Solvothermal synthesis of ZnO spherical particles and VOC sensor application

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We synthesized micrometer-sized ZnO spherical particles solvothermally from the solutions of zinc acetate anhydride, hexamethylenetetramine (HMT), ethylene glycol (EG) and water, and examined the gas sensing properties. The spherical powders were composed of nano particles, which were radially aligned along the c-axis. We obtained particles with smaller crystallites under conditions of higher EG concentrations and shorter reaction period. Spherical powder made of crystallites of 3–5 nm was precipitated in the 95 vol %-EG solvent by heating at 120°C for 4 h. The ZnO powder annealed at 450°C worked as a gas sensor device for volatile organic compounds (VOC) gases. The sensitivity was the best in the case of ethanol gas at 350°C.

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1. Introduction

Zinc oxide (ZnO) is a wide-bandgap semiconductor with a large exciton binding energy. It is widely used for the electronic applications, such as varistors, surface acoustic wave filters, transparent electrodes, phosphors, and gas sensors. Among many ZnO fabrication techniques, solution processes are expected to make complex nanostructures by environmentally friendly and simple methods at low temperatures. Recently, review papers on the synthesis of ZnO precipitates and thin films by solution-based processes including chemical bath deposition, hydrothermal deposition and electro-deposition were published and a wide variety of ZnO morphologies (e.g., nanowires, rods, plates, stars, flowers, rings, and spheres) were reported. These nanostructured ZnO materials have been expected for sensor applications due to their high surface-to-volume ratio.

ZnO hierarchical structures receive attention in the morphology and the orientation control. One of the methods to synthesize ZnO hierarchical structures is the ethylene glycol (EG)-assisted solvothermal process using mixtures of water and EG as solvents. Because EG has affinity for water, the conditions of hydrothermal processes can be optimized by adjusting the mixing ratio of EG to water. Round shaped ZnO particles such as spheres, doughnuts and flowers have been synthesized. The particles often showed hierarchical structures, where component crystallites were radially aligned along the c-axis.

Previously we reported a novel solvothermal condition to synthesize spherical ZnO particles from zinc acetate anhydride and hexamethylenetetramine (HMT) in a mixed solution of EG and water. The chemical reactions of zinc acetate and HMT in aqueous solutions are as follows:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^{-} \\
\text{Zn(} \text{CH}_3\text{COO})_{2} \rightarrow \text{Zn}^{2+} + 2\text{CH}_3\text{COO}^{-} \\
\text{Zn}^{2+} + 2\text{OH}^{-} \rightarrow \text{ZnO} + \text{H}_2\text{O}
\]

When HMT in aqueous solutions are heated, HMT decomposes to formaldehyde and ammonia, which acts as a base and induces ZnO precipitation. Spherical ZnO particles with hierarchical structures built of small crystallites were obtained at lower temperatures than the cases in the absence of HMT. The volume ratio of EG to water played a critical role in the formation of spherical particles. In addition, EG restricted the growth of ZnO microcrystals and particles were composed of smaller crystallites at higher ratio of EG to water in solvents. It occurred due to the capping effect, which was commonly observed in the EG-assisted solvothermal synthesis of ZnO particles.

Nanostructures with small size, good crystallinity, and less-agglomerated configurations have advantages. In this study, we selected a high EG concentration condition, the 95 vol %-EG solvent, for ZnO spherical particles made of small crystallites, and investigated the effects of the aging period and temperature on the morphology of the ZnO powder. We tried to make gas sensor devices by using porous spherical particles and evaluate the gas sensing properties for volatile organic compounds (VOC) gases.

