In-decorated NiO Nanoigloos Gas Sensor with Morphological Evolution for Ethanol Sensors

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Abstract

We investigated the facile and effective strategy for sensitive and selective C$_2$H$_5$OH sensors based on the In-decorated NiO nanoigloos. The In-decorated NiO nanoigloos is fabricated by RF sputtering using 750 nm-diameter polystyrene beads using a soft-template. The morphological evolution based on the Van der Drift model was generated through a heterojunction between In metal and NiO, resulting in a pyramidal rough surface. Upon decorating the In on the NiO surface, high sensitivity and selectivity to C$_2$H$_5$OH were observed, and gas sensing mechanism was demonstrated by a high surface-to-volume and double Schottky barrier. We are confident that the method presented in this study will have a significant impact on the fabrication of effective nanostructures and their application for the gas sensors.

Keywords: Gas sensors, Metal oxide semiconductors, NiO, Morphological evolution, Heterojunction

1. INTRODUCTION

According to the World Health Organization (WHO) statistics for 2019, indoor and outdoor air pollution is the most significant environmental factor that can affect the human body [1]. More than 7 million people die each year from causes related to air pollution. The main reason of the air pollution is considered as certain gases such as particulate matter (PM), ozone (O$_3$), nitrogen dioxide (NO$_2$) and volatile organic compounds such as benzene (C$_6$H$_6$), xylene (C$_8$H$_10$), toluene (C$_7$H$_8$), and ethanol (C$_2$H$_5$OH). Especially, exposure to ethanol can cause health problems such as difficulty breathing, headache, drowsiness, eye irritation, and liver damage [2]. In general, these gases have been generated from power plants, factories, and transportation, and inhalation may cause headaches, respiratory mucosae, and eventually results in cancer.

To detect and monitor air pollutants, high sensitivity and single-gas selectivity are highly demanded. Compared with various types of sensors including optical gas sensors and electrochemical sensors, metal oxide semiconductor based sensors have been extensively studied because of their simplicity, cost-effectiveness, and high sensing performance [3,4]. The mechanism of the metal-oxide sensors has been universally demonstrated through the changes in electrical conductivity caused by the adsorption and desorption of gas molecules on the surface of the semiconductors [5]. However, the challenges, including single-target detection, humidity tolerance, and long-term stability, still remain [6,7]. To overcome these drawbacks, a number of approaches have been conducted through doping, heterojunction, catalyst decoration, and morphological evolution [8-10]. Thompson et al., demonstrated morphological evolution based on the Van der Drift growth model as a facile and effective strategy for gas sensor development [11,12]. As a polycrystalline thin film grows in a specific direction, its morphological evolution is accompanied by a shape change in the direction of minimal strain, surface, or interface energy, and this preferred orientation leads to a large chemical potential on the surface [13-15]. As our previous report, a decoration of heterophase nanoparticles on a metal-oxide surface is an effective way to generate the morphological evolution and realize high-performance NO$_2$ sensors [16].

In this study, we investigated the morphological evolution induced by a heterojunction of NiO nanoigloos decorated with In$_2$O$_3$ nanoparticles. The morphological evolution of pyramidal...
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rough surface with a (111) plane preferred orientation was observed by SEM and XRD upon decorating the hetero junction of NiO and In$_2$O$_3$. In addition, the gas sensing properties of the fabricated samples were evaluated using various gases, and a superior C$_2$H$_5$OH detection was observed. The mechanism of the morphological evolution and gas detection was demonstrated through the Van der Drift model and catalytic effect of the heterojunctions.

2. EXPERIMENTAL

2.1 Fabrication process

Interdigitated electrodes (IDEs) were fabricated using a Pt/Ti (150/30 nm) on a 4 inch SiO$_2$/Si substrate through photolithography. The distance between Pt electrodes is 5 μm. Before drop coating polystyrene (PS) beads, the surface of Pt-IDEs was treated to enhance hydrophilicity using a microwave plasma Asher based O$_2$ plasma (Plasma Finish V15- G) at an RF power of 100 W for 5 min. To fabricate In-decorated NiO nanoigloos, an aqueous suspension of 750 nm-diameter polystyrene beads (2.6 wt %, Polysciences, Warrington) was used as a soft template. Then Pt-IDEs dried at room temperature with a 60 Hz vibration for a uniform monolayer polystyrene bead. We deposited In nanoparticles before and after the deposition of 150 nm-thick NiO film to synthesize double-side In-decorated NiO using RF sputtering with a base pressure, working pressure, and Ar flow rate of $3 \times 10^{-6}$ Torr, 10 mTorr, and 30 sccm, respectively. The RF power and growth rate of the In nanoparticles were 20 W and 4 nm/min, and the nickel oxide thin films were 100 W and 20 nm/min, respectively. The fabricated samples were annealed in ambient air at 550 °C for 2 h to evaporate the PS beads and to crystallize the In-decorated NiO nanoigloos with hollow structure.

2.2 Characterization & Gas sensor measurements

Field-emission SEM (Inspect F50) was performed out to examine the morphologies of the fabricated samples with an accelerator voltage of 15 kV and a working distance of 10 nm. To investigate the crystallinity of the In-decorated NiO nanoigloos, glancing-angle XRD (D8 advance) was utilized over a range of 20–80° at a fixed incident angle of 2° with CuKα radiation (1.5418 Å wavelength) as the X-ray source.

The gas sensing properties by externally heating a quartz tube in a box furnace. The gas flow rate was maintained at 1000 sccm

![Fig. 1. Schematic of fabrication procedures of In-decorated NiO nanoigloos.](image)

![Fig. 2. SEM images of (a) PS beads, and the (b) bare and (c) In-decorated NiO nanoigloos. Cross-sectional images of (b) and (c) are (d) and (e), respectively. (f) XRD of bare and In-decorated NiO nanoigloos.](image)