Morphology of SnO₂ Layers Prepared by the Electrospraying Pyrolysis Method

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1. Introduction

The morphology of material films is generally important as well as the chemical composition. For example, tin dioxide has been used for gas sensors and transparent conductive films. The required morphologies are on the opposite extremes between the two applications. Gas sensors are to have a large specific surface area with porous morphology in order to keep contact with gas molecules, although transparent conductive films have to be dense with small grains so that the light scattering at the grain boundaries is suppressed. The authors previously reported that SnO₂ gas sensors prepared by an electrospraying pyrolysis deposition (ESPD) method showed good sensitivity for H₂ gas without any sensitizer. In the ESPD method, alcohol solution of a metal chloride or nitrate is typically electrospayed onto a heated substrate. This method has advantages in the simplicity of the apparatus and wide applicability to various materials. Since devices are prepared only by spraying a precursor solution, the ESPD method is suited for continuous production. The unique morphology of the obtained layers is also characteristic, compared to other spray pyrolysis methods. Gas sensors, transparent conductive films, transparent electrochemical electrodes of lithium ion batteries and electrochemical electrodes of lithium ion batteries have been prepared with the ESPD method.

The electrospraying technique has been applied to a liquid atomizer and a particle generator. The electrospraying phenomena have been thoroughly investigated with both a physical and engineering interest. The liquid is broken up into droplets at the tip of a metal capillary because of the electrostatic instability. The size distribution of the droplets is known to be narrow. The empirical scaling laws to estimate the droplet size are proposed. The commonly referred one expresses the droplet size \( D_0 \) as:

\[
D_0 = G(\varepsilon) \left( \frac{Q e_0}{\varepsilon K} \right)^{1/3}
\]

Where, \( \varepsilon_0 \) is the dielectric permittivity of the vacuum. \( \varepsilon \), \( Q \) and \( K \) are the dielectric constant, the flow rate and the electric conductivity of the liquid, respectively. \( G(\varepsilon) \) is the function of the dielectric constant. The evaluated droplet size in our configuration is a few micrometers under the typically operated electrospraying conditions.

The morphology of the layers obtained in the ESPD method has been investigated by Chen et al. and Stelzer et al., who are the pioneers in developing the ESPD method for ceramic layers. They explained the formation process of the layer with the generation of the droplets, the vaporization of the solvent, the Coulomb explosion of the droplets because of the Rayleigh instability, the preferential landing on the substrate, the discharge and droplet spreading, and drying and the reaction. The Rayleigh instability arises from the limit of the maximum charge a droplet can attain. The droplet ruptures into smaller droplets beyond the limit. By adding the solvent with the high boiling point, a unique three-dimensional (3-D) structure was reported for Li₃MnO₂, LiCO₂ and TiO₂ layers.

There is actually an ambiguity in the deposition processes. For example, if the droplets undergo the Coulomb explosion at step 3, the particle sizes should be inhomogeneous and cannot be controlled or predicted. However, the SnO₂ layers from the SnCl₂-ethanol solution consisted of uniform-sized spherical particles. The diameter was ~ 100 nm, which was comparable to the value estimated by Eq. (1) and the precursor concentration.

The deposited layers were not yet characterized well because the nature of the deposited film is strongly dependent on the precursor and SnCl₂ has been scarcely used in spray pyrolysis methods. The layers showed the broad peaks in the X-ray diffraction (XRD). The peaks did not develop with the subsequent heat treatments up to 800°C. It is not clear whether the peak broadening originates from the amorphous nature or the smallness of the crystallites.

The investigation of the deposition process and the character of the layers are quite important in order to widely apply the method to the ceramic layer deposition. This paper
describes SnO$_2$ layers with various morphologies in the ESPD method. The possible deposition processes are also proposed.

2. Experimental

The laboratory-made electrospraying apparatus was used, which is illustrated in Ref. 1. The SnCl$_2$-ethanol solution was used as the precursor. The commercial reagent of SnCl$_2$ (99%, Kanto Kagaku K. K.) was solved in ethanol (99.5%, Kanto Kagaku K. K.) at a concentration between $1 \times 10^2$ and $1 \times 10^{-1}$ mol m$^{-3}$. The precursor solution was filled in a glass syringe and was supplied to a metal capillary by a syringe pump at a flow rate of 4.0 cm$^{-1}$ h$^{-1}$. The inner and outer diameters of the capillary were 0.3 and 0.4 mm, respectively. The capillary tip was carefully rounded. The Pyrex glass sheets with the dimensions of $10 \times 10 \times 1$ mm$^3$ were used for the substrates. A heater beneath it heated the substrate. The separation between the metal capillary and the substrate surface varied between 20 and 60 mm. The applied voltage was adjusted between 10 and 14 kV to keep the cone-jet mode of the electrospray.\textsuperscript{20,32} The deposited layers were characterized using XRD (Rigaku, RAD-IIb) with Cu K$_\alpha$ radiation. The layer morphology and the particles were observed by scanning electron microscopy (SEM) (Philips, XL-30) and transmission electron microscopy (TEM) (Hitachi, H700C).

