZnO nanostructures can be synthesized by various methods, sensors utilizing these nanostructures have several drawbacks. For example, vapor-phase reaction approaches[7,8] require severe environmental conditions 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. However, the reaction time required for the growth of 1D ZnO nanostructured materials is relatively long (usually several hours).[9-11] In our previous study, we reported a simple and fast sonochemical route to produce vertically aligned ZnO nanorod arrays on various substrates under ambient conditions.[12,13] However, the application of this sonochemical route to a resistive-type H_2 gas sensor was not investigated.

In this paper, we report a method for fabricating a H_2 gas sensor based on vertically aligned ZnO nanorod arrays synthesized by the sonochemical method. The H_2 gas sensing properties of the sonochemically grown ZnO nanorod arrays are also described.

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Methods and Materials

A shown Figure 1(a), the sensor substrate had interdigitated comb-like Pt electrodes on the front side and a resistive heater on the back side of an alumina substrate (8 × 10 mm^2). Zn (40 nm) thin-films were successively sputtered on the interdigitated Pt electrodes. Then, the sensor substrate was immersed in 0.01 M equimolar aqueous solutions of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine ($(CH_2)_6N_4$). Ultrasonic wave (frequency: 20 kHz) was introduced in the solution at an intensity of 39.5 W/cm^2 for 1 h under ambient conditions. The sensor substrate was carefully washed with deionized (DI) water after ultrasonication, and then dried in an oven at 60 °C. Ultrasonication was performed by a sonochemical apparatus in

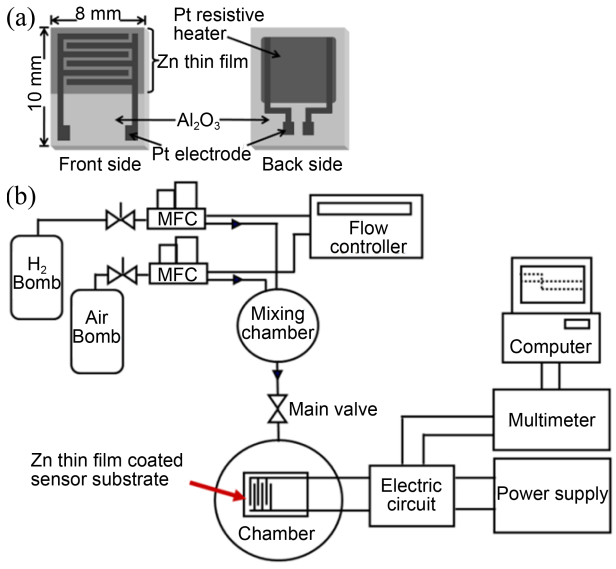

Figure 1. Schematics of (a) a sensor substrate and (b) gas sensor measurement system.

order to grow vertically aligned ZnO nanorod arrays. The morphology of as-synthesized ZnO nanorod arrays was observed by field emission scanning electron microscope (SEM, Hitachi S-4200). The crystalline properties were investigated by transmission electron microscope (TEM, JEOL JEM-2010) and X-ray diffraction (XRD, Rigaku D/Max-2500).

Figure 1(b) shows a schematic of the gas sensor measurement system. As-prepared ZnO nanorod-based sensor substrate was fixed between the pin connectors in the test chamber (1.0 L). The target gas was diluted with dry air and the diluted H_2 gas (70, 125, 250, and 500 ppm) was injected into the test chamber. The total flow rate of the diluted H_2 gas was 500 sccm. The electrical response of the sensor was measured with an automatic analysis system, controlled by a personal computer.

In this paper, the response is defined as follows:

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

where R_a and R_g are the electric resistance in dry air and H_2 gas, respectively.

Results and Discussion

Figures 2(a) and (b) show the SEM images of the ZnO nanorod arrays synthesized by ultrasound on the sensor substrate. The diameter and length of the ZnO nanorods are 50 nm and 400 nm on an average, respectively. From the TEM images and the corresponding selected area electron diffraction (SAED) patterns in Figures 2(c)-(e), it can be observed that the ZnO nanorod is highly crystalline with a lattice spacing of ~0.26 nm. This lattice spacing corresponds to the interlayer spacing of the (0002) planes in the ZnO crystal. ZnO nanorods grew preferentially due to the higher crystal growth rate along the [0001] direction.[14] The detailed growth mechanism of ZnO nanorod arrays by using ultrasonic irradiation has been previously described.[12,13]

