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Highly sensitive VOC sensors using NiO-decorated ZnO nanowire networks: the effect of radial p-n junction

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Abstract

The pristine, NiO-decorated, and NiO-doped ZnO nanowires were prepared by vapor phase reaction and their gas sensing characteristics were investigated. The decoration of p-type NiO on n-type ZnO nanowires significantly enhanced the responses to volatile organic compounds such as C_2H_5OH and HCHO. In contrast, the doping of NiO into the lattice of ZnO NW deteriorated the gas sensing characteristics. The enhanced gas sensing characteristics of NiO-decorated ZnO nanowires were explained by the extension of the electron depletion layer due to the formation of nanoscale p-n junctions between p-type NiO and n-type ZnO.

Key words: Nanowires, Volatile Organic Compounds, Gas Sensors, p-n junctions

Introduction

Oxide semiconductor nanowire (NW) networks are promising gas sensing materials with high gas response, good stability and fast responding kinetics on account of their high surface area to volume ratio, excellent crystallinity and gas accessible networked structures [1]. The gas sensing characteristics can be enhanced by the the addition of noble metal catalysts [2]. The metal oxide additives can be also used to design a high performance gas sensor via controlling donor density, changing the acid-base properties of surface, and varying electronic interaction between additives and sensing materials. In particular, when the p-type oxide material such as NiO are added to n-type sensing materials such as SnO_2 and ZnO, the p-type additive can either incorporate into n-type semiconductors or form second phase. Accordingly, the incorporation of Ni-species into the lattice of n-type semiconductor and the formation of a secondary NiO phase will have a completely different impact on the gas sensing behavior, i.e., a change in donor density and an extension of the electron depletion layer near the interface of the p-n junction, respectively

In this study, the role of p-type NiO additive in the gas sensing reaction of n-type ZnO NWs were determined using three different ZnO NW network sensors: (1) pristine ZnO NW networks; (2) NiO-decorated ZnO NW networks (ZnO NW networks decorated with discrete form of p-type NiO particles, p-n junction) and (c) Ni-doped ZnO NW networks (NiO-doped ZnO networks, incorporation of Ni into ZnO lattice).

Experimental

ZnO NWs were grown on the alumina substrates (size: 1.5 ×1.5 mm^2) with two Au electrodes (on its top surface) by thermal evaporation using a mixture of ZnO powders (99.9%, Aldrich), graphite powders (<20 micron, Aldrich) and Sn powders (99.8%, Acros). The source (ZnO: graphite: Sn = 1 : 1 : 0.01 by weight%) was loaded in the Al_2O_3 boat and was located in the center of the quartz tube (diameter: 2.5 cm). The alumina substrates were placed 5 cm downstream from the source. After evacuating the quartz tube to ~ 9 x 10^{-2} torr using a rotary pump, the furnace temperature was increased to 900°C. The NiO-decorated ZnO NWs were prepared using the following procedures. The as-grown ZnO NWs on the patterned Al_2O_3 substrates and $NiCl_2$ powders (99.99%, Aldrich) were placed in the left and right part of Al_2O_3 boat (length 4 cm), respectively. After evacuating the quartz tube to ~ 9 x 10^{-2} torr using a rotary pump, the furnace temperature was increased to 500 °C. The lenticular/angular configuration of nano-scale NiO islands could be coated on the surface of the ZnO NWs by a reaction between the source and Ar gas (Ar: 200 sccm). The Ni-doped ZnO NWs were prepared using 2 zone quartz tube reactor. $NiCl_2$ (99.99%, Aldrich) powders were

located at the 1st zone (temperature: 600 °C). The mixture between ZnO powders (99.9%, Aldrich), graphite powders (< 20 micron, Aldrich) and Sn powders (99.8%, Acros) were located at the 2nd zone (temperature: 900 °C). An alumina substrate was located on the top of the mixture. The distance between $NiCl_2$ and the mixture 10 cm. Argon gas was flowed while increasing or decreasing the temperature of the reactor. The Ni-doped ZnO NWs were formed by a reaction between the sources and Ar-O_2 mixture gas (Ar: 100 sccm, O_2:1 sccm).

