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Bimetallic Pd/Pt nanoparticle-functionalized SnO_2 nanowires for fast response and recovery to NO_2

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ABSTRACT

Bimetallic Pd/Pt nanoparticles were used to functionalize networked SnO_2 nanowires in order to realize a fast response and recovery ability in their NO_2-sensing performance. Pd and Pt nanoparticles with diameters of 10–40 nm were uniformly decorated on networked SnO_2 nanowires via a sequential γ-ray radiolysis. The NO_2-sensing performance in terms of response and recovery times of the bimetallic Pd/Pt-functionalized SnO_2 nanowire sensor was compared to the ones based on bare SnO_2 nanowires, or functionalized by either Pd or Pt nanoparticles, respectively. The bimetallic functionalized SnO_2 nanowire sensor revealed faster response (13 s) and recovery (9 s) times due to the synergic effect of individual Pd and Pt nanoparticles. The results indicate that the approach of a functionalization by bimetallic nanoparticles has a promising potential to enhance the sensing performances of oxide nanowires.

1. Introduction

Continuous progress in metal oxide-based nanomaterials, such as nanowires [1], nanofibers [2], nanorods [3], nanobelts [4], and hollow structures [5] has led to the rapid development of devices in the field of gas sensors. In recent years, nanowires have received considerable attention because of their excellent gas response and good thermal stability due to their small dimension, as well as unique physical and chemical properties. Accordingly, considerable efforts have been directed towards the development of a novel method of sensor fabrication based on oxide nanowires to improve their gas response, selectivity, and response/recovery times. Such chemical gas sensors, based on oxide nanowires, are usually fabricated using a single nanowire. However, single-nanowire sensors have a number of drawbacks and are unlikely to be the material of choice in future chemical sensor devices. The difficulties using a single nanowire are attributed to the complicated fabrication processes, poor reproducibility, and high costs. Attempts to resolve the problem of single-nanowire sensors have involved the use of either a vertically aligned nanowire array [6] or randomly networked nanowires [7]. Comparing with single-nanowire sensors, networked nanowire sensors were fabricated with excellent reproducibility in a cost-effective way [8–10].

Although semiconducting metal oxide nanowires have been used for the detection of toxic gases and various volatile organic compounds, their sensing performances need to be improved to expand their present fields of application. One of the routes to improving the sensing performances is to functionalize the surface of nanowires with catalytic nanoparticles [11]. In recent years, some research groups have made tremendous efforts toward the synthesis of oxide nanowires with nanosized noble metals, by using various methods [12–14]. To date, metallic catalysts, such as Ag [15], Au [16], Pd [17], Pt [18], and Rh [19] nanoparticles were used to enhance the sensing capabilities of oxide nanowires

In our earlier studies [13,17], the effects of individual Pd- and Pt-functionalized groups on the gas sensing characteristics of SnO_2 nanowire sensors were investigated. Compared to pure SnO_2 nanowires, the nanowires functionalized with either Pd or Pt nanoparticles showed improved sensing capabilities. In particular, on the one hand, the Pd functionalization led to a faster response time [17]. On the other hand, a faster recovery time was achieved by the Pt functionalization [13]. Accordingly, it seems to be interesting to know whether a bimetallic Pd/Pt functionalization can induce synergic effects, that is, faster response and recovery times.

In this work, we fabricated networked SnO_2 nanowires on the basis of a selective growth technique of oxide nanowires. Their surfaces were functionalized by bimetallic Pd/Pt nanoparticles via γ-ray radiolysis in order to achieve a combination of the two advantages of individual Pd and Pt functionalization. To the best of our knowledge, no work has been carried out on the gas-sensing performances of SnO_2 nanowires coated by bimetallic Pd/Pt nanoparticles.

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2. Experimental details

First, networked SnO_2 nanowires were grown by the vapor-phase growth method. For the selective growth of SnO_2 nanowires, patterned-interdigital electrodes (PIEs) were made on SiO_2-grown Si(1 0 0) substrates using a conventional photolithographic process. The details of the PIEs were as follows. The total number of electrode pads consisting the PIEs was 96. One electrode pad was 6.8 mm long and 20 μm wide. The gap between the neighboring electrode pads was 10 μm.

The electrode was a try-layer consisting of Au (3 nm)/Pt (200 nm)/Ti (50 nm) that had sequentially been deposited by a sputtering technique. The Au top layer served as a catalyst for the selective growth. The substrates, on which the PIEs had been created, were introduced into a horizontal quartz tube furnace, in which an alumina crucible containing Sn powders (99.9%) was placed. The furnace was then evacuated by a rotary pump down to a pressure of 8×10^{-2} Torr and heated to 900 °C for 5 min. During the VLS growth of the SnO_2 nanowires, N_2 and O_2 flowed through the quartz tube at rates of 300 and 10 standard cubic centimeter per minute (sccm), respectively. The experimental condition used to synthesize SnO_2 nanowires are described in detail in our previous report [20].

