

Gas Sensing Characteristics of Sb-doped SnO₂ Nanofibers

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Abstract

Undoped and Sb-doped SnO₂ nanofibers were prepared by electrospinning and their responses to H₂, CO, CH₄, C₃H₈, and C₂H₅OH were measured. In the undoped SnO₂ nanofibers, the gas response (R_a/R_g , R_a : resistance in air, R_g : resistance in gas) to 100 ppm C₂H₅OH was very high(33.9), while that to the other gases ranged from 1.6 to 2.2. By doping with 2.65 wt% Sb, the response to 100 ppm C₂H₅OH was decreased to 4.5, whereas the response to H₂ was increased to 3.0. This demonstrates the possibility of detecting a high H₂ concentration with minimum interference from C₂H₅OH and the potential to control the gas selectivity by Sb doping.

Keywords : Gas Sensors, Electrospinning, Nanofibers; Sb-SnO₂, Selective Detection

1. INTRODUCTION

Oxide semiconductor gas sensors give a conductance change according to the chemical interaction between the reducing/oxidizing gases and surface adsorbed species. To enhance the gas response, the particle size needs to be decreased to the thickness level of the electron depletion layer[1,2]. However, the strong agglomeration between primary particles often hampers the diffusion of analyte gas toward the entire sensing surface, which decreases the gas response[3,4].

In this respect, the less agglomerated configurations of nanostructures are good gas sensing materials. Among various nanostructures, one-dimensional nanofibers are promising candidates because they provide a high surface area due to the presence of many primary particles within each nanofiber, effective gas diffusion via the less agglomerated nanofiber network, and the short diffusion path in the nanofibers[5]. Moreover, Schottky barriers are formed not only between nanofibers but also between primary particles within the nanofibers. All of these can maximize the gas response.

Electrospinning is a facile chemical route to prepare one-dimensional nanofibers on a large scale[6]. Although this process was suggested in the beginning of the 20th century[7], intensive research on the fabrication and applications of electrospun nanofibers has been carried during the recent several years[8]. In particular, the gas sensor is one of the most promising applications for nanofibers. To date, the representative gas sensing materials such as SnO₂[9], TiO₂[10], ZnO[11], In₂O₃[12], and WO₃[13] have been prepared in the form of nanofibers for sensor applications.

The remaining challenges are the control of selectivity using electrospun nanofibers. It is relatively easy to add various additives in the precursor solution for electrospinning. Thus, the compositional control of nanofibers, the preparation of composite nanofibers, and the addition of catalyst materials can be considered as the effective approaches to improve gas selectivity in the nanofiber-based sensors. In this contribution, undoped and Sb-doped SnO₂ nanofibers are prepared via electrospinning and their responses to H₂, CO, C₃H₈, CH₄, and C₂H₅OH are studied. The main focus of this study is placed on the control of gas selectivity and relative gas response by the compositional manipulation of gas sensing materials.

2. EXPERIMENTAL

The experimental procedures are shown in Fig. 1. A 8.5

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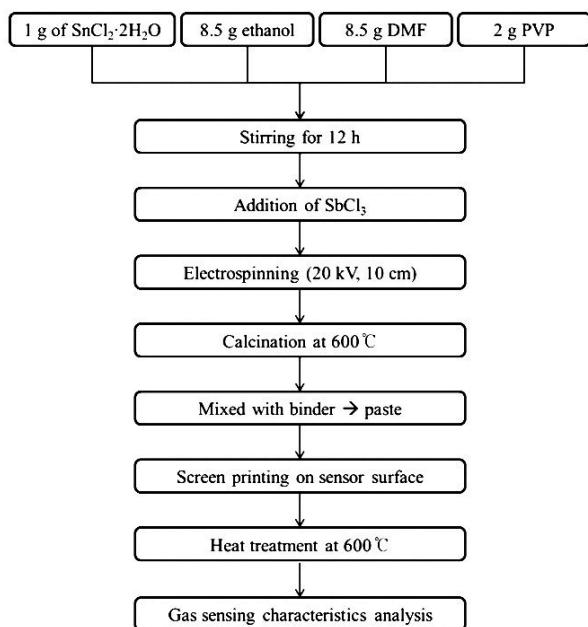


Fig. 1. Schematic diagram of experimental process.