Result and Discussion

The ZnO NWs were grown directly on the alumina substrate with two gold electrodes and discrete configuration of NiO nanoclusters were decorated on ZnO NWs by vapor phase reaction (Fig. 1a). The gold electrodes acted as a catalyst for the growth of ZnO NWs by the vapor–liquid–solid mechanism, which facilitated networking between NWs with highly porous structures and increased the connectivity between the electrodes and NWs. The NiO-decorated ZnO NWs were 30-70 nm thick (Fig. 1b).

Pristine ZnO NWs showed the clean surface and were identified as single crystalline ones (Fig. 2a). The surfaces of NiO-doped NWs were also clean (not shown). Figure 2b shows the TEM image of NiO-deocorated ZnO NWs. The NiO nanoparticles were uniformly formed on the surface of ZnO NWs, and the size of NiO nanparticles ranged from 10 to 40 nm. In the lattice-resolved TEM image (Fig. 2c), of the NiO-decorated ZnO NWs, the $(01\bar{1},10)$ fringes of ZnO were seperated by 2.81 Å and the (220) fringes of NiO nanoparticles were seperated by 1.47 Å (Fig. 3(c)). This indicates that rough surfaces of NWs in Fig. 1b emanate from the formation of NiO nanoclusters.

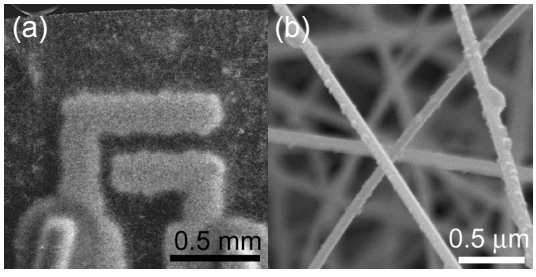

Fig. 1: SEM images of NiO-decorated ZnO nanowire sensor on alumina substrate

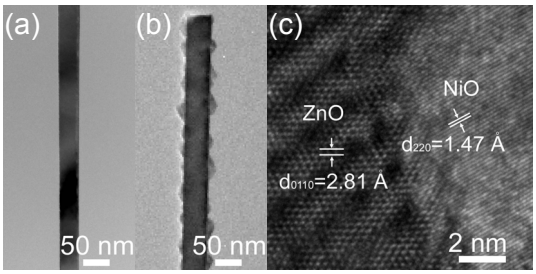

Fig. 2: TEM images of (a) pristine ZnO NW; (b) and (c) NiO-decorated ZnO NW

The high-angle annular dark field (HAADF) scanning TEM (STEM) image and the elemental mapping of Zn, Ni and O (Fig. 3) by the energy dispersive X-ray spectroscopy (EDS) clearly showed the nanoparticles on the surface of the ZnO NW to be NiO. Both the lattice image (Fig. 2c) and the compositional profile (Fig. 3) indicates the distinct interface between ZnO NW and NiO nanoparticles.

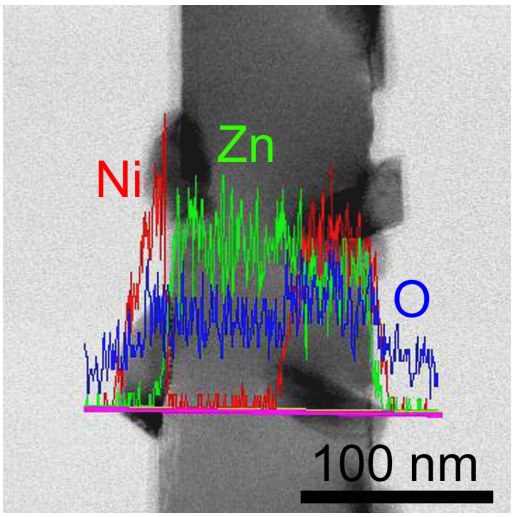

Fig.3: High-angle annular dark field (HAADF) scanning TEM (STEM) image and EDS elemental mapping of Zn, Ni, and O

The formation of discrete NiO nanoclusters and the incorporation of Ni into ZnO lattice in NiO-decorated ZnO NWs and Ni-doped ZnO NWs, respectively, were verfied by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and the sensor resistance in air.

