ZnO Nanowire-Based CO Sensors Prepared at Various Temperatures

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Abstract

In recent years, one-dimensional (1D) nanowires and nanorods have attracted great attention in the field of gas sensors. Compared with bulk and thin film gas sensors, 1D nanowire gas sensors should be able to provide us with a larger response due to their large length-to-diameter aspect ratio and high surface-to-volume ratio. ZnO nanowires have been synthesized by various methods. Recently, we reported the growth of ZnO nanowires on patterned ZnO:Ga/SiO$_2$/Si templates by a two step oxygen injection method without catalysts. Preliminary results of ZnO nanowire-based CO sensors prepared on patterned ZnO:Ga/SiO$_2$/Si templates have been reported. This study discusses the fabrication of ZnO nanowire-based CO sensors prepared at various temperatures. Detailed properties of the fabricated sensors are also discussed.

Experimental

Prior to the growth of ZnO nanowires, a Si substrate was thermally oxidized to form a 500 nm thick SiO$_2$ film. A 100 nm thick Ga-doped ZnO thin film was deposited subsequently onto the SiO$_2$ film by radio frequency magnetron sputtering. X-ray diffraction (XRD) measurement revealed that the sputtered ZnO:Ga film was oriented along the (002) direction, as shown in Fig. 1a. Using four-point resistance measurement, the sheet resistance of the sputtered ZnO:Ga film was around 200 Ω/□. Standard photolithography and etching (1% HCl for 7 min) were applied to define electrode regions and then active arm regions on the template. In the active arm region, the etching mask was designed to make the fingers of the comb-like pattern 10 μm wide and 80 μm long with a spacing of 10 μm, as shown in Fig. 1b. Two small pieces of glass were then used to cover the electrode regions so that the ZnO:Ga film was exposed only in the arm regions. The template was then placed together with 0.25 g Zn powder on an alumina boat, which was inserted into a quartz tube. To grow the ZnO nanowires, argon and oxygen gases were introduced into the reaction quartz tube. The argon flow rate and the chamber pressure were kept at 54.4 sccm and 10 Torr, respectively, throughout the growth. Then, the temperature was ramped up at 30°C/min. Initially, only Ar was introduced into the furnace. When the temperature reached 450°C, the oxygen gas started to pour into the chamber with a flow rate of 0.8 sccm.

Figure 1. (Color online) (a) XRD patterns of the ZnO:Ga thin film. (b) Schematic diagram of the patterned ZnO:Ga/SiO$_2$/Si templates.
When the temperature reached the growth temperatures (i.e., either 600, 650, 700, 750, or 800°C), the temperature ramping process that continuously grew the ZnO nanowires was stopped. The total growth time was 40 min. After the growth, photolithography and lift-off were used to deposit Au/Pd (80%:20%) onto the electrode regions of the substrate. The substrate was then annealed at 350°C for 15 min in Ar ambient to form good ohmic contacts between Au/Pd and the underlying ZnO:Ga film, completing the fabrication of ZnO nanowire gas sensors.

A JEOL JEM-2100F high resolution transmission electron microscope (HRTEM) operated at 200 kV and a JEOL JSM-6500F field emission scanning electron microscope (FESEM) operated at 5 keV were then used to characterize structural properties of the as-grown ZnO nanowires. Cathodoluminescence (CL) was also used to evaluate the quality of the deposited ZnO nanowires. During CL measurements, the electron beam power was kept at 0.405 W (accelerated at 5 keV with an emission current of 81 μA). To measure gas sensing properties of the nanowires, the sample was placed in a sealed chamber and the resistivity of the sample in air measured from the two electrodes of the patterned ZnO:Ga film at 320°C. Then, 500 ppm CO gas was injected into the chamber and the resistivity of the sample was measured again at 320°C in the presence of CO gas.

Results and Discussion

Figure 2a shows a top-view FESEM image of the ZnO nanowires grown at 600°C. It was found that ZnO nanowires were grown on both the conducting ZnO:Ga finger regions and the insulating SiO2 spacer regions. It was also found that ZnO nanowires grown on ZnO:Ga finger regions were well aligned in the vertical direction. The vertical nanowires observed in these regions should be attributed to the fact that ZnO nanowires were grown along the columnar grains of the underneath sputtered ZnO:Ga film. In contrast, ZnO nanowires grown on SiO2 spacer regions were randomly oriented. Notably, these randomly oriented ZnO nanowires provide electrical paths between the neighboring fingers. With these randomly oriented ZnO nanowires in the spacer regions, the two electrodes were no longer electrically open. Hence, the resistivity of the sample could thus be determined. Figure 2b plots current-voltage (I-V) characteristics measured from the two electrodes in air. The linear behavior reveals that good ohmic contacts were formed between the nanowires and the electrodes. Figure 3 shows the HRTEM image taken from the edge portion of the ZnO nanowires. It can be seen clearly that the ZnO crystal lattices are well oriented in this region. Such a result indicates our ZnO nanowires are structurally uniform and single crystal. Selected area electron diffraction (SAED) image of the ZnO nanowires is shown in the upper right portion of Fig. 3. The observed diffraction pattern again indicates that our ZnO nanowires are single crystal with wurtzite structure.