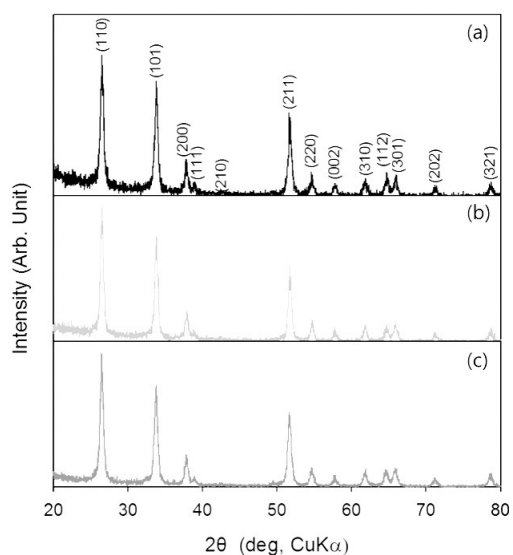


Fig. 2. X-ray diffraction(XRD) patterns of (a) undoped SnO₂, (b) 0.88Sb-SnO₂, and (c) 2.65Sb-SnO₂ nanofibers heat-treated at 600 °C for 2 h.

g of ethyl alcohol(99.9 %, J. T. Baker Chemical Co., Ltd., USA) was mixed with 8.5 g of N, N-dimethylformamide (99.5%, Samchun Chemical Co., Ltd., Korea). Into these mixed solvents was dissolved 1 g of SnCl₂ · 2H₂O(98+%, Acros organics, Belgium) and the solution was homogenized for 2 h by stirring. After the addition of 2 g of polyvinylpyrrolidone(Mw=1,300,000, Sigma-Aldrich

Co., Ltd., USA), the solution was stirred again for 10 h. This led to a clear Sn-precursor solution for the preparation of SnO₂ nanofibers. In order to prepare the Sb-doped SnO₂ nanofibers, the corresponding amount of SbCl₃(98.0 %, Kanto Chemical Co., Ltd., Japan) was added to the Sn-precursor solution and homogenized for 12 h by stirring. The doping amount of Sb was 0.88 or 2.65 wt% of SnO₂. Hereinafter, for simplicity, the 0.88 wt% Sb-doped and 2.65 wt% Sb-doped SnO₂ nanofibers will be referred as '0.88Sb-SnO₂ nanofibers' and '2.65Sb-SnO₂ nano-fibers', respectively.

The precursor solution was loaded in a plastic syringe and electrospun by applying 20 kV at an electrode distance of 10 cm. The as-spun nanofibers were heat-treated at 600 °C for 2 h to convert the precursor nanofibers into undoped or Sb-doped SnO₂ nanofibers. Heat-treated nanofibers were dispersed in isopropanol(99.5 %, Sigma-Aldrich Co., Ltd., USA) by ultrasonic treatment and subsequently dried at 80 °C for 24 h. The nanofibers were mixed with organic binders(ethyl cellulose: α-terpineol = 1:14 by wt%) and printed on the SiO₂/Si substrate with Pt/Ti electrode patterns. The sensor was dried at 80 °C for 2 h and heat-treated again at 600 °C for 2 h to decompose the organic contents.

The morphologies of the nanofibers were observed by scanning electron microscopy(SEM, S-4800, Hitachi) and transmission electron microscopy(TEM, FEI Tecnai 20, Philips). The crystal phase was studied using X-ray diffraction(XRD, Rigaku D/MAX-2500). The gas concentration was controlled by changing the mixing ratio of dry parent gases and dry synthetic air. A flow-through technique with a constant flow rate of 500 sccm was used. The gas responses ($S = R_a/R_g$) to 100 ppm H₂, 100 ppm CO, 500 ppm CH₄, 100 ppm C₃H₈, and 100 ppm C₂H₅OH were measured at 400 °C by comparing the sensor resistance in air (R_a) with that in target gases (R_g). The dc 2-probe resistance of the sensor was measured using an electrometer interfaced with a computer.

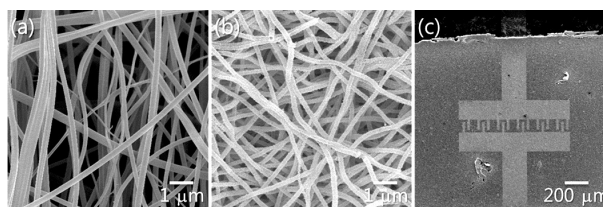


Fig. 3. SEM images of (a) as-spun, Sn-precursor nanofibers, (b) SnO₂ nanofibers heat-treated at 600 °C for 2 h, and (c) SnO₂ sensor surface.