2. Experimental

Zinc acetate anhydride (Wako Pure Chemical Industries) 2.202 g and HMT (Wako) 1.682 g were dissolved in each 20 ml of mixed solution of 95 vol %-EG solvent by heating at 120°C for 4 h. The mixed solutions were placed in Teflon lined stainless steel cylindrical chambers of 50 ml capacity and were then heated in an oven at 95–120°C for 3–12 h. After cooling to room temperature, the precipitates were separated by centrifugation. Washing with ethanol and ultrasonication was repeated three times. The resultant powders were dried at room temperatures. The particles were observed by using scanning electron
microscopy (SEM; HITACHI, S-5000). The cross-section of the spherical particle was observed by transmission electron microscopy (TEM; JEOL, JEM-2100F) with field emission gun, operated at 200 kV. We tried to determine the orientation of crystallites by selected area electron diffraction (SAED). The powder was dried at 250°C for 1 h and then the relative surface area of the powder was measured by using a surface area analyzer (Autosobe-1, Quantachrome Instruments).

The ZnO powder prepared at 120°C for 4 h was annealed at 450°C for 4 h in air. The slurry dispersed in ethanol was drop-deposited on the gold interdigital electrode with 100 nm pitch sputtered on a glass substrate and dried. The electric resistance under gas flow (1000 ppm H₂, 50-ppm ethanol and 50-ppm toluene) was measured in air at 350°C as a function of time. Air and the target gases were alternately flowed into a measurement system at 70 sccm. A standard resistor was connected with the sensor, and the voltage across the standard resistor was measured under an applied DC voltage of 4 V to evaluate the electrical resistance of the device. The gas sensitivity ($R_{\text{air}}/R_{\text{gas}}$) was defined as the ratio of the sensor resistance in air ($R_{\text{air}}$) to that in the object gas ($R_{\text{gas}}$).

3. Results and discussion

We obtained micron-sized ZnO spherical particles under the preparation conditions at 95–120°C in 95 vol%-EG solvents. Figure 1 shows a typical SEM photograph of ZnO particles prepared by heating at 120°C for 4 h. The particle size was 1–5 μm and the average diameter was 2.5 μm. The particle size did not so much depend on the preparation conditions and was comparable to the previous results prepared in 87.5 vol%-EG solvents at 95°C.5)

Newly precipitated powders were porous, and the surface of the aged powders was covered with plate-like patches. Induction periods before precipitation of spherical particles were about 6 and 3 h at 95 and 120°C, respectively. SEM photographs of the ZnO particles are shown in Fig. 2. When particles were prepared by heating for 6 h at 95°C, the crystallites at the surface was about 30 nm [Fig. 2(a)]. The surface was porous and there were holes about 50 nm. When the particles were aged for 12 h, the surface was completely covered with plates about 0.2 μm as shown in Fig. 2(b). When particles were prepared by heating for 4 h at 120°C, the surface was composed of small particles about 20–30 nm, which were separated individually [Fig. 2(c)]. The surface aged for 12 h shown in Fig. 2(d) was covered with plates about 0.3 μm.

The inner structures of the ZnO spherical particle were observed by TEM. The cross-sectional images of the spherical particles are shown in Fig. 3. Radial contrast was observed for all samples. The ZnO spherical particles were revealed as agglomerates of nano-particles. In Fig. 3(a), the images of the particles made by heating for 6 h at 95°C are shown. The surface was rough and holes about 50 nm were found at the surface, which was also observed by the SEM [Fig. 2(a)]. There were triangle-shaped particles about 30 nm at the surface and the inside was made of crystallites about 5 nm. The surface aged for 12 h in Fig. 3(b) was covered with a dense layer of triangle particles about 0.2 μm, which formed due to abnormal grain growth at surface. The triangle shape is the sectional image of pyramid-shaped crystallites, which were also observed for the sample previously prepared in 87.5%-EG solution.15) The plate-like patches at the surface of the spheres observed by the SEM [Fig. 2(b)]

Fig. 1. SEM photograph of the spherical ZnO particles prepared by heating at 120°C for 4 h.

Fig. 2. SEM photographs of the spherical ZnO particles prepared by heating for (a) 6 h at 95°C, (b) 12 h at 95°C, (c) 4 h at 120°C and (d) 12 h at 120°C.
were found to be the surface of pyramid-shaped particles. The inner side of the surface layer was composed of nano particles about 10 nm. When particles were prepared by heating for 4 h at 120°C, the crystallite size was 3–5 nm [Fig. 3(c)]. The smallness of the particles was attributed to higher degree of super saturation at higher temperatures. The inside of the particles was almost dense and the surface was more homogeneous than that prepared at 95°C.