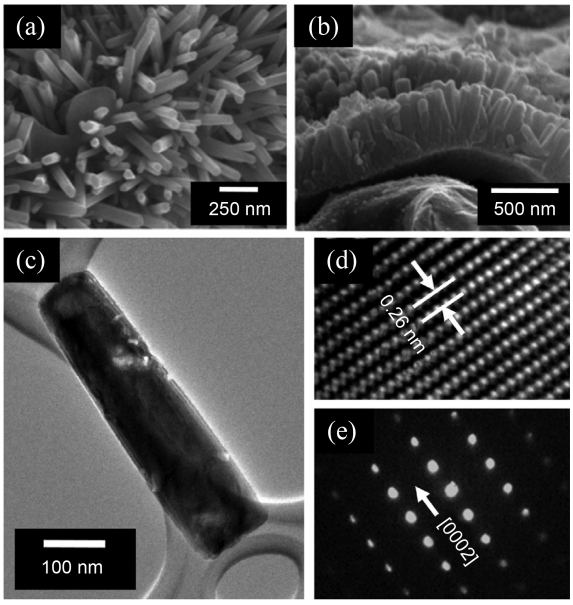

Figure 2. FE-SEM images of (a) top and (b) side view of the ZnO nanorod arrays synthesized by ultrasonication. (c) TEM, (d) HR-TEM images, and (e) ED patterns of an individual ZnO nanorod.

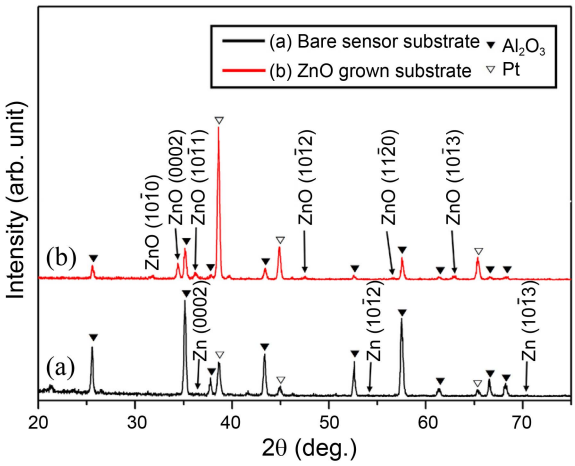

Figure 3. XRD patterns of (a) Zn thin-film deposited and (b) ZnO grown sensor substrate.

Figure 3(a) shows the XRD pattern of the substrate before ZnO nanorod growth. The Pt, Al_2O_3, and Zn peaks from the Zn thin-film are observed and showed very small intensity. The peaks of Pt and Al_2O_3 are attributed to the Pt electrode and the alumina substrate, respectively. After ZnO nanorod growth, new peaks in the XRD pattern of the substrate appeared, as shown in Figure 3(b). This finding means that the ZnO nanorod arrays with the pure hexagonal wurtzite structure, were successfully grown on the sensor substrate by a sonochemical method.

Figures 4(a) and (b) show the effect of operating temperature on sensing properties with 1% H_2 gas in dry air. The response of the sensors is affected by an operating temper-

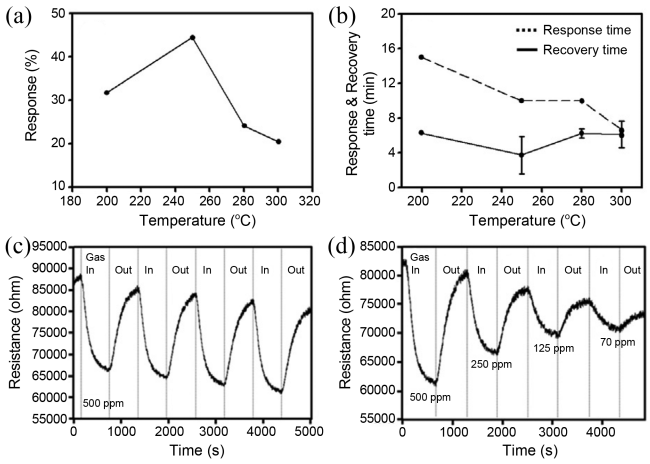

Figure 4. (a) The effect of operating temperature on response of the sensor based on ZnO nanorod arrays with 1% H_2 in dry air. (b) Response and recovery times as a function of the temperature of the ZnO nanorod-based H_2 sensor. (c) Isothermal response curves of the ZnO nanorod arrays with 500 ppm H_2 gas at 250 °C. (d) The dynamic response curves of the ZnO sensor with different H_2 gas concentrations ranging from 70 to 500 ppm at 250 °C.