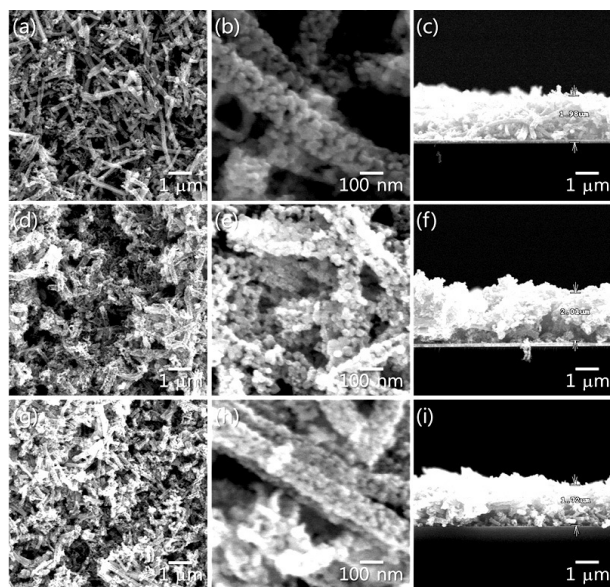


Fig. 4. SEM images of sensor surface: (a-c) undoped SnO₂, (d-f) 0.88Sb-SnO₂, and (g-i) 2.65Sb-SnO₂ nanofibers heat-treated at 600 °C for 2 h.

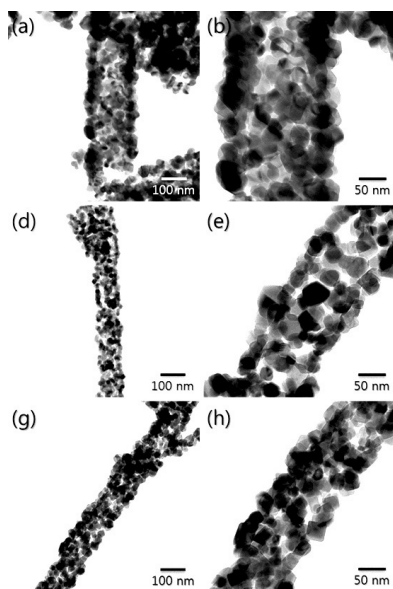


Fig. 5. TEM images of (a), (b) undoped SnO₂, (c), (d) 0.88Sb-SnO₂, and (e), (f) 2.65Sb-SnO₂ nanofibers heat-treated at 600 °C for 2 h.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction(XRD)

The undoped SnO₂ nanofibers after heat treatment at 600 °C for 2 h were identified as having a rutile structure

(JCPDS # 77-0447) (Fig. 2a). The 0.88Sb-SnO₂ and 2.65Sb-SnO₂ nanofibers showed similar XRD patterns (Fig. 2b and 2c). The Sb-related phases such as Sb, Sb₂O₅, and Sb₂O₃ were not found in the XRD patterns, which indicates that Sb is incorporated into the SnO₂ lattice.

3.2 SEM and TEM analysis

The as-spun Sn-precursor nanofibers showed clean surface morphology (Fig. 3a) with a diameter ranging from 200 to 300 nm and a length of several tens of micrometers. The undoped SnO₂ nanofibers after heat treatment at 600 °C for 2 h showed rougher surface morphology (Fig. 3b). This morphology can be explained by the burn-out of organic content in the Sn-precursor nanofibers. The SnO₂ nanofibers were uniformly coated on the surface of the substrates with electrodes (Fig. 3c). The morphologies of the Sb-doped Sn-precursor nanofibers and Sb-doped SnO₂ nanofibers were similar to Fig. 3a and 3b, respectively (data not shown).

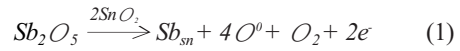
High magnification images of the sensor surfaces are shown in Fig. 4. All the undoped and Sb-doped SnO₂ nanofibers on the sensor surface were several micrometers long (Fig. 3a,d,g). This is significantly shorter than the length of the as-spun precursor nanofibers and the heat-treated SnO₂ nanofibers (several tens micrometers, for example, as shown in the SEM images in Fig. 3a and 3b), which can be explained by the breaking of the nanofibers during their ultrasonic dispersion. All the nanofibers consisted of small primary particles (Fig. 4b,e,h). The thicknesses of the sensor films determined from the cross-sectional images were ~1.98, 2.01, and 1.72 μm for the undoped SnO₂, 0.88Sb-SnO₂ and 2.65Sb-SnO₂ nanofibers, respectively (Fig. 4c,f,i).

