Highly selective and sensitive xylene sensors using Ni-doped branched ZnO nanowire networks

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ABSTRACT

Branched ZnO nanowires (NWs) doped with Ni were grown by a three-step vapor phase method for the sensitive and selective detection of *p*-xylene. ZnO NWs were directly grown on sensor substrates with Au electrodes, which were transformed into NiO NWs by the thermal evaporation of $NiCl_2$ powder at 700 °C. ZnO branches doped with Ni were grown from NiO NWs by the thermal evaporation of Zn metal powder at 500 °C. The stem NiO NWs played the role of catalyst for the growth of ZnO branches through vapor–liquid–solid mechanism. The Ni-doped branched ZnO NWs showed enhanced gas response (S = resistance ratio) to methyl benzenes, especially to 5 ppm *p*-xylene (S = 42.44) at 400 °C. This value is 1.7 and 2.5 times higher than the responses to 5 ppm toluene (S = 25.73) and C_2H_5OH (S = 16.72), respectively, and significantly higher than the cross-responses to other interfering gases such as benzene, HCHO, trimethylamine, H_2, and CO. The selective detection of xylene was attributed to the catalytic role of the Ni component. This novel method to form catalyst-doped hierarchical ZnO NWs provides a promising approach to accomplish superior gas sensing characteristics by the synergetic combination of enhanced chemiresistive variation due to the increased number of branch-to-branch Schottky barrier contacts and the catalytic function of the Ni dopant.

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1. Introduction

Volatile organic compounds (VOCs) such as benzene, toluene, xylene (BTX), and HCHO are representative indoor pollutants. Since people spend most of their lives indoors, which leads to prolonged exposure, even low concentrations of VOCs can significantly affect human health. Distinguishing a single gas among the BTX gases using a simple handheld device is important and necessary because of their different effects on human health; but it still remains challenging due to similar chemical properties of aromatic hydrocarbons. Although there have been conventional analytical devices for detecting VOCs, most of them require expensive equipment and tedious sample preparation steps [1,2]. Metal oxide semiconductor nanowires (NWs) and their networks with excellent crystallinity, high surface-to-volume ratio, superior gas accessibility, and high stability are viable alternatives to achieve highly sensitive, rapid-responding, portable, stable, and cost-effective VOC sensors [3–5]. Unlike nanoparticles, porous NW network structures have a lower tendency to form agglomerates, and thus, comparably higher surface area and wire-to-wire contacts can contribute to the enhanced gas sensing reaction. Accordingly, many oxide semiconductor NWs such as ZnO, SnO_2, In_2O_3, and CuO NWs have been widely explored in the fields of gas sensors [6–10]. In most cases, they often showed the highest response to highly reactive C_2H_5OH. Accordingly, the addition of a catalytic material by either doping or surface modification is required in order to achieve selective and sensitive detection of other analyte gases such as BTX.

In general, the gas responses of p-type metal oxide semiconductors such as NiO, CuO, Cr_2O_3, and Co_3O_4 are known to be lower than those of n-type metal oxide semiconductors, such as SnO_2, ZnO, In_2O_3, and TiO_2, with the same morphological configuration [11]. Thus, the design of gas sensors using p-type oxide semiconductors is still in the nascent stage of research. However, owing to their multi-valence properties and abundant oxygen adsorption [12], p-type metal oxide semiconductors are known as excellent catalysts to promote the oxidation of relatively less reactive BTX gases at low temperature [13,14], indicating that the p-type oxide semiconductors can be doped or added to n-type oxide semiconductor gas sensors to enhance the selectivity to BTX gases without deteriorating the high gas response.

The gas response of oxide NW networks can be enhanced by increasing the number of chemiresistive wire-to-wire contacts

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[15,16]. In this perspective, the brush-like hierarchical oxide nanostructures or the branched ZnO NWs are excellent nano-architectures because high gas-sensing reaction can be achieved via involving a large number of chemiresistive wire-to-wire contacts. Previously, we demonstrated that Co-doped branched ZnO NWs can be grown by vapor phase reaction on CoO NWs and exhibit unique gas sensing characteristics such as selective detection of xylene [17]. Accordingly, in this study, in order to confirm the validity of the aforementioned novel concept on the growth mechanism and enhanced gas sensing characteristics of branched oxide NW networks, we prepared branched Ni-doped ZnO NWs by a three-step vapor phase reaction (the growth of ZnO NWs, the transformation of ZnO NWs into NiO NWs, and the growth of branched Ni-doped ZnO NWs on the stem NiO NWs) and investigated their gas sensing characteristics. The similarity or difference in the transformation from ZnO into NiO NWs, the growth of Ni-doped ZnO branches, and the catalytic activity of the Ni component in gas sensing characteristics, will lead to either the possibility of tuning gas sensing characteristics or the confirmation of a general concept. The main focus of the study is directed at the formation mechanism and material characterization of Ni-doped branched ZnO NWs and the reason for the selective detection of p-xylene with negligible interference from gases such as C_2H_5OH, toluene, benzene, and HCHO.

