ZnS modified ZnO nano-heterojunction for efficient trace H2S gas detection

Pei Ding1, a, Dongsheng Xu1, b, Haiyun Huang1, c, Pengcheng Xu2, d and Dan Zheng1, *

1School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China
2State Key Lab of Transducer Technology, Shanghai Institute of Microsystem and information Technology, Chinese Academy of Sciences, Shanghai 200050, China

*Corresponding author e-mail: zhengdan@sit.edu.cn, a dingdingpei@qq.com, b 1398899150@qq.com, c haiyunhuang@sina.cn, d xpc@mail.sim.ac.cn

Abstract. ZnO nanowires (NWs), with 200nm diameter, are synthesized by a hydrothermal method and in situ grown on the surface of a micro-sensor for detecting trace H2S gas. A chemical conversion of ZnO to ZnS is adapted to create a ZnS shell over single crystalline ZnO nanowires. The morphology and composition of both ZnO nanowires and ZnO-ZnS core-shell heterojunction are characterized and analyzed using SEM and EDS imaging. Experimental sensing results show that the core-shell geometry results in minimization of the band gap, therefore causing an improvement of sensitivity to H2S gas. At 10ppm H2S gas atmosphere, the response of ZnO-ZnS core-shell nano-heterojunction is 0.67, significantly higher than pure ZnO NWs (0.28). Therefore, modifying ZnO to form ZnO-ZnS nano-heterojunction is an effective method to improve ZnO sensor sensitivity to H2S gas.

1. Introduction
H2S is a colorless, toxic, flammable corrosive gas with a toxicity comparable to that of CO. When people inhale a small amount of H2S, it will not only cause their sense of smell to deteriorate, but also seriously damage their nervous system. In addition to harming human health, it also has adverse industrial and environmental effects such as catalyst poisoning and causing acid rain. The sensitive materials in the gas sensor are critical in detecting trace H2S and other toxic gases. Currently, the most commonly used sensitive materials include: organic compound (amino acids, vitamins), semiconductor metal oxides (tin oxide, indium oxide, zinc oxide), carbon materials (carbon nanotubes, graphene), and biological materials (enzymes, antibodies) [1-4]. Among these materials, the semiconductor metal oxides have been widely used for the monitoring of toxic and inflammable gases in ambient air due to their miniature dimensions, low cost, and high compatibility with the microelectronic fabrication process.

In recent years, the choice of sensor-sensitive materials used to detect trace amounts of H2S gas has focused on composite sensitive ZnO thin films [5], ZnO films with catalyst [6], Cu-doped SnO2 [7], heterostructure formed by SnO2 and other oxides [8], and so on. In those studies, many deficiencies have also been exposed, such as high cost, complex preparation process, high detection limit, high operating temperature, poor selectivity, and short material life.

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In order to obtain H$_2$S sensors with better quality and superior performance, in this paper, ZnO nanowires were selected as the research material. The 200nm ZnO nanowires were prepared by low temperature hydrothermal method, and a highly sensitive intrinsic ZnO nanowires gas sensor was fabricated using microelectromechanical system (MEMS) technology, achieving high sensitivity detection of trace H$_2$S gas. By modifying ZnS on the surface of ZnO nanowires to form ZnO-ZnS heterojunctions, the sensitive value at the same H$_2$S concentration is more than twice that of pure ZnO. This method provided a new way for improving the sensitivity of ZnO semiconductor gas sensors.

2. Experiment Section

2.1. Preparation of micro sensor chip

The micro-hotplate sensor chip was fabricated using MEMS technology (see Figure 1). The sensor substrate is silicon and the following four layers were integrated respectively on the substrate: SiNx (1um), Ti/Pt (20/200nm), SiO$_2$ (500nm) and Au / Cr (300/50nm). The SiNx layer acts as a mechanical support for the upper heating plate; the Pt/Ti layer is a micro heater that provides a suitable operating temperature for the sensor; the SiO$_2$ insulating layer can separate the Pt/Ti layer from the Au/Gr layer to prevent the two from communicating and affecting the experiment results; the Au/Gr interdigital electrode layer is the test electrode of the chip, and ZnO nanowires grow in the interdigitated gap.

2.2. Growth of ZnO nanowires and ZnO-ZnS heterojunctions

The ZnO nanowires were directly grown on the surface of the sensor interdigital electrodes by the hydrothermal method. First, the sensor chips were washed with acetone, ethanol and deionized (DI) water, and then dried with N$_2$. The seed solution (5 mM zinc acetate in ethanol) was uniformly dispensed in the interdigitated electrode area, which is then dried in air for 10 seconds, rinsed with acetone and blown with N$_2$. The above work was repeated 3-5 times to form seed films. Second, the sensor chips were placed in a 350°C tube furnace and calcined for 20 minutes, taken out and cooled; the calcined sensor chips were kept in sealed glass bottles which contains 50 mM aqueous solution of Zinc nitrate and hexamethylenetetramine of 1:1 molar ratio. Grown reaction was carried out in the laboratory oven at 90°C for 12h. Further, ZnO nanowires grown substrates were naturally cooled to room temperature and cleaned using DI water. ZnS shell formation was facilitated in 10 mM Na$_2$S solution, wherein primarily grown ZnO NWs films were dipped into Na$_2$S solution for 1h at 70°C. Surface treated NWs films were cleaned in DI water and ethanol to remove the residual sulfur from the nanowires surface.
3. Results and Discussion

Typical SEM image of the sensor chip is shown in Figure 2 (a), the size of which is 100μm×90μm, and the gap width of the Au test interdigital electrode is 10μm. The sensor has a suspended bottom heating structure which is insulated by air. The structural features can provide better thermal insulation due to the low thermal conductivity of air.

