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Design of a highly sensitive and selective C_2H_5OH sensor using p-type Co_3O_4 nanofibers

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Abstract

The Co_3O_4 nanofibers were prepared by electrospinning of solution containing Co-nitrate, N,N-dimethylformamide, and polyvinylpyrrolidone and subsequent heat treatment at 500, 600, and 700°C. The response to 100 ppm C_2H_5OH of Co_3O_4 nanofibers was significantly higher than those to 100 ppm CO, C_3H_8, and H_2 in all three sensors. In particular, the Co_3O_4 nanofibers heat-treated at 500 and 600°C showed higher response and selectivity to C_2H_5OH. The variation of gas sensing characteristics were explained and discussed in relation to the gas sensing mechanism of a p-typesemiconductor and the morphology ofspecimens.

Key words:Co_3O_4 nanofibers, Gas sensor, Electrospinning, p-type, Gas sensing mechanism

Introduction

Electrospinning of a solution containing metal precursors and subsequent heat treatment is a facile route to prepare well-defined oxide nanofibers. Polycrystalline oxide nanofibers prepared by electrospinning are promising nanostructures for high-performance gas sensors on account of their high surface area to volume ratio, less agglomerated network configuration, and chemoresistive contacts between primary particles within a nanofiber. Thus far, various n-type oxide semiconductors such as SnO_2, ZnO, TiO_2, In_2O_3, WO_3, and Fe_2O_3 have been prepared into nanofibers or nanotubes by electrospinning for gas sensor applications.

In n-type oxide semiconductor gas sensors, the adsorption of oxygen with negative charge forms the electron depletion layer near the surface of the particles. Thus, the chemoresistive variation is dominated by the conduction across the resistive electron depletion layers at the inter-particle contacts. In contrast, hole accumulation layer is established near the surface of p-type oxide semiconductor particles by the adsorption of negatively charged oxygen. The thinning of hole accumulation layer by the oxidation of reducing gases is responsible gas sensing reaction. Accordingly, the gas sensing reactions in n-type and p-type oxide semiconductor gas sensors should be understood under the completely different frameworks.

To date, researches on the gas sensing characteristics of p-type nanofibers are in an early stage, although NiO [1], Cr_2O_3[2], $LaFeO_3$ [3], and LaOCl-NiO [4] nanofibers have been explored.In this study, Co_3O_4 nanofibers are prepared by electrospinning and their gas sensing characteristics such as gas response, selectivity, and response time were investigated in relation to the morphological configuration of nanofibers.

Experimental

$Co(NO_3)_2 \cdot 6H_2O$ (1 g) was dissolved in 17 g of a solvent mixture of C_2H_5OH and N,N-dimethylformamide (C_2H_5OH : N,N-dimethylformamide = 1 : 1 by wt%) and kept under magnetic stirring for 2 h. Then polyvinylpyrrolidone (2 g) was added to the solution. After stirring for 24 h, a clear solution was attained. The as-prepared homogeneous solution was loaded in a plastic syringe and electrospun using a 21-gauge needle with a flow rate of 0.5 mL/h at an applied voltage of 20 kV over a collection distance of 15 cm.The as-spun nanofibers were dried at 70°C for 24 h to remove the residual solvents, then they were converted into Co_3O_4 nanofibers by heat treatment at 500, 600, and 700 °C for 2 h in an air atmosphere. The heating rate was fixed at 5 °C/min. For simplicity, hereinafter, the Co_3O_4 nanofibers formed by heat treatment at 500, 600, and 700 °C will be referred to as 'Co_3O_4-500', 'Co_3O_4-600', and 'Co_3O_4-700' nanofibers, respectively. The Co_3O_4 nanofibers were dispersed in isopropanol (Sigma-Aldrich Co.,

Ltd., USA) and subsequently dried at 70°C for 24 h. The Co_3O_4 nanofibers were mixed with organic binders (ethyl cellulose: terpinol = 1: 14 by wt%) and printed on the alumina substrate (size: 1.5 x 1.5 mm^2) with two Au electrodes (on its top surface) and a micro-heater (on its bottom surface). The sensor was heated at 508°C for 2 h using micro-heater to remove any residual organic contents.

