



Fabrication of SnO₂ Particle-Layers using the Electrospray Method and Gas Sensing Properties for H₂

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Abstract. The particle layers of SnO₂ were prepared using the electrospray pyrolysis method from SnCl₂ ethanol solution on the glass substrates heated at 773 K. Pyrex and quartz glass were used for the substrates. The effects of the concentration and the conductivity of the precursor solutions on the morphology and gas sensitivity of the SnO₂ layers were investigated. The sensitivity measurements were carried out for 0.5% H₂ in synthetic air at the operating temperature of 573 K and that was defined by the resistance ratio of the specimen under synthesized dry-air (R_{air}) and 0.5% H₂ (R_{gas}), $R_{\text{air}}/R_{\text{gas}}$. Among the examined concentrations of 1×10^{-4} , 1×10^{-3} and 1×10^{-2} mol · dm⁻³, the layer prepared at 1×10^{-3} mol · dm⁻³ exhibited the maximum sensitivity of 20. The particle sizes were 110(30), 160(40), and 150(35) nm in diameter at 1×10^{-4} , 1×10^{-3} , and 1×10^{-2} mol · dm⁻³, respectively. The values in the parentheses indicate the standard deviation of the measured data. On the other hand, the conductivity of the solution exerted no significant influence on the sensitivity, which was adjusted by the addition of dilute hydrochloric acid. The particle size decreased with the conductivity and became 134(30), 105(20) and 87(20) nm in diameter at 7.8, 27.0 and 86.6 $\mu\text{S} \cdot \text{cm}^{-1}$, respectively. Under all the conditions the layers had the dendrite-like structure, indicating the in-flight particle formation. The crystallite size was evaluated to be 6 nm from XRD using the Scherrer's equation. These particles of 87–160 nm was thought to consist of smaller primary particles (crystallites). The Pd doping by 1 wt% to SnO₂ enhanced the gas sensitivity by a factor of 4.

Keywords: tin dioxide, gas sensor, electrospray, particle layer, palladium

1. Introduction

The electrospray is an aerosol generator which can provide monodispersion droplets from a highly biased metal-capillary. The formation of ceramics films on substrates using the electrospray method through pyrolysis of precursor solutions was reported in 1994 [1, 2]. In this method the solution containing the precursors such as metal acetates and chlorides is sprayed toward a heated substrate. The precursors decompose into oxides after or before reaching the substrate so as to form the film of the metal oxides on the substrate. The surface morphology of deposited layers depends on the electrospraying conditions such as the properties of solvents and a substrate temperature. The resulting film

becomes the porous layer composed of particles, the dense powdery film or the monolithic gel film (sometimes with cracks) when the surface is kept dry, partially wet or completely wet, respectively, during the deposition [3–6].

SnO₂ is one of the promising materials for the gas sensor. It is well known that the additives of the noble metals such as Pd and Pt enhance the sensitivity for flammable gases. However, the cost-effective method without neither any additive nor post-heat-treatment is desirable for the industrial application. The electrospray pyrolysis method is a candidate satisfying the requirement for the fabrication of the SnO₂-based gas sensor, because of the simultaneous fabrication of the sensing element while the synthesis of the material, the porosity of the resulting film and the easy set-up of the apparatus. The attempt to prepare the SnO₂-based gas sensor using the electrospray pyrolysis method was

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carried out by Gourari et al. [7, 8]. They reported that the pure SnO₂ film prepared by this method exhibited the poor sensitivity less than 5 to 0.2% H₂ in N₂ at the operating temperature of 648 K, and that the addition of Mn₂O₃ at the ratio of 1:10 to SnO₂ activated the sensitivity to 28 at the maximum. In their studies the SnCl₄·5H₂O ethanol solution in the concentration range of 1×10^{-2} to 1×10^{-1} mol · dm⁻³ with (CH₃COO)₂Mn · 4H₂O was examined. On the other hand, our previous work showed that the elaboration of the synthetic condition resulted in the as-sprayed SnO₂ layers exhibiting the good sensitivity comparable to that by Gourari, for 0.5% H₂ in synthetic air at 573 K [9].

