

Synthesis and Sensing Properties of Pd Nanoparticle-Functionalized SnO₂ Nanowires

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Abstract

Networked SnO₂ nanowires were uniformly functionalized with Pd nanoparticles via γ -ray radiolysis. The Networked SnO₂ nanowires were fabricated through a selective growth method. The sensing properties of the Pd-functionalized SnO₂ nanowires were analyzed in terms of their response to NO₂ and CO gases. The response time and sensitivity of the sensors were significantly improved for NO₂ at lower temperatures by the Pd functionalization. The enhancement in the sensing properties is likely to be due to the spillover effect of the Pd nanoparticles.

Keywords : Gas Sensor, Nanowire, Pd-SnO₂, Functionalization

1. INTRODUCTION

Oxide nanostructures have been widely studied for their potential use in chemical gas sensors. Specially, one-dimensional oxide nanowires have received much attention, in comparison to traditional sensors based on thin or thick films of nanoparticles, due to their peculiar physical and chemical properties. One-dimensional oxide nanostructures based on nanowires, nanotubes and nanoribbons exhibit excellent sensitivity for gas detection due to their exceptionally high surface-to-volume ratio, single crystalline nature, and semiconducting electrical behavior[1-3].

However, sensors based on single nanowire have some shortcomings which restrict their practical applications[4]. First, their fabrication requires a careful photolithography process, usually involving tedious fabrication steps. Second, an expensive measurement unit is required for gauging the infinitesimal current change due to the interaction of gaseous species with the surface of the nanowires. Third, the different sizes of each nanowire used for sensing may alter the current values. In comparison to single nanowire sensors, networked nanowires are superior in terms of fabrication and reproducibility, but suffer with lower sensitivity and longer response times. These properties need to be improved in order to see them applied

practically.

Meanwhile, metallic nanoparticles can be used as a catalyst to enhance the properties of gas sensors[5]. These metallic catalysts facilitate a spillover effect, which involves a dissociation of gaseous species into ions or neutral chemical species, resulting in superior gas sensing capability[6]. Various methods have been attempted to functionalize oxide nanowires with metallic catalysts[7-9]. Radiolysis is one effective route for synthesizing metallic nanoparticles and can also be employed to functionalize nanowires[10-12].

In this work, we fabricate networked SnO₂ nanowires via a selective growth method. Subsequently, the nanowires are Pd-functionalized through γ -ray radiolysis. We investigate the sensing properties of the Pd-functionalized SnO₂ nanowires at different temperatures in terms of their response to NO₂ and CO.

2. EXPERIMENTAL DETAILS

The fabrication of Pd-functionalized SnO₂ networked nanowire sensors involves two steps. First, the SnO₂ nanowires were selectively grown on patterned interdigital electrodes(PIEs) by the well-known vapor-liquid-solid growth method. Second, the Pd nanoparticles were functionalized on the surface of the SnO₂ nanowires by γ -ray radiolysis. The PIEs were prepared on SiO₂/Si(100) substrates using a conventional lithography process followed by the deposition by sputtering of tri-layers

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composed of Au(3 nm)/Pt (100 nm)/Ti (100 nm). The Ti (100 nm) layer was deposited to provide better adhesion between the Pt and SiO₂ layers. The SnO₂ nanowires with network junctions were selectively grown on 10-nm-spaced PIEs. The conditions used for fabrication of the SnO₂ nanowires are described in detail in our previous report[13].

The precursor solution for the functionalization of the SnO₂ nanowires with Pd nanoparticles was prepared by dissolving 0.051 mM of palladium chloride(PdCl₂, Kojima Chemicals Co.) in a mixed solvent of acetone(50 vol%) and 2-propanol(50 vol%). The prepared solution was stirred for 24 h. Then the fabricated networked SnO₂ nanowires were immersed in the precursor solution. The solution was illuminated with ⁶⁰Co γ -rays for 3 h in ambient air at room temperature at the Korea Atomic Energy Research Institute(KAERI). The prepared samples were heat treated at 500 °C for 1 h in air.

The microstructure of the Pd-functionalized SnO₂ nanowires was investigated using field-emission scanning electron microscopy(FE-SEM) and transmission electron microscopy(TEM). Their responses to NO₂ and CO were measured using a custom-made sensing system. The measurements were taken at various temperatures. The response(R) was estimated as $R = R_g/R_a$, where R_a is the resistance in the absence of NO₂ and R_g is the resistance measured in the presence of NO₂. The converse was applied for the case of CO.

3. RESULTS AND DISCUSSIONS

Fig. 1a and 1b show the plan- and the cross-section views of the networked SnO₂ nanowires, which demonstrate the formation of networked junctions on the PIEs by the selective growth method. The Pd nanoparticles were anchored to these nanowires by γ -ray radiolysis. Fig. 2a and 2b show low and high magnification images of the Pd-functionalized networked SnO₂ nanowires. Fig. 2b clearly shows that the Pd nanoparticles were uniformly deposited on the surface of SnO₂ nanowires. The average diameter of the Pd nanoparticles is ~20 nm. The microstructure of the Pd nanoparticles on the surface of SnO₂ nanowires was further investigated by TEM. The results are shown in Fig. 3. Fig. 3a clearly reveals a uniform dispersion of the Pd nanoparticles on the surface of an SnO₂ nanowire. The high resolution TEM image in Fig. 3b displays the lattice fringes of an SnO₂ nanowire and Pd nanoparticles. The lattice spacing confirms the

successful formation of single-crystalline SnO₂ nanowires and Pd nanoparticles.

