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Enhancement of gas sensing properties by Functionalization of Networked SnO_2 Nanowires with Metal Nanoparticles

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Abstract

Networked SnO_2 nanowires were functionalized with Ag and Pd nanoparticles through γ-ray radiolysis. Selective growth method was used to grow the networked SnO_2 nanowires.The sensing properties of Ag and Pd-functionalized SnO_2 nanowires were investegated in NO_2. The Ag and Pd-functionalized SnO_2 nanowires showed reasonablely higher sensing properties. The mechanism of the enhancement in the sensing properties is discussed.

Key words: Gas sensors, Pd-SnO_2, Ag-SnO_2, nanowires, Functionalization

Introduction

The large surface-to-volume ratio of one dimensional semiconducting metal oxide nanostructures makes them highly sensitive in gas sensors [1,2]. In terms of the fabrication process and reliability, networked nanowires sensors show excellence except showing a decreased sensitivity and response time compared to single nanowire sensors. Therefore, improving those properties in networked nanowires is essential in practical application of such nanowires to chemical gas sensors. The sensitivity and response time to certain gases in nanowire gas sensors may be enhanced by functionalizing the surfaces of oxide nanowires with nanoparticles of noble metals [3]. For the purpose of synthesizing metal nanoparticles, various methods such as photochemistry, chemical, electrochemical, radiolysis, and sonochemistry have been attempted [4-6].]. γ-Ray radiolysis is one of the methods for synthesizing metallic nanoparticles and can be an effective way to functionalize network nanowires [7-9].

In this work, we have fabricated networked SnO_2 nanowire sensors based on a selective growth of nanowires by the vapor-liquid-solid growth method and functionalized them with Ag and Pd nanoparticles via γ-ray radiolysis. The distribution of metal nanoparticles on nanowires was deliberately controlled and the effects of the surface area of metal nanoparticles on the sensing properties were investigated.

Experimental

Networked SnO_2 nanowires selectively grown on patterned-interdigital electrodes (PIEs) by vapor-liquid-solid growth method, followed by metal-functionalization of SnO_2 nanowires via γ-ray radiolysis. The PIEs with 10 nm-spacing were prepared on SiO_2/Si(100) substrates using conventional lithography process. The subsequent tri-layers of Au(3 nm)/Pt (100 nm)/Ti (100 nm) deposited by sputtering method. The top Au layer function as catalytic layer for selective growth. The fabrication conditions of SnO_2 nanowires are described in detail in the previous report [10].

The precursor solutions for functionalization of SnO_2 nanowires with Ag and Pd nanoparticles are as follows. The Pd precursor solution was prepared by dissolving 0.051 mM of palladium chloride ($PdCl_2$, Kojima Chemicals Co.) in a mixed solvent of aceton (50 vol%) and 2-propanol (50 vol%). And the Ag precursor solutions were prepared by dissolving 0.0002 to 0.02 mM of silver nitrate ($AgNO_3$, Sigma-Aldrich) in a mixed solvent of deionized water (90 vol%) and 2-propanol (10 vol%). The prepared solutions was stirred for 24 h. The prepared networked SnO_2 nanowires were then immersed into the precursor solutions and illuminated with ^{60}Co γ-rays at 10 kG h^{-1} under ambient air at room temperature at the Korea Atomic Energy Research Institute (KAERI). All samples were heat treated at 500 ^{o}C for 1 h in an air atmosphere.

The microstructure of networked SnO_2 fibers and Ag and Pd-functionalized SnO_2 nanowires was investigated using field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4200) and transmission electron microscopy (TEM, Philips CM-200). The sensing characteristics of Ag and Pd-functionalized networked SnO_2 nanowires were measured for NO_2 using a custom-made gas dilution and sensing system. The measurements were performed at various temperatures. The sensitivity (S) was estimated according to the formula: $S = R_g/R_a$, where R_a is the resistance in the absence of gas and R_g is the resistance measured in the presence of gas.