According to the empirical equation, the droplet size generated in the electrospray is expressed by Eq. (1) for the liquids with high enough conductivities and/or viscosities [10], where the parameters originated from the liquid properties were put into the coefficients A and B such as the relative dielectric constant, the surface tension and the density. D_d , Q , and K are the droplet size, the liquid flow rate, and the conductivity of the liquid.

$$D_d = A(Q/K)^{1/3} - B(1/K^2)^{1/3}. \quad (1)$$

The size of the particle precipitating from a droplet was estimated using the formula weight (M_{SnO_2}), the density (ρ_{SnO_2}) of SnO₂, the concentration C , and D_d .

$$d_p = (M_{\text{SnO}_2} C / \rho_{\text{SnO}_2})^{1/3} D_d \quad (2)$$

In the present work, the effects of the easily accessible parameters of C and K in the electrospray on the morphology and the sensitivity of the resultant layers were investigated. The palladium doping in this method was also examined.

2. Experimental

The illustration of the apparatus was shown elsewhere, which was basically the same as the previous report [9]. SnCl₂ ethanol solution was chosen as the precursor. The commercial reagent of SnCl₂ (98.9%, Kanto Kagaku K. K.) was solved in ethanol (99.5%, Kanto Kagaku K. K.) at the given concentration. Pyrex and quartz glass were used for the substrates in the experiments of the concentration and conductivity effects, respectively. The solution filled in the glass syringe was supplied to the metal capillary by a syringe pump at flow rates of $1.0 \text{ cm}^3 \cdot \text{h}^{-1}$ for the Pyrex substrate and $4.0 \text{ cm}^3 \cdot \text{h}^{-1}$

for the quartz glass substrate. The separations between the capillary and the substrate were 5.0 and 2.0 cm for the Pyrex and quartz glass, respectively. These conditions were determined in the preliminary conducted deposition experiments. The electrospray was operated in the cone-jet mode. The applied voltage was typically in the range from 8 to 15 kV. The capillary end was carefully rounded. The inner and outer diameters of the capillary were 0.3 and 0.4 mm, respectively. The substrate with the dimensions of $10 \times 10 \times 1 \text{ mm}^3$ was heated at 773 K from the backside and was masked by a synthetic mica sheet with a circular aperture of 9 mm in diameter. The layer morphology was observed using the scanning electron microscope (SEM) (XL-30, Philips). The particle size was calculated by averaging over 100 particles in a sample in SEM photographs. At least 10 samples were prepared for each condition. The identification of the deposited layer and the estimation of the crystallite size were carried out using the X-ray diffractometer (RAD-IIc, Rigaku) with Cu K α radiation.

The sensitivity measurements were carried out for 0.5% H₂ in synthetic air. The operating temperature of the sensor was 573 K. The comb-type Au electrode with a 0.4 mm strip was evaporated on the substrate before the deposition. The sensitivity was defined by the resistance ratio under air (R_{air}) and 0.5% H₂ (R_{gas}), $R_{\text{air}}/R_{\text{gas}}$.

For the concentration effects, the precursor solutions of 1×10^{-4} , 1×10^{-3} and 1×10^{-2} mol · dm⁻³ were examined. To exclude another effect, e.g. the layer thickness, the amount of sprayed solute was set to be equal so that the spray times were 10, 1 and 0.1 h for 1×10^{-4} , 1×10^{-3} and 1×10^{-2} mol · dm⁻³, respectively.

For the conductivity effects, the concentration was fixed at 1×10^{-3} mol · dm⁻³. A trace amount of dilute hydrochloric acid was added to the solution. The conductivity of the solution was measured by a conductivity meter (DS-12, Horiba, Ltd.). The palladium doping was carried out by solving the palladium acetylacetonate (99%, Merck & Co., Inc.) in the precursor solution at the concentration of 1 wt% Pd to SnO₂.

3. Results

3.1. Layer Morphologies

For the gas sensor application, a high specific surface area should be retained. The solvent in the droplet has