For the synthesis of bimetallic Pd/Pt nanoparticles, γ-ray radiolysis was used. The precursor solutions for the γ-ray radiolysis were prepared as follows. A solution for Pd was prepared by dissolving 0.051 mM of palladium chloride ($PdCl_2$, Kojima Chemicals Co.) in a mixed solvent of acetone (50 vol.%) and 2-propanol (50 vol.%) at room temperature under vigorous stirring for 24 h. A solution for Pt was prepared by dissolving 1.0 mM of hydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot nH_2O$), $n = 5.8$, Kojima Chemicals Co.) in a mixed solvent of deionized water (94 vol.%) and 2-propanol (6 vol.%) at room temperature under the identical stirring for 24 h. The fabricated networked SnO_2 nanowire sensors were first immersed into the Pd-precursor solution and subsequently illuminated with ^{60}Co γ-rays. During this process, Pd nanoparticles were decorated on the SnO_2 nanowires. The Pd-functionalized SnO_2 nanowires were next immersed into the Pt-precursor solution, and illuminated with ^{60}Co γ-rays. By this two-step sequential γ-ray radiolysis, the bimetallic Pd/Pt nanoparticles were successfully decorated on the SnO_2 nanowires. The γ-ray radiolysis conditions used for both cases are as follows: exposure time of 1 h and dose rate of 10 kGy h^{-1}. After γ-ray illumination, the samples were taken out of the precursor solution and heat treated at 500 °C for 1 h in air to remove residual solvents that may remain on the surface of the samples. The γ-ray radiolysis was done at the Korea Atomic Energy Research Institute (KAERI). The whole procedure including the synthesis of networked nanowires and the preparation of Pd/Pt bimetallic nanoparticles on the nanowires, and the dimension of the fabricated sensor is schematically described in Fig. 1.

The microstructure and phase of the synthesized bimetallic Pd/Pt nanoparticles were examined by field-emission scanning electron microscopy (FE-SEM, Hitach, S-4200) and transmission electron microscopy (TEM, Philips, CM 200), and x-ray diffraction (XRD, CuKα), respectively. The sensing performances of the bimetallic Pd/Pt-functionalized SnO_2 nanowires to various gases including NO_2, CO, C_6H_6, and C_7H_8 were investigated with a custom-made gas sensing system and compared with those of bare SnO_2 nanowires, and ones functionalized with either Pd or Pt nanoparticles. A schematic for the sensing-measurement system is shown in Fig. 2. The sensors were placed in a horizontal-type tube furnace and the measuring temperature was varied between 200 and 400 °C. The gas concentration was controlled by changing the mixing ratio of the dry air-balanced target gas and the dry air through accurate mass flow controllers (MFCs). The dry air-balanced target gases were purchased from the manufacturer

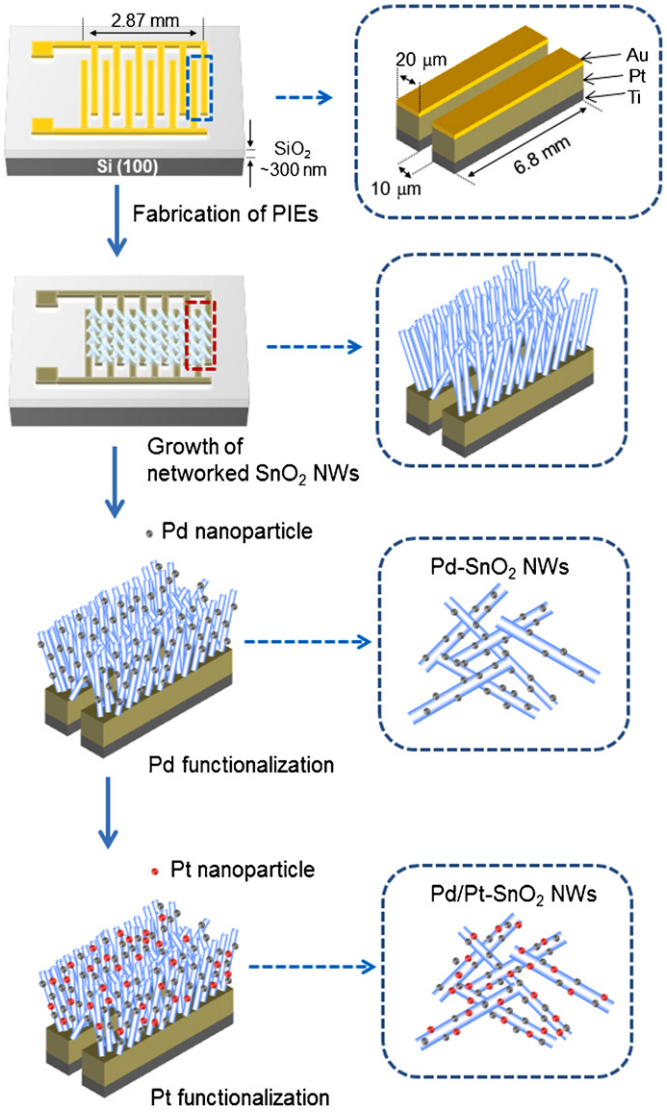

Fig. 1. A schematic showing the whole procedure including the synthesis of networked nanowires and the preparation of Pd/Pt bimetallic nanoparticles on the nanowires, and the dimension of the fabricated sensor.

(Daeduk Gas Co., Korea) and the concentration of the target gases was 100 ppm. The full ranges of the MFCs for regulating the dry air-balanced target gas and the dry air were 50 and 1000 sccm, respectively. With these dry air-balanced target gases and the use

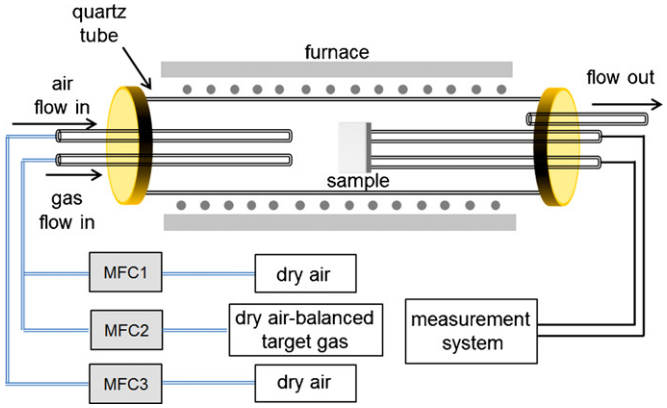

Fig. 2. A schematic showing the experimental set-up used in this study for measuring the sensing properties.