3. Results and discussion

3.1 Substrate temperature

3.1.1 Morphology

The substrate temperature is known as an important parameter because the morphology is affected whether the solvent is vaporized or not before reaching the substrate surface.\textsuperscript{7,8} Figures 1(a)–(d) show the morphology of the SnO$_2$ layers at $5 \times 10^0$ mol m$^{-3}$, at (a) 218, (b) 250, (c) 281, and (d) 297°C. These values are the temperature measured with a K-type thermocouple at the surface before electrospraying.

Cracks were shown in the films prepared below 250°C. The surface was partially wet during the deposition because of the incomplete vaporization of the solvent. The precursor gel films were formed on the substrate and shrank with the pyrolysis to SnO$_2$.

The cracks disappeared at 250°C and the deposits began to link together. A unique network structure appeared at 281°C. A somewhat similar structure was reported for Li$_3$Mn$_2$O$_4$, LiCoO$_2$, and TiO$_2$ layers in the literature,\textsuperscript{6,9,10,12} when solvent with a high boiling point such as butyl carbitol was added. According to Ref. 6, droplets of such solvent were not completely vaporized during the flight and they reached the substrate surface. The vaporization on the substrate took place from the rims of the droplets, which led to the 3-D cross-linked structure. On the other hand, only ethanol was used in this work. The network structure is not attributed to the drying process of a solvent. In order to investigate the pyrolysis behavior, SnCl$_2$ powder was heated in a crucible at various temperatures and time. Figure 2 shows the XRD patterns of the products in the crucible after the heat treatments. The pyrolysis rate was dependent on the temperature and was found to be low at lower temperatures. Although the pattern coincided with the starting SnCl$_2$ after the heat treatment at 350°C for 1 h, the heat treatment for 10 h at the same temperature produced SnO$_2$. A temperature of 430°C was needed to pyrolyze bulk SnCl$_2$ powder by the 1 h heat treatment. The SnCl$_2$ is solid at room temperature and the melting point is 248°C, which is close to the temperature where the linkage

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Morphology of SnO$_2$ layers prepared with $5 \times 10^0$ mol m$^{-3}$ solution at (a) 218, (b) 250, (c) 281, and (d) 297°C, respectively.}
\end{figure}
between the particles began to be observed. The network structure at 281°C is probably attributed to the formation of the molten SnCl₂ layer on the substrate, and the release of a by-product gas with the pyrolysis.

The layers became powdery above 281°C and up to 500°C. Figure 3 is a typically obtained thick layer prepared at 500°C with the $5 \times 10^{-3}$ mol m$^{-2}$ solution. The thick layer showed a dendrite-type structure (Fig. 3(a)). The layer from the top view appears to be a group of cauliflowers (Fig. 3(b)). The dendrite-type structure is characteristic of the thick layers, because it was observed at a different concentration. The layer is composed of particles of 100 nm in size, as shown in the magnified image of the layer (Fig. 3(c)). The pyrolysis of SnCl₂ is completed before reaching the substrate and the particles are formed during the flight. It is contrasted to the fact that the SnCl₂ is pyrolyzed on the substrate at 281°C and below. The arriving particles preferentially land on those previously deposited on the substrate by the electrostatic force, because the electric field is stronger at the place where the curvature is large. The local curvature is larger at the deposited particles than that on the flat surface. Such preferential landing has been proposed by Chen et al. and the dendrite-type morphology of the thick layers supports the idea.

The electrostatic force also affected the deposition yield. The evaluated deposition yield in the present work was relatively high. More than 80 mass% of the sprayed solute was deposited within a $50 \times 50$ mm$^2$ square area with the capillary-substrate separation of 50 mm. The traveling particles were not dispersed in the atmosphere by the convection on the heated substrate, although the liquid flow rate was as small as 4 cm$^3$ h$^{-1}$.