2. Experimental

2.1. Sample preparation

ZnO NWs were grown on alumina substrates (1.5×1.5 mm^2, thickness, 0.25 mm) with two gold electrodes (electrode length, 1 mm; separation, 0.2 mm) by thermal evaporation of a mixture of ZnO (99.9%, Sigma Aldrich), graphite (<20 μm, Sigma Aldrich), and Sn (99.8%, Acros) powders (Fig. 1a). The source powder (ZnO: graphite: Sn = 1: 1: 0.1 wt%) was loaded in an Al_2O_3 boat that

was located at the center of a quartz tube (diameter: 2.5 cm) and the alumina substrates were placed 5 cm downstream from the source. The Sn powder was added as growth catalyst of ZnO NWs along the [0 1 $\bar{1}$ 0] direction with high reproducibility [18,19]. The inside of the quartz tube was evacuated to ∼9×10^{-2} Torr using a rotary pump and the furnace temperature was increased to 900 °C. The ZnO NWs were grown for 20 min by the reaction between the source powder and mixture of Ar-O_2 gas (Ar, 100 sccm, O_2, 0.2 sccm). The gold electrodes on the substrate acted as the catalyst for the vapor–liquid–solid (VLS) mechanism, which enabled the formation of NW networks with highly porous structures and improved the connectivity between the NWs and the electrodes. The as-grown ZnO NWs were transformed into NiO NWs via the cation exchange reaction by thermal evaporation of $NiCl_2$ powder (99.99%, Sigma Aldrich) at 700 °C (Fig. 1b). The quartz tube was evacuated to ∼9×10^{-2} Torr and Ar (200 sccm) was flowed for 10 min. The NiO NWs were placed 0.5 cm from the Zn powder (99.995%, Sigma Aldrich) in the Al_2O_3 boat that was placed at the center of the quartz tube in the horizontal furnace. After evacuating the tube using a rotary pump to ∼9×10^{-2} Torr, the furnace was heated to 500 °C and was kept for 10 min under mixed Ar/O_2 gas (Ar, 200 sccm, O_2, 1.0 sccm). The corresponding reaction resulted in the growth of Ni-doped ZnO branches from the NiO NWs in which NiO acted as the growth catalyst for the VLS mechanism (Fig. 1c and d) [20].

2.2. Characterization

The morphologies of pristine ZnO NWs, NiO NWs, and Ni-doped branched ZnO NWs were analyzed using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEOL, JEM-2100F). The phase and crystallinity of the NWs were analyzed by X-ray diffraction (XRD, Rigaku D/MAX-2500-V/PC) using Cu Kα radation. The
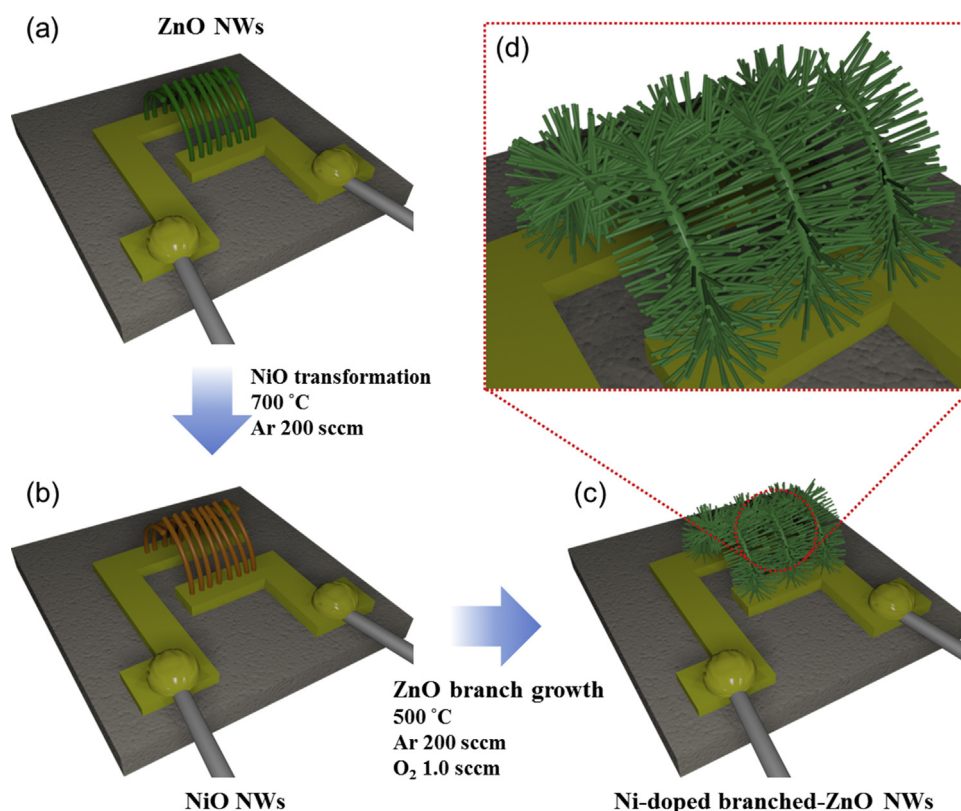

Fig. 1. (a) Growth of ZnO NWs on alumina substrate with Au electrodes, (b) transformation of ZnO NWs into NiO NWs, and (c and d) growth of ZnO branches from NiO NWs.