The gas responses of pristine, NiO-decorated and Ni-doped ZnO NW network sensors to 5 ppm C_2H_5OH, HCHO, CH_3CHO, CO, C_3H_8, H_2, benzene, toluene, and p-xylene were measured at 450 °C. All the sensors showed n-type gas

sensing behaviors. In particular, n-type gas sensing in NiO-decorated ZnO NWs confirms that conduction occurs along continuous n-type ZnO NWs rather than the discrete configuration of p-type NiO nanoparticles. Regardless of sensors, the responses to C_2H_5OH and HCHO were higher than those to other gases. However, the abosolute values of gas response were significantly different according to the sensor configuration. The response (R_a/R_g, R_a: resistance in air and R_g: resistance in gas) to 5 ppm C_2H_5OH of NiO-decorated ZnO NWs at 450 °C was 29.04, which was 7.96-fold higher than that of pristine ZnO NWs (3.65) (Fig. 4). It is interesting that the doping of NiO deteriorated the response to 5 ppm C_2H_5OH down to 2.18.

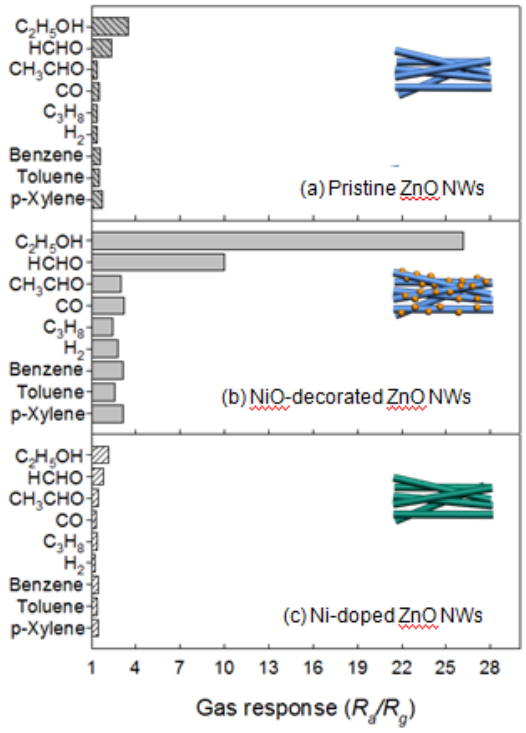

Fig. 4: Gas responses (R_a/R_g, R_a: resistance in air and R_g: resistance in gas) to C_2H_5OH, HCHO, CH_3CHO, CO, C_3H_8, H_2, benzene, toluene, and p-xylene at 450 °C.

The doping of Ni to ZnO NWs decreased the R_a value and deteriorated gas sensing characteristics. It has been reported by He *et al*, that the electrical conductivity of Ni-doped ZnO NWs was 10-20 times higher than that of pristine ZnO NWs due to the co-existence of Ni^{3+} and Ni^{2+} [3]. In contrast, the decoration of p-type NiO nanoparticles on n-type ZnO NWs increased the R_a value two orders of magnitude by the extension of electron depletion layer near the p-n junction and greatly enhanced the responses and selectivity to C_2H_5OH and HCHO (Fig. 3). This clearly indicates that the sensing mechanisms of NiO-decorated and Ni-doped ZnO NW sensors should be understood in the completely different framework.

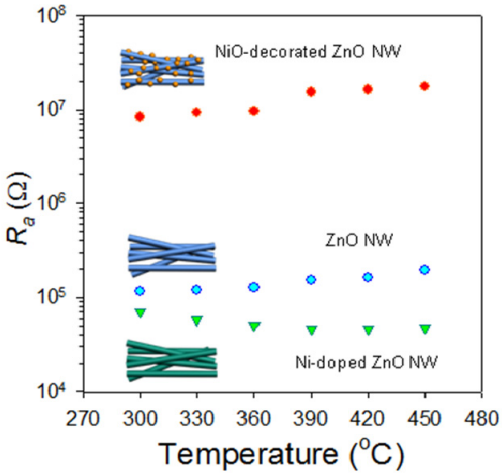

Fig. 5: Resistance in air (R_a) values of NiO-decorated ZnO NW, ZnO NW, and Ni-doped ZnO NW

Summary

The role of NiO in the gas sensing characteristics of ZnO nanowires was investigated. The gas response and selectivity to C_2H_5OH and HCHO were significantly by the decoration of NiO nanoclusters on ZnO nanowires. In contrast, gas responses C_2H_5OH and HCHO were deteriorated by the incorporation of NiO into ZnO lattice. The enhancement of gas responses was attributed to the extension of electron depletion layer near the p-n junctions.

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