

ZNO NANOTUBE ETHANOL GAS SENSOR

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Introduction

In recently years, ZnO is a chemically and thermally stable n-type semiconductor with a large exciton binding energy of 60 meV and large bandgap energy of 3.37 eV at room temperature. ZnO nanotubes can be synthesized by various methods. *Duan et al.* synthesized ZnO nanotubes using a Polyethylene Glycol (PEG 2000) method [1]. *Yu et al.* fabricated highly oriented ZnO nanotubes by a general low-temperature route [2]. *Kong et al.* synthesized ZnO nanotubes on Au-coated silicon substrate by physical evaporation [3]. It has been shown that these ZnO nanotubes can be used for applications such as optoelectronic devices, field emitter and gas sensors.

For gas sensing, ZnO sensors with various forms, such as thick films, thin films, heterojunctions, nanoparticles and nanotubes have all been demonstrated. In general, oxygen-related gas sensing mechanism involves chemisorption of oxygen on the oxide surface followed by charge transfer during the reaction between chemisorbed oxygen reducing and target gas molecules. This leads to a change in surface resistance of the sensor element. Accordingly, 1D ZnO nanotubes should be able to provide us a large sensitivity due to their large length-to-diameter ratio and surface-to-volume ratio, as compared to bulk ZnO and ZnO films. In this study, we report the growth of ZnO nanotubes on sapphire (i.e., Al_2O_3) substrates by reactive evaporation. Ethanol gas sensor was then fabricated using these ZnO nanotubes. Details of the growth of ZnO nanotubes and properties of the fabricated ethanol sensor will also be discussed.

Experimental

Prior to the growth of ZnO nanotubes, we first screen printed two 15- μm -thick L-shaped Au patterns on both sides of the sapphire substrates, separately, followed by 900°C annealing for 40 min in air. As shown in figure 1, we designed the mask during screen printing so that width, length and separation of the Au patterns were 380, 1500 and 780 μm , respectively. We subsequently screen printed a ruthenium-oxide (RuO_2) layer on the backside of sapphire substrates. The samples were then annealed at 850°C for 60 min in air again. Under high current injection, this RuO_2 layer should serve as a good heater. We then grew ZnO nanotubes on front-side surface of the samples. To grow the ZnO nanotubes, we used 99.99% Zn metal powder as the zinc vapor source. We placed the

patterned substrate and Zn powder on an alumina boat, and inserted them into a quartz tube. Evaporation was then performed in the quartz tube (5-cm diameter, 120-cm long) in a horizontal tube furnace (40-cm long). We placed the zinc vapor source on the upstream side and sample was placed 16 cm away from the Zn source. The growth of ZnO nanotubes was divided into two steps. The first step was to ramp the temperature up at 30°C/min. Initially, only Ar gas was introduced into the furnace at a flow rate of 54.4 sccm. When the temperature reached 400°C, oxygen gas was poured into the chamber at a flow rate of 0.8 sccm to start the growth of ZnO nanotubes. When the temperature reached 600°C, the temperature ramping was terminated and the chamber temperature was maintained at 600°C to grow the ZnO nanotubes continuously (the temperature of the templates region was around 350°C due to the temperature gradient). The chamber pressure and the total growth time were kept at 10 Torr and 40 min, respectively. After the growth, we soldered Pt wires onto the terminals of the Au lines, as shown in figure 1. During sensitivity measurements, we closed the outlet port and injected ethanol gas into the chamber through a gas-injecting syringe. At this stage, we measured the resistivity of the sample continuously in the presence of ethanol gas (i.e., air+ethanol). After the chamber was stabilized, we opened the outlet port so that the air pump can pump the ethanol gas away.

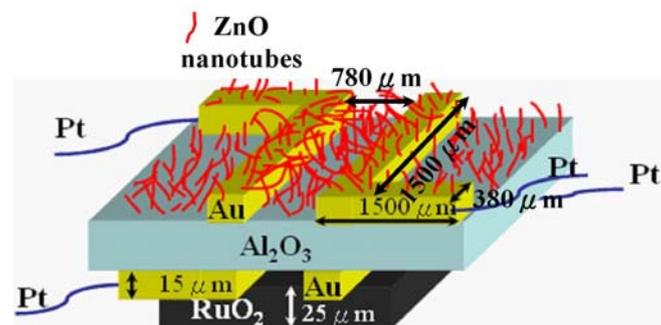


Fig.1 Schematic diagram of the fabricated ZnO nanotube ethanol gas sensor.

Result and discussion

Figure 2 shows current-voltage characteristics measured in air from the two front-site Pt wires. It can be seen that the measured current increased linearly with the applied bias. Such linear behavior reveals that good ohmic contacts were formed between the nanotubes and the underneath Au patterns.