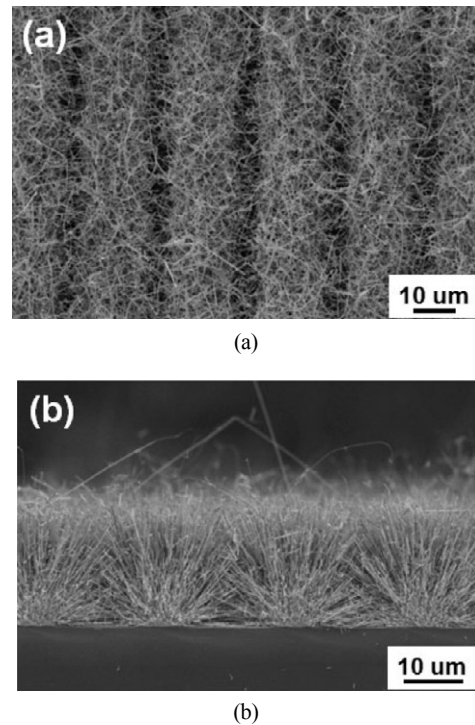


Fig. 1. (a) Plan view of the networked SnO₂ nanowires grown on patterned electrodes via the selective growth method. (b) Cross-sectional view of the networked SnO₂ nanowires.

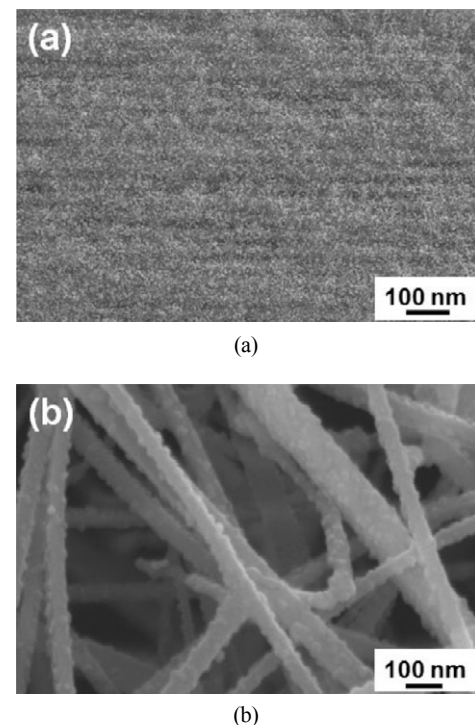


Fig. 2. (a) Plan view of the networked SnO₂ nanowires functionalized with Pd nanoparticles through γ -ray radiolysis. (b) Microstructure of the Pd nanoparticles on the surface of the SnO₂ nanowires grown under 10 kG h⁻¹ ⁶⁰C γ -rays for 3 h.

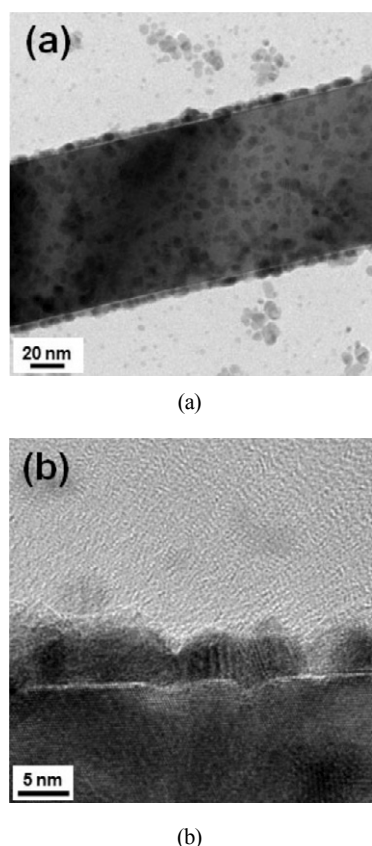


Fig. 3. TEM images of the Pd nanoparticles on the surface of the SnO₂ nanowires at (a) low and (b) high magnification.

The sensing properties of the Pd-functionalized networked SnO₂ nanowires were tested in temperatures from 50 to 300 °C for NO₂. The obtained results are shown in Fig. 4. The resistance of the Pd-functionalized SnO₂ nanowires tracked the supply/cut off of NO₂ well. The response time decreases from 140 to 20 s as the temperature is raised from 50 °C to 200 °C. Whereas at 300 °C, the response time has risen back to 100 s. The best sensing properties were obtained at 200 °C, as shown in Fig. 4d. The inset of the figure shows an enlarged part of the result obtained at 0.1 ppm NO₂ for clarity. This variation in resistance of the Pd-functionalized networked SnO₂ sensors can be explained by the n-type semiconductor mechanism and the spillover effect of the Pd nanoparticles.