Results and Discussion

As-electrospun Co-precursor nanofibers showed the clean and dense surfaces (not shown). The diameters of nanofibers were in the range of 300 – 1000 nm. After heat treatment at 500-700°C, the nanofibers are converted into porous Co_3O_4 nanofibers (Fig. 1). The fibrous morpohologies were maintained after heat treatment at 500 (Fig.1a) and 600 °C (not shown), while the fibers are disintegrated into primary particles or shorter nanofibers after heat treatment at 700 °C (Fig. 1b). According to X-ray diffraction analyses, all the nanofibers prepared by heat treatment of electrospun Co-precursor fibers at 500-700°C are identified as cubic Co_3O_4 phase. The average sizes of primary particles in Co_3O_4-500, Co_3O_4-600, and Co_3O_4-700 nanofibers were determined to be 51.8 ± 21.1 nm, 105.8 ± 42.7 nm, and 143.0 ± 64.5 nm from the analyses of TEM images.

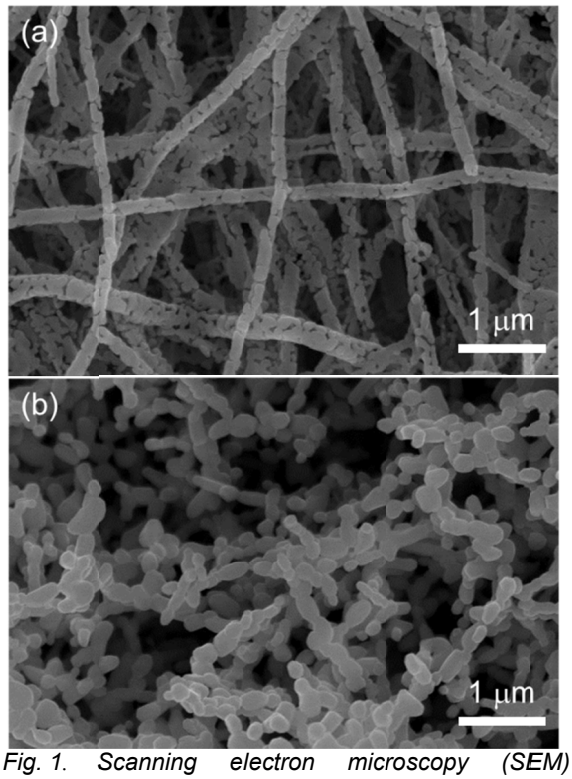

Fig. 1. Scanning electron microscopy (SEM) images of (a) Co_3O_4 nanofibers heat-treated at 500°C and (b) Co_3O_4 nanofibers heat-treated at 700°C.

Gas sensing characteristics of Co_3O_4 nanofibers were measured at 301 °C. The sensors showed typical p-type gas sensing characteristics, the resistance increase upon exposure to reducing gases (Fig. 2a,c,e). In all three different Co_3O_4 sensors, the responses ($S=R_g/R_a$, R_g: resistance in analyte gas, R_a: resistance in air) to 100 ppm C_2H_5OH were significantly higher than those to 100 ppm CO, C_3H_8, and H_2 (Fig. 2b,d,f). In particular, The Co_3O_4-500, Co_3O_4-600 sensors showed the sensitive and selective detection of C_2H_5OH (R_g/R_a=51.2 and 45.3 to 100 ppm C_2H_5OH) (Fig. 2b,d). The response to 100 ppm C_2H_5OH became significantly lower (R_g/R_a=6.0) when the heat treatment temperature was increased to 700 °C (Fig. 2f).

The particle sizes, the inter-fiber contacts, and connectivity between primary particle within a nanofiber can be considered as the key parameters to determine the gas response of p-type oxide semiconductors. The particle size of Co_3O_4-600 sensor are ~ 2 times larger than that of Co_3O_4-500 sensor. Nevertheless, the responses to 100 ppm C_2H_5OH in Co_3O_4-500 and Co_3O_4-600 sensors are similar with each other. In contrast, the gas response to 100 ppm C_2H_5OH of Co_3O_4-700 sensor (R_g/R_a=6) are significantly lower than that of Co_3O_4-600 sensor (R_g/R_a=45.3), while the particle size of Co_3O_4-700 sensor are only ~1.35 times larger than that of Co_3O_4-600 sensor. This reflects that, except the particle size, another parameters to determine gas response should be taken into account.

In order to investigate the effect of 1-dimensional connectivity in Co_3O_4 nanofibers on the gas response, the connective configuration of Co_3O_4-600 nanofibers were broken into nanoparticles by ultrasonic treatment for 1 h in slurry condition (not shown). The response to 100 ppm C_2H_5OH of the Co_3O_4-600-NP sensor at 301°C was 2.71 (Fig. 3b), which was significantly lower than that of the Co_3O_4-600 sensor (47.5) (Fig. 3a). This value is also lower than that of the Co_3O_4-700 sensor (6.8) (Fig. 2f). Above results clearly verify that, in p-type oxide semiconductor gas sensors, long 1-dimensional nanostructures are more advantageous to achieve a high gas response than less-elongated nanofibers or nanoparticles.

