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 C₂H₅OH 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 SnO₂ 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 mm²) 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 Al₂O₃ 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 Al₂O₃ substrates and NiCl₂ powders (99.99%, Aldrich) were placed in the left and right part of Al₂O₃ 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. NiCl₂ (99.99%, Aldrich) powders were
located at the 1\textsuperscript{st} 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 2\textsuperscript{nd} zone (temperature: 900 °C). An alumina substrate was located on the top of the mixture. The distance between NiCl\textsubscript{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\textsubscript{2} mixture gas (Ar: 100 sccm, O\textsubscript{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-decorated ZnO NWs. The NiO nanoparticles were uniformly formed on the surface of ZnO NWs, and the size of NiO nanoparticles ranged from 10 to 40 nm. In the lattice-resolved TEM image (Fig. 2c), of the NiO-decorated ZnO NWs, the (01\textsubscript{1}-10) fringes of ZnO were separated by 2.81 Å and the (220) fringes of NiO nanoparticles were separated by 1.47 Å (Fig. 3c). This indicates that rough surfaces of NWs in Fig. 1b emanate from the formation of NiO nanoclusters.

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.

The gas responses of pristine, NiO-decorated and Ni-doped ZnO NW network sensors to 5 ppm C\textsubscript{2}H\textsubscript{5}OH, HCHO, CH\textsubscript{3}CHO, CO, C\textsubscript{3}H\textsubscript{8}, H\textsubscript{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 C₂H₅OH and HCHO were higher than those to other gases. However, the absolute values of gas response were significantly different according to the sensor configuration. The response \((R_a/R_g, \text{ resistance in air and } R_g: \text{ resistance in gas})\) to 5 ppm C₂H₅OH 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 C₂H₅OH down to 2.18.

Fig. 4: Gas responses \((R_a/R_g, \text{ resistance in air and } R_g: \text{ resistance in gas})\) to C₂H₅OH, HCHO, CH₃CHO, CO, C₃H₆, H₂, 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 Ni³⁺ and Ni²⁺ [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 C₂H₅OH 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 C₂H₅OH and HCHO were significantly by the decoration of NiO nanoclusters on ZnO nanowires. In contrast, gas responses C₂H₅OH 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.

**References**