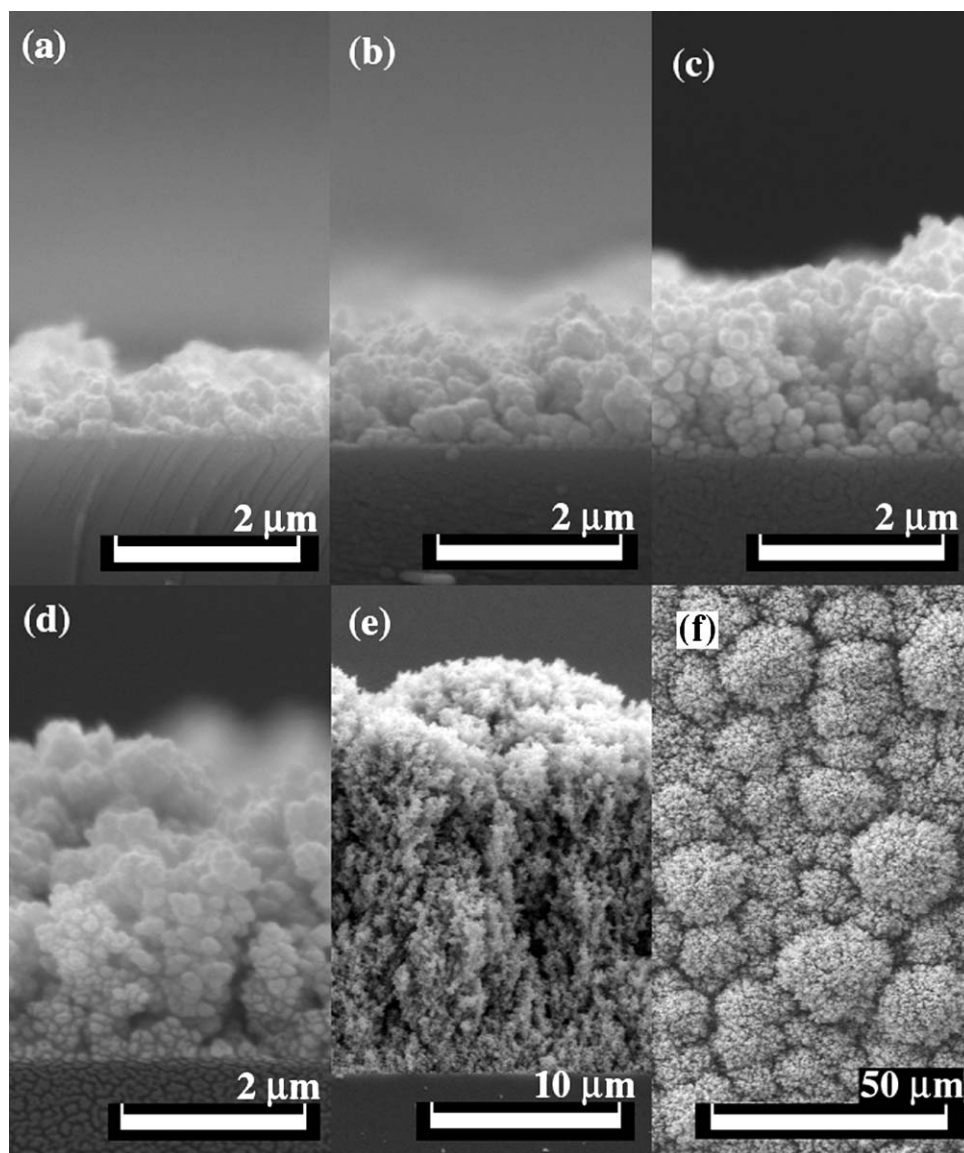


Fig. 1. SEM images of the SnO₂ layers prepared at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ on the quartz glass substrates: (a) to (e) show the cross sections of the layers sprayed for (a) 0.5 h, (b) 1.0 h, (c) 1.5 h, (d) 2.0 h and (e) 12.0 h and (f) is the surface of the layer sprayed for 12.0 h.

to be completely vaporized before reaching the substrate. In order to confirm this, the morphology change against the spray time was investigated. Figure 1 shows the SEM images of the layers prepared at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ on the quartz glass substrate with 2.0 cm separation between the capillary and the substrate. Figure 1(a)–(e) show the cross sections of the layers. The spray times were (a) 0.5 h, (b) 1.0 h, (c) 1.5 h, (d) 2.0 h and (e) 12.0 h. All the layers constituted of the well-defined particles and the distinct dendrite-like structure

was observed. This result indicated the in-flight particle formation during the deposition. Figure 1(f) is the surface of the layer sprayed for 12.0 h. The particles constituted the aggregations like a cauliflower in shape. The aggregation became larger with the spray time. On the layer sprayed for 12.0 h that was 10–30 μm as shown in Fig. 1(f) (see also Fig. 5).

The layer thickness increased linearly at the rate of $1.5 \text{ μm} \cdot \text{h}^{-1}$ under this electro-spraying condition and the deposition rate depended on the precursor

concentration and the separation between the capillary and the substrate.