The TEM images of all the specimens showed a bright contrast in the core region (Fig. 5). This indicates the hollow morphology of the undoped SnO₂, 0.88Sb-SnO₂ and 2.65Sb-SnO₂ nanofibers, which facilitated the diffusion of analyte gases toward the entire sensor surface. In general, hollow nanofibers have been prepared by coaxial two-capillary electrospinning of two immiscible liquids [14,15]. In this study, however, the hollow nanofibers were prepared by single capillary design, which offers the advantage of simplifying the fabrication process. The size of the primary particles within the oxide nanofibers ranged from 20 to 50 nm.

3.3 Gas sensing characteristics

The sensing transients to 100 ppm H₂, 100 ppm CO, 500 ppm CH₄, 100 ppm C₃H₈, and 100 ppm C₂H₅OH at 400 °C are shown in Fig. 6. The sensor showed typical n-type semiconductor characteristics, i.e., the resistance was decreased by exposure to the reducing gases. The R_a value of ~ 9 × 10⁶ Ω in the undoped SnO₂ nanofiber sensor(Fig. 6a) was decreased to ~ 8 × 10⁴ Ω by doping with 0.88 wt% Sb(Fig. 6b), and was decreased further to 5 × 10³ Ω by doping with 2.56 wt% Sb(Fig. 6c). Babar et al.[16] prepared Sb-doped SnO₂ thin films by spray pyrolysis of the solution containing SnCl₄ and SbCl₃ at 475 °C and observed that the resistivity of the thin film was decreased as the Sb doping concentration was increased. The XPS analysis results confirmed the dominance of Sb⁵⁺ over Sb³⁺ and attributed the decrease of resistivity to the increase of

electron concentration by the incorporation of Sb⁵⁺ ions into Sn⁴⁺ sites. Accordingly, the Sb in this study was thought to exist in the form of Sb⁵⁺ rather than Sb³⁺ and Sb⁵⁺ can decrease the resistance by the following reaction[17-19].



The times to reach 90 % variation in resistance upon exposures to gas and air are defined as the 90 % response time(τ_{res}) and 90 % recovery time(τ_{recov}), respectively. The τ_{res} values were relatively short(0.6 ~ 72.4 s) while the τ_{recov} values were long(60.8 ~ 703 s). The short response kinetics implies that the in-diffusion of analyte gas and its oxidation with negatively charged surface oxygen occurred rapidly. Such rapid gas diffusion can also be applied to the in-diffusion of oxygen in the recovery reaction. Thus, the slow recovery suggests that the serial surface reactions

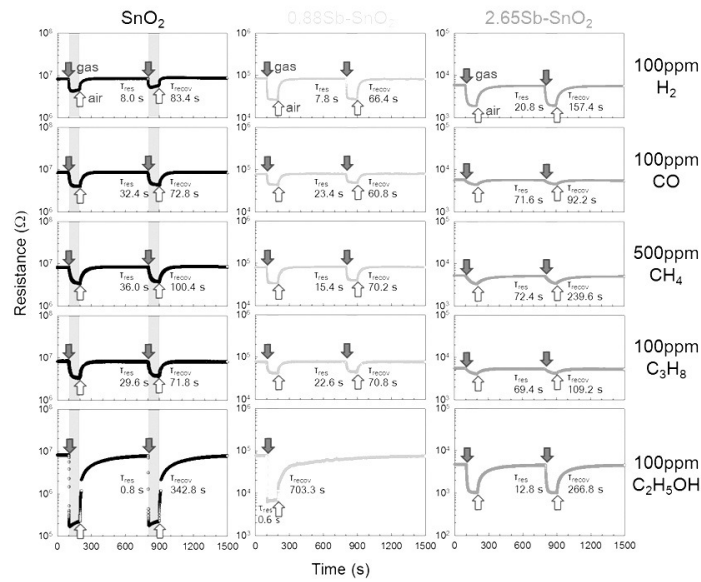


Fig. 6. Dynamic gas sensing transients at 400 °C.