In bare SnO₂ nanowires, the resistance increases upon exposure to NO₂ and decreases upon removal of NO₂. The NO₂ molecules adsorbed on the surface of SnO₂ nanowires are likely to extract electrons from the surface region of SnO₂ nanowires, enhancing the surface depletion of each SnO₂ nanowire. The extracted electrons are then transferred back to the conduction band of the SnO₂

nanowires in conjunction with the desorption of the NO₂ molecules.

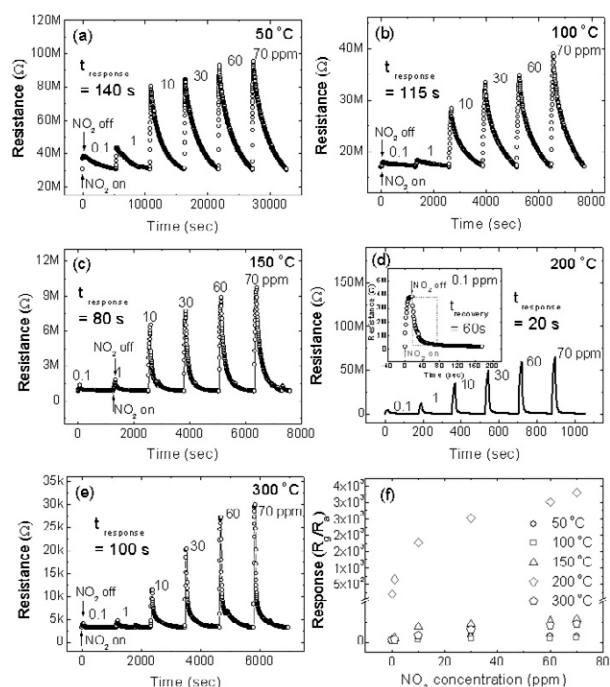


Fig. 4. Response curves of the Pd-functionalized SnO₂ nanowire sensor to NO₂ at (a) 50 °C, (b) 100 °C, (c) 150 °C, (d) 200 °C and (e) 300 °C. (f) Summary of responses obtained from the Pd-functionalized SnO₂ nanowires.

The Pd nanoparticles on the surface of the SnO₂ nanowires provide more active sites for adsorption of NO₂ molecules through the spillover effect[6]. The spillover effect facilitates the adsorption of NO₂ molecules. More adsorption of NO₂ molecules is likely to enhance the depletion region and suppress the underlying conducting channel more. The overall effect reduces the conductance, which ultimately lowers the response time and enhances the sensitivity. Another possibility is that the Pd nanoparticles induce catalytic effects and dissociate the NO₂ into ions or neutral chemical species, such as NO, O, NO₂⁻, NO⁺ and NO⁻[14-17]. These chemical species tend to capture the electrons in SnO₂ nanowires, enhancing the sensing properties.

The sensitivity of the Pd-functionalized SnO₂ nanowires at different temperatures is shown in Fig. 4f. They show an exceptionally high response at 200 °C. As the temperature is raised, the response also increases gradually. This is likely to be due to the faster adsorption and desorption of chemical species at higher temperatures.

The sensing behavior of the Pd-functionalized SnO₂ nanowires was also investigated in the presence of CO at

temperatures from 100 °C to 300 °C. A typical response curve we obtained is shown in Fig. 5. The sensor shows a relatively long response time and a low response to CO. The best response time of 60 s was obtained at 200 °C. The response is summarized in Fig. 5d. According to the results, it is reasonable to conclude that the Pd-functionalized SnO₂ nanowires are more sensitive to NO₂ than to CO.

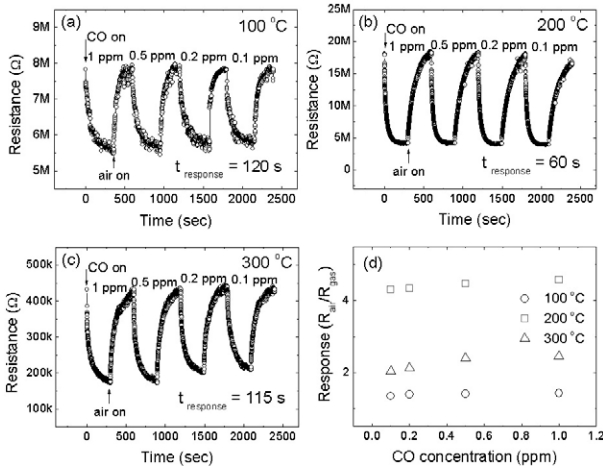


Fig. 5. Response curve of the Pd-functionalized SnO₂ nanowire sensor to CO at (a) 100 °C, (b) 200 °C, and (c) 300 °C. (d) Summary of responses obtained from the Pd-functionalized SnO₂ nanowires.

4. CONCLUSIONS

Pd nanoparticles were successfully functionalized on the surface of the networked SnO₂ nanowires via γ -ray radiolysis. The Pd-functionalized SnO₂ nanowires showed reasonable response times and responses to NO₂ at 200 °C. On the other hand, the sensor was not sensitive to CO.

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