3.2. Concentration Effects

The concentration effects on the sensitivity were examined with the layers prepared at three different concentrations of 1×10^{-4} , 1×10^{-3} , and $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ on Pyrex substrates. The SEM observation showed that they had the comparable thickness of $0.4 \mu\text{m}$ and that the particle sizes were 110(30), 160(40), and 150(35) nm in diameter at 1×10^{-4} , 1×10^{-3} , and $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, respectively. The values in the parentheses indicate the standard deviation of the measured data. Although the concentration varied in two orders of magnitude, the change in the particle diameters was no more than 1.5. This results from the competition between K in Eq. (1) and C in Eq. (2). From Eq. (1), the droplet size D_d of the solution with the higher concentration becomes smaller, because the conductivity increases with the concentration. On the other hand, the amount of the solute in a droplet increases with C and therefore the particle size d_p in Eq. (2) increases.

The sensitivity change with the concentration is shown in Fig. 2. The error bar indicates the standard deviation of the data. The SnO_2 layer prepared from $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ solution showed the poor sensitivity less than 2. The maximum sensitivity of 20 was attained at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and decreased at $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$. The main factor determining the difference in the sensitivity is still unclear. At least there was no distinct correlation between the sensitivity and the morphology (particle size, roughness and thickness) in the SEM observation.

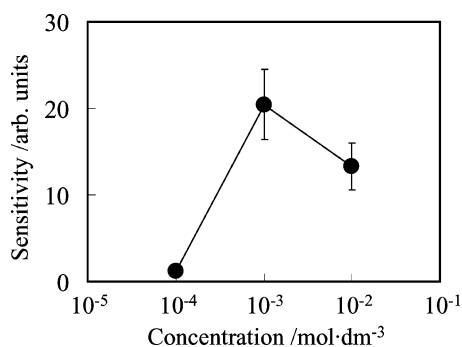


Fig. 2. Sensitivities of the SnO_2 layers on the Pyrex substrate prepared at the different concentrations.

3.3. Conductivity Effects

To examine the conductivity effects the concentration was set constant at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, because the sensitivity showed maximum at this concentration as shown in the previous section. The solution at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ had the conductivity of $7.8 \mu\text{S} \cdot \text{cm}^{-1}$. To increase the solution conductivity a trace amount of hydrochloric acid was added. The particle size showed the decreasing tendency with the increasing conductivity. They were 134(30), 105(20) and 87(20) nm at 7.8, 27.0 and $86.6 \mu\text{S} \cdot \text{cm}^{-1}$, respectively. The values in the parentheses indicate the standard deviation. From Eq. (1), the droplet size D_d decreases with K and therefore d_p in Eq. (2) decreases with C constant. It is known that the sensitivity of the gas sensor of the sintered SnO_2 is enhanced when the grain size is in the order of a few tens of nanometer. The attempt to reduce the particle size to that size range with the higher conductivity failed because of the instability of the electrospray. The electrospray became unstable above $100 \mu\text{S} \cdot \text{cm}^{-1}$.

Figure 3 shows the sensitivity of the SnO_2 layer prepared at the different conductivities on the quartz glass substrate. The doping effect of Pd was also shown in this figure. The error bar indicates the standard deviation of the data. The sensitivity was almost constant around 17 in spite of the increase of the conductivity to 27.0 and $86.6 \mu\text{S} \cdot \text{cm}^{-1}$ by the addition of hydrochloric acid. Figs 2 and 3 showed that the type of the substrate didn't influence the sensitivity of the layer, although it was expected that no contamination of alkali metal from the substrate to the SnO_2 layer enhanced the sensitivity on quartz glass. The SnO_2 layer at the same concentration had the comparable sensitivity of 20 for Pyrex and 17 for quartz glass. The Pd doping by 1 wt%

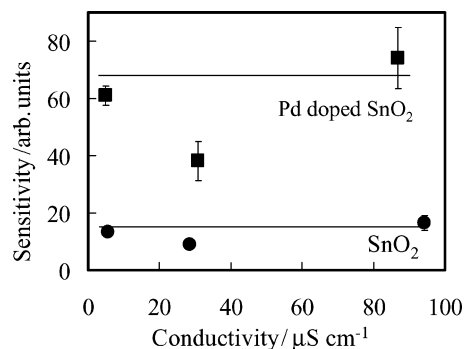


Fig. 3. Sensitivities of the SnO_2 and Pd doped SnO_2 layers prepared at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ with the different conductivities.

enhanced the sensitivity by a factor of 4 for all the conductivities. The dispersion state of Pd in SnO₂ layer didn't change regardless of the solution conductivity.