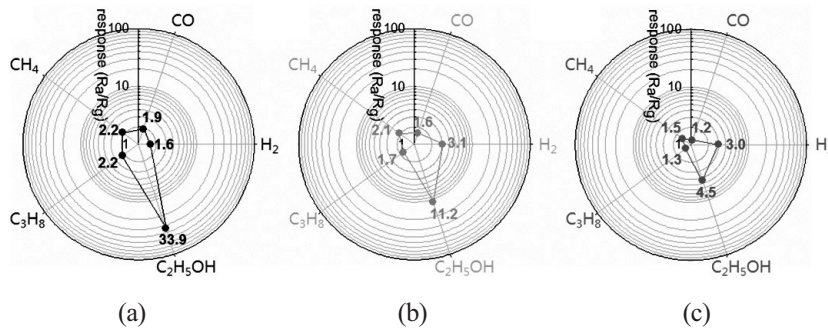


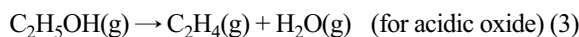
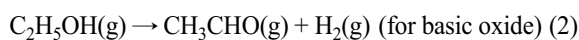
Fig. 7. Gas responses to 100 ppm H₂, 100 ppm CO, 500 ppm CH₄, 100 ppm C₃H₈ and 100 ppm C₂H₅OH of the sensors according to the variation of Sb-doping concentrations: (a) undoped SnO₂, (b) 0.88Sb-SnO₂, and (c) 2.65Sb-SnO₂ nanofibers(sensor temperature = 400 °C).

such as adsorption, dissociation, and ionization of oxygen are sluggish.

The responses to 100 ppm H₂, 100 ppm CO, 500 ppm CH₄, 100 ppm C₃H₈, and 100 ppm C₂H₅OH at 400 °C are shown as polar plots in Fig. 7. The gas responses were closely dependent upon the Sb doping. As shown in Fig. 7a, the response to 100 ppm C₂H₅OH was very high(33.9) while that to other gases ranged from 1.6 to 2.2. This indicates that C₂H₅OH can be detected in a selective manner using the undoped SnO₂ nanofibers. By doping with 0.88 wt% Sb, the response to 100 ppm C₂H₅OH was decreased to 11.2, whereas that to H₂ was approximately doubled(3.1). The response to 100 ppm C₂H₅OH was further decreased to 4.5 by doping with 2.56 wt% Sb, whereas the response to H₂ remained similar(3.0). Thus, increasing Sb doping concentration facilitates the detection of a high H₂ concentration(for example > 200 ppm) with minimum interference from C₂H₅OH. Moreover, the different sensing pattern to various gases can be used in artificial olfaction for the recognition and quantization of gases.

3.4 Discussion

The sensing of C₂H₅OH is closely dependent upon the acid-base properties of the sensing materials[20,21].



For the oxidation reaction, CH₃CHO + H₂ consumes more surface oxygens with negative charge than C₂H₄ + H₂O. Moreover, the oxidization of chemically stable C₂H₄ into CO₂ and H₂O is difficult. Thus, the addition of basic oxides such as La₂O₃, Sm₂O₃ and Gd₂O₃ is known to enhance the response to C₂H₅OH significantly[20,22]. The greater electronegativity of Sb(2.05) than that of Sn (1.96) means that Sb is more acidic. Therefore, the decrease of response to C₂H₅OH by Sb doping can be explained by the promotion of reaction (3) rather than reaction (2).

Zima et al.[23] reported that the doping of SnO₂ with Sb significantly enhances the response to H₂, which is consistent with the present results. This again suggests that the H₂ sensing reaction is promoted by the catalytic activity of Sb. This is feasible considering that Sb is one of the important catalytic materials for the oxidation reaction[24, 25]. Thus, Sb doping can be used as an effective additive to enhance the response to H₂ while suppressing the response to C₂H₅OH.

4. CONCLUSION

Undoped and Sb-doped SnO₂ nanofibers were prepared by electrospinning and their sensing characteristics to H₂, CO, CH₄, C₃H₈ and C₂H₅OH were investigated. The undoped SnO₂ nanofibers demonstrated the selective detection of C₂H₅OH. As the Sb doping concentration was increased to 2.65 wt%, the response to C₂H₅OH was decreased significantly while the response to H₂ was enhanced. The effect of Sb doping concentration on the selectivity was explained by the acid-base properties and catalytic function of Sb.

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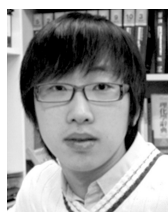
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