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ZnO Nanowire-Based CO Sensors Prepared at Various Temperatures

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1. Introduction

ZnO is an interesting chemically and thermally stable n-type semiconductor with a large exciton binding energy of 60 meV and a large bandgap energy of 3.37 eV at room temperature [1]. With these properties, ZnO is widely used in nanoelectronics, optoelectronics and detectors sensitive to toxic and combustible gases [2]. In recently years, one-dimensional (1D) nanowires and nanorods have attracted great attention in the field of gas sensor. Compared with bulk and thin film gas sensors, 1D nanowire gas sensors should be able to provide us larger response due to their large length-to-diameter aspect ratio and high surface-to-volume ratio. Recently, we reported the growth of ZnO nanowires on patterned ZnO:Ga/glass and patterned ZnO:Ga/SiO2/Si templates by two step oxygen injection method without catalysts [3.4]. Preliminary results of ZnO nanowire-based CO sensors prepared on patterned ZnO:Ga/SiO_2/Si templates have also been reported [4]. In this study, we report the fabrication of ZnO nanowire-based CO sensors prepared at various temperatures. Detailed properties of the fabricated sensors will also be discussed.

2. Experiments

The same gas sensor structures and the process of growth have also been accepted [3]. In this study, the mainly change various growth temperatures (i.e., either 600°C, 650°C, 700°C, 750°C or 800°C).

A JEOL JSM-6500F FESEM operated at 5 keV was then used to characterize structural properties of the as-grown ZnO nanowires. CL was also used to evaluate quality of the deposited ZnO nanowires. The measurement systems of the gas sensor have also been reported [4].

3. Results and discussion

Figures 1(a), 1(b), 1(c), 1(d) and 1(e) show cross-sectional FESEM images of the ZnO nanowires grown at 600°C, 650°C, 700°C, 750°C, and 800°C, respectively. The high density vertical well-aligned ZnO nanowires were grown on the conducting ZnO:Ga finger regions while randomly oriented ZnO nanowires were grown on the insulating SiO_2 spacer regions [4]. The vertical nanowires are observed in these regions because they were grown along the columnar grains under the sputtered ZnO:Ga film [3]. The average diameter and length of the nanowires grown at different temperatures varied significantly. Notably, the scale bars in figures 1(a) and 1(e) differed from those in Figures 1(b), 1(c) and 1(d). The average length of the ZnO nanowires increased when the growth temperature was increased from 600°C to 700°C. It is known that saturated vapor pressure of zinc in the chamber increased rapidly as the growth temperature increased. Thus, we observed an increase in average length of ZnO nanowires as we increased the growth temperature from 600°C to 700°C. At the same time, the amount of oxygen molecules that passed through the Zn vapor source decreased. Previously, Tseng et al. demonstrated that the diameter of the ZnO nanowires decreased as the oxygen flow rate decreased [6]. Thus, the average diameter became smaller as we increased the growth temperature from 600°C to 700°C. As we further increased the growth temperature, it was found that average length of the nanowires became smaller probably due to shortage of Zn with the same growth time. Figure 2 shows room-temperature CL spectra of the ZnO nanowires prepared at various temperatures. A clear sharp strong peak located at approximately 380 nm was observed from all five samples. This sharp CL peak originates from the near band-edge emission of ZnO [7]. For some samples, deep level emission (i.e., green-yellow band) was also observed as a broad peak. This deep level emission is related to the singly ionized oxygen vacancy in ZnO [8]. From these spectra, it was found that UV-to-visible CL intensity ratios were 40, 4.3, 0.5, 10.3 and 11.3 for the ZnO nanowires grown at 600°C, 650°C, 700°C, 750°C and 800°C, respectively. These values suggest that the density of oxygen vacancies is the largest for the ZnO nanowires grown at 700°C.

For ethanol gas sensing, the oxygen sorption plays an important role in electrical transport properties of ZnO nanowires. It is known that oxygen ionosorption removes conduction electrons and thus lowers the conductance of ZnO. Thus, the conductance of ZnO nanowires will increase as CO gas is introduced into the test chamber due to the exchange of electrons between ionosorbed species and ZnO nanowires [9]. Figure 3 shows detector responses of the ZnO nanowire-based CO gas sensors measured at 320°C. During these measurements, we introduced 500 ppm CO gas into a sealed chamber and measured the resistivities of the sensors both in air (R_a) and in CO gas (R_b).