4. Discussion

It was shown that the sensitivity of the SnO₂ layer depended on the concentration but not on the conductivity. Although the particle sizes varied in the range of 87 and 160 nm depending on the experimental conditions, at least there was no distinct correlation between the sensitivity and the particle size. Figure 4 shows the XRD patterns of the layer at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ for 12.0 h. The thickness was 18 μm . The lower pattern is that of the as-sprayed layer. The middle and upper patterns are those of the layers after heat treatment at 773 K for 1 h and 1073 K for 8 h, respectively. All the peaks were indexed based on the cassiterite structure. The peaks have the relatively large full width at half maximum (FWHM) and only a slight evolution was seen in the peaks after the heat treatment. Because the pyrolysis of the starting chloride and the crystallization of SnO₂ must be completed at least in the layer heated at 1073 K for 8 h, the peak broadening was due to the small crystallite of the particle. Although the absolute value of crystallite size is hardly evaluated using XRD in this dimension range, the Scherrer's equation for 101 reflection resulted in the crystallite size of about 6 nm. The reason that the significant grain growth didn't take place after the heat treatment even at 1073 K for 8 h was probably due to the difficulty of tin dioxide in sintering and poor contact among the crystallites in the particles. From these

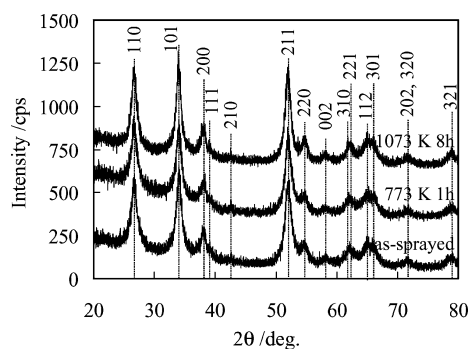


Fig. 4. XRD patterns of the SnO₂ layer sprayed for 12.0 h on the quartz substrate. Lower: as-sprayed, middle: after heat treatment at 773 K for 1 h and upper: after heat treatment at 1073 K for 8 h. Indices are based on the cassiterite structure.

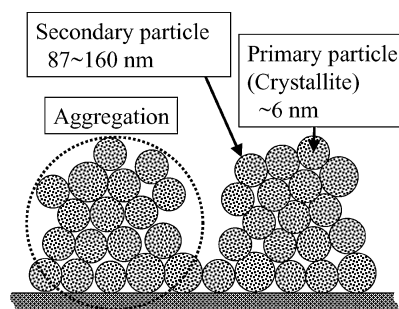


Fig. 5. Schematic illustration of the structure model of the SnO₂ layer obtained in the present work.

facts the sensing property was presumed to depend on the state of the primary particles (crystallites) precipitating in the droplet. The structure of the particle layer discussed here is schematized in Fig. 5. Of the electro-spraying conditions the concentration was important to the sensitivity. The concentration probably affected the state of precursor in the solution and therefore the crystallite formation precipitating in the droplet during the electro-spray.

5. Conclusions

In this work, the particle layers of SnO₂ were deposited on the glass substrates (Pyrex and quartz glass) using the electro-spray pyrolysis method. The effects of the concentration and the conductivity of the solution on the morphology and the sensitivity of the deposited layers were investigated. The layer thickness increased linearly with the spray time and the deposition rate was dependent on the experimental conditions such as the precursor concentration and the separation between the capillary and the substrate. The dendrite-like structure of the deposited layers indicated that the particles were formed in flight before reaching the substrate surface under the conditions we examined. The sensitivity strongly depended on the precursor concentration but not on the conductivity. Among the examined concentrations of 1×10^{-4} , 1×10^{-3} and $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, the layer prepared at $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ showed the maximum sensitivity of 20 for 0.5% H₂. The particle size showed the decreasing tendency as increasing the solution conductivity with the HCl addition. The crystallite size estimated from the Scherrer's equation in XRD was about 6 nm. Therefore the particles of 87–160 nm prepared in this method consisted of the primary particles (crystallites) of ~6 nm in size. It was inferred

that these primary particles (crystallites) played the important role on the sensitivity of the layer. The palladium doping enhanced the sensitivity by a factor of 4.

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