ature because it exerts a strong influence on adsorption and desorption of gases on the surface of sensing materials such as metal oxides.[3] As shown in Figure 4(a), the sensor based on ZnO nanorod arrays reached a maximum response at 250 °C. In addition, the shortest recovery time of the sensor occurred at 250 °C. The operating temperature increased in the range of 200 to 300 °C, and the response time gradually decreased. The response time is defined as the time needed for the sensor to reach 63% of the maximum resistance change after the sensor is exposed to a target gas.[15] As a result, we selected the temperature of 250 °C as an operating temperature for sensing of H_2 gas with our ZnO nanorod sensor.

It is well known that oxygen molecules are 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. The stable oxygen ions are O_2 below 100 °C, O between 100 and 300 °C, and O^2 above 300 °C.[3] In the following reaction,

$$H_{2(ads)} + O^-_{(ads)} \rightarrow H_2O_{(gas)} + e^- \quad (2)$$

when the ZnO nanorods are exposed to H_2 gas, the H_2 gas reacts with the adsorbed O^- ions on the surface of ZnO nanorods. Then, the concentration of electrons on the surface of ZnO nanorod arrays increases and the resistance of the ZnO layer decreases, because the O^- ions assist in the oxidation of H_2 molecules and the electrons of oxygen ions are reinjected to the conduction band of the ZnO nanorods. Therefore, the electron concentration of ZnO nanorods increases and the resistance of the ZnO sensor decreases.

Figure 4(c) shows the isothermal response curves with 500 ppm of H_2 gas at the optimum operating temperature (250 °C). When the H_2 gas was injected into the test chamber, the resistance of the ZnO sensor decreased. The average response and recovery times were 148 and 385 s, respectively. The reversible cycles of the response curve demonstrate the stability and reproducibility of our ZnO nanorod array sensor. Figure 4(d) shows the dynamic response curves with different H_2 gas concentrations ranging from 70 to 500 ppm at 250 °C. At this temperature, the responses of the sensor were calculated by equation (1) to be 4.5, 16.3, 10.4 and 24.8% for 70, 125, 250 and 500 ppm of H_2, respectively. The maximum response of our ZnO sensor was 24.8% when 500 ppm of H_2 gas was injected. Then, the response and recovery times were 147 and 379 s, respectively. The detection limit of our ZnO nanorod-based sensor was 70 ppm with a response time of 277 s at 250 °C. In comparison with the previously reported ZnO nanorod array sensor grown by the hydrothermal method,[6] our ZnO sensor demonstrated a 1.5-fold higher response. The hydrothermal method produces ZnO nanostructured materials at low temperatures (below 200 °C).[9-11] On the other hand, the sonochemical approach can synthesize ZnO nanorods at higher temperature than the hydrothermal process, because this method uses a cavitation effect produced by ultrasound.[12,16] Thus, the ZnO nanorods synthesized by ultrasound have higher crystallinity than those synthesized by a hydrothermal method.

When we carefully compared the crystallinity of ZnO nanorods synthesized by hydrothermal (ZnO_{hyd}, in a previous report)[6] and sonochemical (ZnO_{sono}, in this report) methods, the crystalline sizes of ZnO_{hyd} and ZnO_{sono} nanorods determined by the Debye-Scherrer equation[17] were 17.3 and 28.7 nm, respectively. The ZnO_{sono} nanorods exhibited a larger particle size than the ZnO_{hyd} nanorods. Based on the TEM images and XRD data, we concluded that the ZnO_{sono} nanorods exhibit a relatively high crystallinity with larger particle size in contrast to the ZnO_{hyd} nanorods.

Conclusions

Resistive-type H_2 gas sensors were fabricated based on ZnO nanorod arrays synthesized *via* a sonochemical route under ambient conditions. The highest response of our ZnO sensor was 24.8% when 500 ppm H_2 gas was injected. This response is 1.5-fold higher than that of ZnO nanorods grown by hydrothermal methods. Sonochemical method provides simple, fast, and low cost fabrication of a ZnO-based H_2 gas sensor with excellent detection characteristics. We expect that the proposed process can also be readily utilized for the development of other aligned 1D semiconductor nanomaterial-based chemical sensors.

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