Result and Discussions

Figure 1a and 1b shows the high-magnification FE-SEM iamges of the selectively grown networked SnO_2 nanowires functionalized by Pd and Ag-nanoparticles. They clearly show that the Ag and Pd nanoparticles were throughly disperesed on the surface of SnO_2 nanowires Further, microstructure of Pd nanoparticles on the surface of SnO_2 nanowires was analyzed by TEM. The insets in figure 1a and 1b show the corresponding high-resolution TEM images of Pd and Ag-functionalized networked SnO_2 nanowires, which clearly reveal that the Ag and Pd nanoparticles were simply anchroed on the surface of SnO_2 nanowires. The lattice fringes of the SnO_2 nanowires and Ag and Pd-nanoparticles shows formation of clear interface between them, which signify that the γ-ray radiolysis is an effcient route to functionlize the surface of oxide nanowires with metal nanoparticles without any significant reaction.

The sensing characteristics of Pd and Ag-functionalized networked SnO_2 nanowires were investegated and compaired with bare networked SnO_2 nanowires at temperature 300 ^oC in the presence of 1 ppm NO_2. The sensing results for Pd-functionalized networked SnO_2 nanowires in comparison to bare networked SnO_2 nanowires at 1 ppm is shown in Fig 2. The resistance of Pd-functionalized SnO_2 nanowires followed the supply/cut off of NO_2. The response was increased from 60 to 430, whereas the response and recovery time lowered from 123 to 7 s and 265 to 8 s, respectively by the Pd functionalization.The sensing performance of Ag-functionalized networked SnO_2 nanowires was also tested. The response was increased from 500 to 1800 by the Ag functionalization. And the response and recovery times were greatly shortened.

On the basis of obtained results, it is reasonable to conclude that Ag and Pd-nanoparticles resonably enhace the gas sensing charateristics of networked SnO_2 sensors. The enhancment in sensing characteristics of the Ag and Pd-functionalized networked SnO_2 sensors can be explained on the basis catalytic effect of metal nanoparticles and mechanism of n-type semiconductors [11].

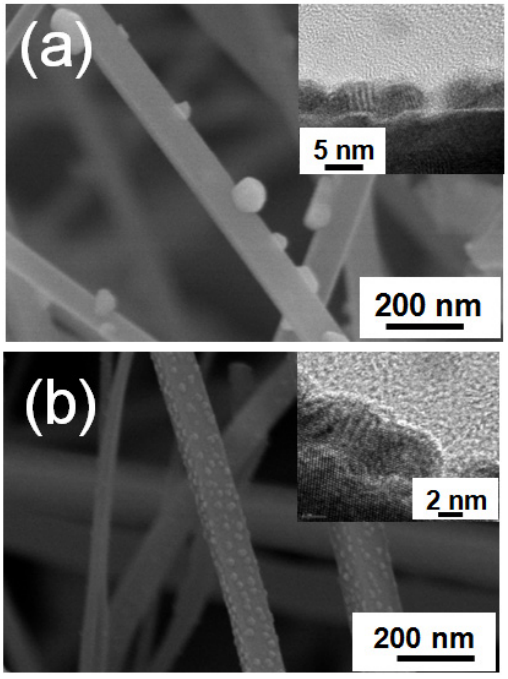

Fig. 1. FE-SEM images of networked SnO_2 nanowires functionalized by (a) Ag and (b) Pd nanoparticles. The inset shows the high resolution TEM images.

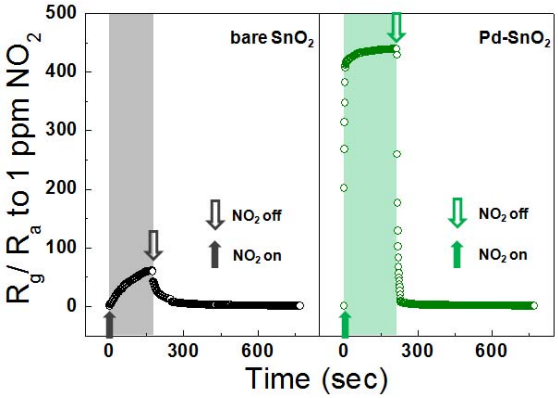

Fig. 2. Response curves of a sensor fabricated with bare networked SnO_2 nanowires and a sensor fabricated with Pd-functionalized networked SnO_2 nanowires to NO_2 1 ppm at 300 ^oC.

Conclusions

Ag and Pd nanoparticles were successfully functionalized on the surface of networked SnO_2 nanowires via γ-ray radiolysis. The Ag and Pd-functionalized SnO_2 nanowires showed reasonablely higher sensing properties than

bare SnO_2 nanowires. The enhancement was likely from the catalytic effects of the metals.

Acknowledgements

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