Figures 4a-e show cross-sectional FESEM images of the ZnO nanowires grown at 600, 650, 700, 750, and 800°C, respectively. As shown in these figures, it was found again that 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 SiO2 spacer regions. It was also found that average diameter and length of the nanowires grown at different temperatures varied significantly. Notably, the scale bars in Fig. 4a and e differed from those in Fig. 4b-d. Figure 5 summarizes the average length and diameter of these ZnO nanowires. It can be seen that average length of the ZnO nanowires increased when the growth temperature was increased from 600 to 700°C. It is known that saturated vapor pressure of zinc in the chamber increased rapidly as the growth temperature increased. Thus, an increase in average length of ZnO nanowires was observed as the growth temperature was increased from 600 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. However, the average diameter became smaller as the growth temperature was increased from 600 to 700°C. As the growth temperature was increased, it was found that the average length of the nanowires became smaller probably due to a shortage of Zn with the same growth time.

Figure 6 shows room-temperature CL spectra of the ZnO nanowires grown on patterned ZnO:Ga/SiO2/Si templates.
wires 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 bandedge emission of ZnO. 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. 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, 650, 700, 750, and 800°C, respectively. These values suggest that the density of oxygen vacancies is the largest for the ZnO nanowires grown at 700°C, followed by the ZnO nanowires grown at 650°C. Figure 7 shows detector responses of the ZnO nanowire-based CO gas sensors measured at 320°C. During these measurements, 500 ppm CO gas was introduced 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 \( \frac{(R_a - R_b)}{R_a} \times 100\% \). With this definition, it was found that sensor responses of the ZnO nanowires prepared at 600, 650, 700, 750, and 800°C were 3, 14, 57, 7.5 and 5%, respectively. In other words, the largest sensor response was achieved from the ZnO nanowires grown at 700°C, followed by the ZnO nanowires grown at 650°C. It should be noted that we performed the same experiment at least five times on each individual sample and achieved almost identical responses, which indicates that sensor responses of our devices are reproducible. 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. The reaction kinetics is described as follows:

1. \[ O_2(gas) = O_2(adsorbed) \]
2. \[ O_2(adsorbed) + e^- = O_2^- \]

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Cross-sectional FESEM images of the ZnO nanowires grown at (a) 600, (b) 650, (c) 700, (d) 750 and (e) 800°C. The scale bars in Fig. 3a and e differ from those in Fig. 3b-d.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** (Color online) Average length and diameter of the ZnO nanowires prepared at various temperatures.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Room-temperature CL spectra of the ZnO nanowires prepared at various temperatures.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Detector responses of the ZnO nanowire-based CO gas sensors measured at 320°C.
Thus, the conductance of the ZnO nanowires increases as the reducing gas (CO) is introduced into the test chamber due to the exchange of electrons between the ionosorbed species and the ZnO itself. The reaction between the CO gas and the surface of oxide sensor can be described by

\[ \text{O}_2 + \text{e}^- \rightarrow 2\text{O}^- \]  

Notably, this reaction involves a change of surface state charge. 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, the largest CO sensitivity thus achieved from the ZnO nanowires was prepared at 700°C. Figure 8 shows the response variations of the nanowires growth at 700°C upon exposure to CO gas injection and pumping. These measurements were performed by injecting various amounts of CO gas into the sealed chamber, followed by pumping at 320°C. Using the same definition, it was found that measured responses were around 34, 57, 65, 68, and 71% when the concentration of injected CO gas was 300, 500, 1000, 1500, and 2000 ppm, respectively. In other words, the sensor response increased with an increase of CO gas concentration. It was also found that the measured device resistivity responded rapidly as we injected CO gas into the chamber and pumped them away. Such a result indicates that the response speed of the fabricated sensor is also good.

To ensure reproducibility of the ZnO nanowire-based CO sensors, we prepared five samples at each temperature (i.e., 600, 650, 700, 750, and 800°C). We then measured the resistivities of these samples both in air and in 500 ppm CO gas at 320°C. Using the same definition, we subsequently calculated sensor responses of these samples. Table I summarizes measured sensor responses of these 25 ZnO nanowire-based CO sensors. It can be seen that the results are well reproducible with an inaccuracy within ±1.5%. These values again indicate that the sensors proposed in this study are indeed potentially useful.

**Conclusion**

In summary, ZnO nanowire-based CO gas sensors were fabricated by growing single crystal ZnO nanowires on patterned ZnO:Ga/SiO₂/Si templates at various temperatures. It was found that the average length of the nanowires increased while the average diameter of the nanowires decreased as the growth temperature was increased from 600 to 700°C. It was also found that the nanowires became significantly shorter as the growth temperature increased. By measuring the resistivity change of the samples at 320°C, it was found that the sensor responses were of 3, 17, 57, 7.5, and 5% for the ZnO nanowires grown at 600, 650, 700, 750, and 800°C, respectively. In addition, it was found that the device responsivities measured at 320°C were around 34, 57, 65, 68, and 71% when the concentration of injected CO gas was 300, 500, 1000, 1500, and 2000 ppm, respectively.

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**References**


**Table I.** Five of the same samples at each ZnO nanowire synthesis temperature were measured at CO gas 500 ppm and measured temperature of 320°C.

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