The performance of the sensor was measured as the sensor response, defined by $[((R_a - R_b)/R_a) \times 100\%]$. With this definition, the sensor responses of the ZnO nanowires prepared at 600°C, 650°C, 700°C, 750°C and 800° C were 3%, 14%, 57%, 7.5% and 5%, respectively. In other words, we achieved the largest sensor response from the ZnO nanowires grown at 700°C. A possible mechanism by which ZnO nanowires sense CO gas is as follows. First, reactive oxygen species such as O_2^-, O^{2-} and O^- are adsorbed on the ZnO surface at elevated temperatures. Notably, the chemisorbed oxygen species depend strongly on temperature. At low temperatures, O_2^- is commonly chemisorbed. At high temperatures, O^- is normally chemisorbed while O_2^- disappears rapidly [10]. Accordingly, the response of the fabricated ZnO nanowire CO sensors depends strongly on the number of oxygen vacancies in the nanowires and their length-to-diameter ratio. With a large density of oxygen vacancies and a large length-to-diameter ratio, we thus achieved the largest CO sensitivity from the ZnO nanowires prepared at 700°C.

4. Conclusions

In summary, ZnO nanowire-based CO gas sensors were fabricated by growing single crystal ZnO nanowires on patterned ZnO:Ga/SiO_2/Si templates at various temperatures. It was found that average length of the nanowires increased while the average diameter of the nanowires decreased as we increased the growth temperature from 600°C to 700°C. It was also found that the nanowires became significantly shorter as we further increased the growth temperature. By measuring the resistivity change of the samples at 320°C, we found that the sensor responses were of 3%, 17%, 57%, 7.5% and 5% for the ZnO nanowires grown at 600°C, 650°C, 700°C, 750°C and 800°C, respectively..

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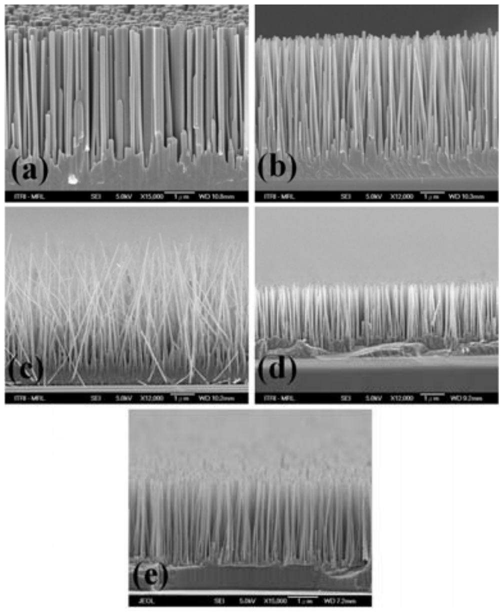

Figure 1 Cross-sectional FESEM images of the ZnO nanowires grown at (a) 600°C, (b) 650°C, (c) 700°C, (d) 750°C and (e) 800°C.

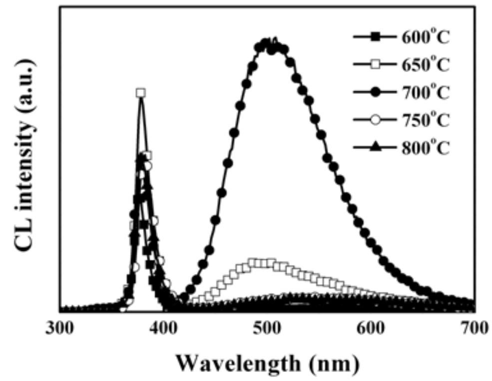

Figure 2 Room-temperature CL spectra of the ZnO nanowires prepared at various temperatures.

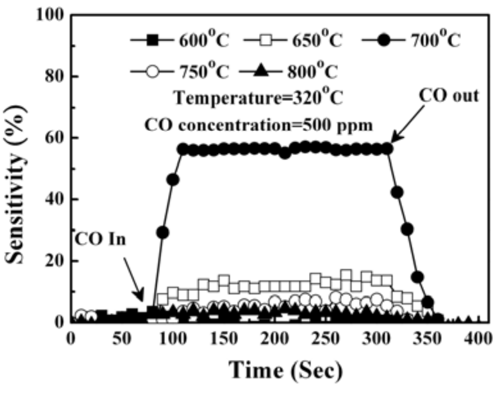

Figure 3 Detector responses of the ZnO nanowire-based CO gas sensors measured at 320°C