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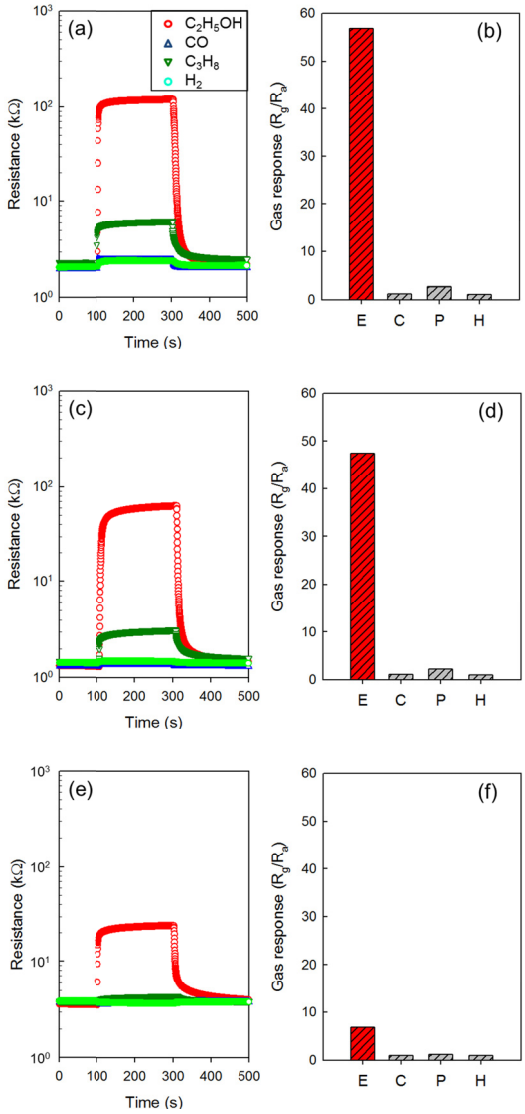

Fig. 2. Gas sensing transients and gas responses (R_g/R_a) to 100 ppm C_2H_5OH, 100 ppm CO, 100 ppm C_3H_8 and 100 ppm H_2 at 301° C: (a),(b) Co_3O_4-500 sensor, (c),(d) Co_3O_4-600 sensor, and (e),(f) Co_3O_4-700 sensor. (E, C, P, H in (d) represent ethanol, carbon monoxide, propane, and hydrogen, respectively.)

The significant decrease of the gas response was explained and discussed in relation to the gas sensing mechanism of a p-type semiconductor, and the connecting configuration between nanoparticles and nanofibers.

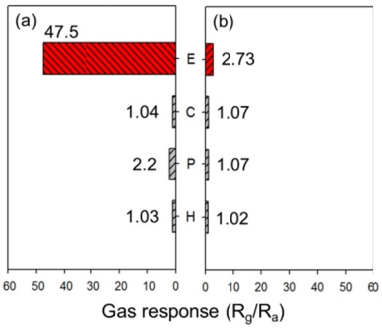

Fig. 3. Gas responses (R_g/R_a) to 100 ppm C_2H_5OH, 100 ppm CO, 100 ppm C_3H_8 and 100 ppm H_2 at 301° C: (a) Co_3O_4-600 sensor, (b) the sensor prepared by heat treatment of Co-precursor nanofibers at 600°C and untrasonic disintegration of Co_3O_4nanofibers into nanoparticles(E, C, P, H in figurerepresent ethanol, carbon monoxide, propane, and hydrogen, respectively.)

Summary

The p-type Co_3O_4 nanofibers were prepared by electrospinning and subsequent heat treatment at 500 – 700 °C. The variation of heat treatment temperature leads to the variation of morphology, particle size and connecting configuration of nanofibers, which changed the gas sensing characteristics. The Co_3O_4 sensors prepared by heat treatment of as-spun nanofibers at 500 and 600°C showed well-developed one-dimensional morphologies and exhibited sensitive and selective detection of C_2H_5OH. By contrast, the most of 1-dimensional morphology of the Co_3O_4 specimen was lost and the response to 100 ppm C_2H_5OH became significantly lower when the heat treatment temperature was increased to 700 °C.

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