Figure 2(b) shows the temperature simulation result of the interdigital region at a working voltage of 1.6V. It can be seen that the temperature distribution is relatively uniform and the temperature of the entire chip area is about 200°C, so we are sure the device can provide a good and stable temperature test condition to those integrated gas sensing materials.

Figure 3 and 4 are scanning electron micrographs (SEM) images of ZnO nanowires and ZnO-ZnS heterostructure which are grown in situ between the interdigitated electrodes. Top view of pure ZnO

![Figure 2. SEM image of Heating-plate sensor chip (a) and simulation result for temperature distribution on the interlacing digital electrodes (b).](image)

NWs film (Figure 3) shows a dense and oriented array of 200nm average diameter. The pure ZnO NWs have a hexagonal structure, flat surface and clear ridge lines. The surface of ZnO-ZnS core-shell heterojunctions (Figure 4) has a large number of defects and the ridge lines are blurred. This indicates that Na₂S and ZnO have undergone ion exchange reaction on the surface of nanowires.

\[
\text{ZnO} + \text{S}^2- + \text{H}_2\text{O} \rightarrow \text{ZnS} + 2\text{OH}^- 
\]

![Figure 3. SEM images of 200nm ZnO nanowires.](image)
The driving force of this reaction comes from the large difference between the solubility of ZnO \( (6.8 \times 10^{-17}) \) and ZnS \( (1.2 \times 10^{-24}) \) under the same temperature. When ZnO and ZnS coexist in the solution, ZnS is more stable, so ZnO will gradually transform to ZnO-ZnS core-shell heterojunction, the shape of ZnO will change significantly in solution containing Na2S.

The EDS spectra of ZnO NWs and ZnO-ZnS heterojunctions are compared in Figure 5 (a) and 5 (b). They have the same elemental peaks: O, Zn and Si which are the elements contained in ZnO and the substrate Si, respectively. A new peak appearing at 2.5V in Figure 5 (b) is the characteristic peak of S element. This new peak verifies the generation of ZnS.

For comparison, the ZnO powder (size between 200-500 nm, see Figure 6(a)) was coated on the interdigitated region of the sensor chip. Its sensitivity to H2S gas is tested under the same testing conditions with ZnO nanowire (200°C). The results show that the ZnO powder does not respond in the 1-5 ppm H2S gas atmosphere, and the sensor only produces a very weak response (approximately 0.05) when the concentration of H2S reaches 20 ppm (see Figure 6 (b)).
The sensitivity curve of 200 nm ZnO nanowires to H2S gas (5-10 ppm) is showed in Figure 7(a). The 200 nm ZnO nanowires have a weak response (0.05) to 5 ppm of H2S gas. The response value increases with H2S concentration, and the response of the sensor reaches 0.28 in the 10 ppm H2S gas atmosphere. The reason is mainly due to the lower bond energy of H2S and the faster chemical reaction rate between the oxygen ions and ZnO NWs. As the H2S concentration increases, the high concentration of H2S consumes more oxygen ions and ZnO, resulting in a reduction of the sensor resistance.

Figure 7 (b) is the sensitivity curve of ZnO-ZnS to H2S. It can be seen that, at the same H2S concentration (5, 6, 7, 8, 9, 10 ppm), the response of the ZnO-ZnS heterojunction is more than double that of the pure ZnO nanowires, and the response speed of the former is faster than the latter.

Using the ZnS particles with a band gap of 3.6eV as the shell layer to cover the 3.37eV ZnO nanowire core layer, the resulting ZnO-ZnS core-shell nanowire has a significantly narrower band gap (Eg = 2.4 eV)[9]. Relative to the uncovered ZnO, the electrons will be more easily captured by other substances (such as oxygen). The amount of oxygen ions generated on the surface of ZnO-ZnS heterojunctions will be much more than that on pure ZnO NWs, which results in more oxygen ions participating in chemical reactions. Therefore, for the same concentration of reduced gas, more electrons will be transferred from the oxygen ions to the ZnO-ZnS heterojunctions which will then create a stronger response signal than the intrinsic ZnO NWs.

4. Conclusion
The 200 nm ZnO nanowires were prepared using the low temperature hydrothermal method and integrated in situ on the sensor chip fabricated by the MEMS process. Then the surface of ZnO nanowires were modified with a layer of ZnS using the ion exchange method to form a ZnO-ZnS heterojunction, and trace H2S gas sensitivity of ZnO nanowires and the ZnO-ZnS heterojunction were tested. It is found that, at lower test temperature (200°C), ZnO particles with size 200-500nm are not sensitive to H2S gas, but 200 nm ZnO nanowires show a extremely sensitive response to H2S. At the same working temperature and gas concentration, the sensitivity of ZnO-ZnS heterojunction to H2S is higher than that of ZnO nanowires, and the response speed of the former is faster than the latter. This fully demonstrates that the ZnS oxygen barrier layer plays a positive role in the gas sensing process, resulting in an improvement of H2S sensitivity than pure ZnO.

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