The SAED patterns shown in Fig. 3 revealed that the crystallites were almost radially aligned along the c-axis for all the three samples. The SAED spots for the present samples were less sharp compared with the previous sample made of larger pyramid-shaped crystallites (30–100 nm), which were prepared in the 87.5 vol%-EG solution at 95°C for 12 h reaction.15)

For the following investigation, we chose the reaction condition at 120°C for 4 h, where ZnO porous powder composed of relatively small crystallites was obtained. The relative surface area of the particles was 3.3 m²/g. Figure 4 shows the SEM photographs of the ZnO powder (a) before and (b) after annealing at 450°C. The spherical shape did not change by annealing. The size of the particles at the surface grew to 50 nm, which is almost twice the size before annealing.

The dynamic response of porous spherical powder of ZnO was first measured by using a mixed gas of H₂ in air (1000-ppm) at 350°C in order to consider the sensing mechanism for the reducing gases. The measured typical dynamic responses of ZnO to the 1000-ppm H₂ in air measured are shown in Fig. 5(a).
The resistance of ZnO powder decreased by about one order of magnitude upon the gas exchange from the air to the H₂-air, and then recovered completely by the reverse exchange. The gas sensing mechanism can be explained as follows: in air atmosphere and at high operating temperatures, oxygen molecules are adsorbed onto the surface of the ZnO sensor to form O⁻ or O²⁻ ions by attracting electrons from the conduction band of the ZnO. When the ZnO gas sensor is exposed to reducing gases, the gas reacts with oxygen ion molecule on the surface and gives back electrons into the conduction band, thereby lowering the resistance of ZnO sensors.\(^1\),\(^2\)

We next studied the sensing property of the ZnO powder to the reducing gases such as H₂, ethanol and toluene. The results are shown in Fig. 5(b), where the sensitivity is defined as the ratio \(R_{\text{air}}/R_{\text{gas}}\). It is confirmed that the ZnO powder has a high sensing property and the sensitivity for the 50-ppm ethanol was the highest value over 20. The value for the 50-ppm toluene is half of the one obtained for 50-ppm ethanol and the value for the 1000-ppm H₂ is the lowest. Thus, we confirmed that the ZnO spherical powder works well as a VOC gas sensor. The best sensitivity of the ZnO spherical powder was obtained for ethanol.

Compared with the sensitivity measured for ethanol gas sensors based on the other ZnO nanomaterials at 50 ppm, such as 17 for nanoflowers at 320°C,\(^15\) 15 for nanowires at 300°C,\(^17\) and 20 for porous nanosheets at 320°C,\(^18\) the sensitivity for the present ZnO powder, which were 20 at 350°C, is comparable. Zhang et al. reported a high sensitivity of 100 at 400°C for ZnO nanosheets, which were synthesized by annealing of the zinc carbonate hydroxide hydrate precursors at 300°C,\(^19\) and they suggested that the high ethanol-sensing performance resulted from the following factors: (1) large specific surface area, (2) 3D network architecture and (3) high single-crystallinity. In order to improve the sensitivity of the present powder, further researches on these factors are expected. Systematical study on the sensing property would be performed in the near future.

4. Summary

Micrometer-sized ZnO spherical particles were synthesized solvothermally by heating the solution of zinc acetate anhydride, HMT, EG and water. The spherical powders were composed of nano crystallites, which were radially aligned along the c-axis. We obtained particles with smaller crystallites under the conditions of higher EG concentrations and shorter reaction period.

Spherical powder made of crystallites of 3–5 nm was precipitated in the 95 vol%‐EG solvent by heating at 120°C for 4 h. The gas sensor devices made by using the ZnO powder annealed at 450°C reacted to reduced gases of H₂, ethanol and toluene and the sensitivity was the best for ethanol at 350°C.

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