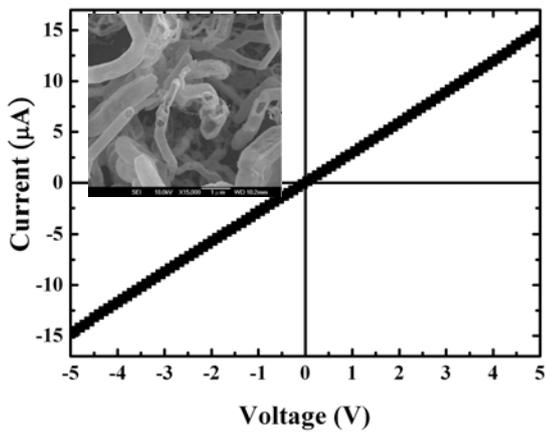


Fig.2 I-V characteristics measured in air from the two front-site Pt wires. (Insert FESEM images of the ZnO nanotubes.)

Figure 3 shows response of the fabricated ZnO nanotube ethanol gas sensor measured at various temperatures. During these measurements, we injected DC currents into backside RuO₂ heater and used a thermocouple to determine the sample temperature. We also introduced 100 ppm ethanol gas into the sealed chamber and measured the resistivity of the sample in air and in the presence of ethanol gas. It was found that measured sensitivities were around 34%, 76%, 77%, 77% and 87% when the gas sensor was operated at 90°C, 120°C, 150°C, 180°C and 230°C, respectively. In other words, the sensor response increased as the temperature increased. This should be attributed to the transformation from O₂⁻ to O₂²⁻ and O⁻ at high temperatures. Thus, ZnO nanotubes will become more conductive at high temperatures. Figure 4 shows the response variations of our ZnO nanotube sensor upon exposure to ethanol gas injection and pumping. These measurements were performed by injecting various amounts of ethanol gas into the sealed chamber, followed by pumping at 230°C. It was found that measured responsivities were around 51%, 61%, 67%, 80% and 87% when the concentration of the injected ethanol gas was 5, 10, 20, 50 and 100 ppm, respectively. In other words, the sensor response increased with an increase of ethanol gas concentration. It was also found that the measured device resistivity responded rapidly as we injected ethanol gas into the chamber and pumped them away. Such a result indicates that the response speed of the fabricated sensor is also good. It should be noted that sensitivity of ZnO nanowire sensor was much smaller. In contrast, sensitivity of ZnO nanotube sensor reported in this study could reach 77% at the same temperature when only 100 ppm ethanol gas was introduced. The much larger sensitivity observed from the nanotube sensor should again be attributed to the much larger surface-to-volume ratio of the nanotubes.

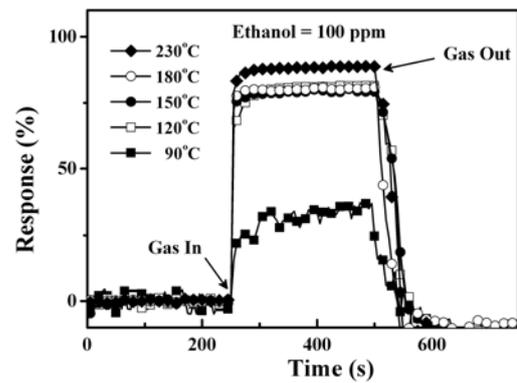


Fig.3: Response of the fabricated ZnO nanotube ethanol gas sensor measured at various temperatures.

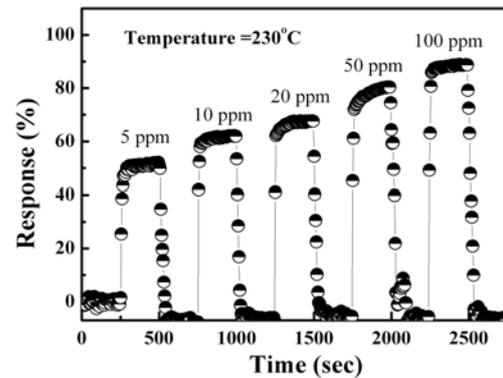


Fig.4 Response variations of ZnO nanotube sensor upon exposure to ethanol gas injection and pumping.

Conclusion

In summary, we report the fabrication of ZnO nanotube ethanol gas sensor. By introducing 100 ppm ethanol gas, it was found that the device sensitivities were around 34%, 76%, 77%, 77% and 87% when the gas sensor was operated at 90°C, 120°C, 150°C, 180°C and 230°C, respectively. Furthermore, it was found that the device responsivities measured at 230°C were around 51%, 61%, 67%, 80% and 87% when the concentration of injected ethanol gas was 5, 10, 20, 50 and 100 ppm, respectively.

References

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