3.1.2 Characterization of the particle layer

The microstructure of ceramic films is also important. For example, the performance of sintered SnO$_2$ gas sensors depends on the grain (crystallite) size as well as the morphology. It is known that sensors composed of smaller grains exhibit higher sensitivity. The XRD peaks of the layers in our previous reports were assigned to the rutile-type SnO$_2$, but the peaks were broadened. The crystallite size estimated from Scherrer’s equation was $\sim 6$ nm. In the literature from previous studies, some authors claimed an amorphous SnO$_2$ in the electrospraying pyrolysis method but the distinction between amorphous and nano-sized crystallites is quite difficult in XRD. The XRD is not necessarily suitable to characterize the grains in this size range. Therefore, we carried out the TEM observation for the particles held on a collodion film. Figure 4 shows the TEM image of the particle with the inset of the electron diffraction pattern. Small crystallites of a few nanometers cohere to form the particle of 120 nm in size. The crystallite size is in the order of that estimated by the network structure.
XRD. The distinct Debye-Scherrer rings in the electron diffraction imply that they are fully crystallized.

3.2 Precursor concentration

Unshaped layers embedded with hollow particles were obtained at higher concentrations of $5 \times 10^3$ mol m$^{-3}$ and above. Figure 5 shows the cross-section of the layer obtained at 500°C with the $1 \times 10^3$ mol m$^{-3}$ solution. The capillary-substrate separation was 20 mm. Such a hollow structure can be applied to a thermal insulator.

Hollow particles are often observed in spray drying processes. Leong investigated the particle shapes in the spray drying process theoretically and experimentally.$^{44,45}$ The hollow particle tends to form with a higher solute mass in a droplet, because the crystallization takes place at the droplet surface where the solute concentration is at a maximum. Since in the present case, the temperature is high enough to accompany the pyrolysis and sometimes the melting of the precursor, the situation is somewhat different from the spray drying described by Leong. However, the trend that the higher concentration brings the hollow particles is consistent with the case of the spray drying. The background, unshaped layer also appears to be the fragments of distorted shells of the hollow particles.

3.3 Comparison of the deposition processes

The possible deposition processes are compared in Fig. 6. The substrate temperature had an effect on both the solvent vaporization and the precursor pyrolysis. The cracked films were obtained below 250°C. It indicated that the substrate surface was partially wet during the deposition. Precursor gel films were formed on the surface and the shrinkage resulted in the cracks. The unique network structure appeared at the middle temperature ($281^\circ$C), which was due to the melting of the precursor SnCl$_2$ on the substrate and the release of a by-product gas.

Although the pyrolysis took place on the substrate at $281^\circ$C and below, it was completed before reaching the substrate above $281^\circ$C. The precursor precipitated in the droplets and the particles were formed during the flight. The formation process of the particles was affected by the concentration. The hollow particles observed at $5 \times 10^3$ mol m$^{-3}$ and above resulted from the shell formation in the droplets during the vaporization of the solvent. On the other hand, the spherical particles of ~100 nm were generated below $5 \times 10^1$ mol m$^{-3}$, which were agglomerates of crystallites of a few nanometers. They deposited on the substrate to construct the dendrite-type thick layers.

As a summary of the nature of the precursor, the cracked films at the lower temperatures seemed a common feature independent of the kind of precursors, because similar films have been reported in the previous literature.$^{7,8}$ The layers obtained above 250°C were specific to the precursor SnCl$_2$. The network morphology at 281°C and the porous packed particle layers obtained above 281°C were dependent on the low volatility of SnCl$_2$. The SnO$_2$ layers prepared from volatile precursors, such as SnCl$_2$ and tin acetate in the spray pyrolysis method sometimes showed the crystal habits,$^{46,47}$ which indicated the crystal growth through the vapor deposition. Such vapor deposition did not take place for SnCl$_2$, because the melting point and the boiling point temperatures of SnCl$_2$ are 248 and 623°C, respectively.

4. Summary

Morphology change was demonstrated by varying the electrospraying conditions. The substrate temperature and the precursor concentration were the crucial factors for the morphology. The formation of the precursor gel films on the substrate led to the cracked films at temperatures lower than 250°C. The unique network structure observed at 281°C originated from the molten SnCl$_2$ layer and the release of a by-product gas. When the temperature was high enough for the pyrolysis, the particles were formed during the flight. Spherical particles of ~100 nm were obtained at concentrations lower than $5 \times 10^1$ mol m$^{-3}$. The deposition manner was affected by the electrostatic force and the particles constructed the dendrite-type thick layers. When the concentration was $5 \times 10^1$ mol m$^{-3}$ and higher, the unshaped layers embedded with the hollow particles were obtained.

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References