Preparation of Hollow Fibers of Tin Oxide with and without Antimony Doping

Hiroaki Imai,* Yukie Iwaya, Kazuhiko Shimizu, and Hiroshi Hirashima
Department of Applied Chemistry, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223-8522

(Received May 2, 2000; CL-000424)

Hollow fibers of tin oxide with and without antimony doping were prepared by a chemical solution deposition technique using cotton fibers as a template. Homogeneous coating of tin dioxide undoped and doped with antimony was achieved on the organic fibers in aqueous solutions of tin difluoride and antimony trifluoride. Crystalline tin oxide hollow fibers were then obtained by removing the organic compounds with combustion in air. Since antimony-doped tin oxide annealed at 500–600 °C showed a low resistivity around 3.5×10^{-3} ohm·cm, the ceramic fibers produced by this technique have great potential as a novel conductive material.

Since antimony-doped tin oxide (SnO_2) exhibits both optical transparency in the visible region and high electrical conductivity, it is widely used in numerous applications, such as solar cells, liquid crystal displays and heat mirrors in window glasses. Various methods including spray pyrolysis,[1,2] chemical vapor deposition[3–5] and sputtering[6] were studied for preparing SnO_2. These techniques usually provide SnO_2 thin films on a flat substrates for the applications. Electrically conductive anisotropic particles are also needed for preparation of SnO_2–polymer composites which can be used to prevent electrification and to shield electromagnetic radiation. Tsugeki et al.[7] prepared SnO_2-coated whiskers by chemical vapor deposition. From this view point, SnO_2 fibers are expected to show better performance for the conductive polymer composites.

Recently, direct deposition techniques using supersaturated chemical solutions have been developed for the preparation of metal-oxide films such as silica,[8] titania,[9–11] and vanadia.[12] One of the authors has reported that tin(IV) oxide films were directly deposited from tin(II) fluoride (SnF_2) solutions.[13] Using these techniques, various substrates having complex shapes can be coated through heterogeneous nucleation. We reported that organic fibers, such as paper and cotton, were coated with titania small particles by the deposition technique in TiF_4 solutions. Anatase nanotubes were also prepared using nanochannels of porous alumina membranes.[14] Here, we describe the preparation of hollow fibers of SnO_2 by the deposition technique in SnF_2 solutions using organic fibers as a template. The scheme of this technique is shown in Figure 1. Ceramic hollow fibers were obtained by removal of the organic compounds with calcination in air.

Precursor solutions were prepared by dissolving SnF_2 (Kanto Chemicals) in purified water and stirred for 1 h. The SnF_2 concentration of the solutions were adjusted to 0.005–0.03 M. Antimony(III) fluoride (SbF_3) (Wako Pure Chemical) was previously dissolved in the purified water for doping of antimony into SnO_2. Cotton fibers were immersed in the solutions and maintained at 60–100 °C for 3 h. In order to measure the resistivity and the composition of the deposited samples, SnO_2 was prepared on a glass slide at the same conditions. Following our previous study,[13] SnO_2 films were deposited in aqueous solutions containing 0.005–0.3 M SnF_2. Hydrolysis and oxidation of SnF_2 in the solution induced the stepwise reactions producing SnO_2 as shown below:

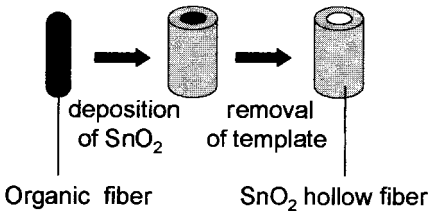

Figure 1. A scheme for preparation of SnO_2 fibers by chemical solution deposition using organic fibers as a template.

$$SnF_2 + O_2 + H_2O \rightarrow Sn(OH)_{4-x}F_x \rightarrow SnO_2 \quad (1).$$

Thin films were prepared through heterogeneous nucleation on various kinds of hydrophilic substrates, such as glass and organic polymers, because the solutions in that condition become gradually supersaturated with SnO_2 produced by the stepwise reactions. The composition of the deposited films was estimated by an X-ray photoelectron spectroscopy (XPS, JEOL JPS-90SX). Since tin(IV) was detected by the tin 3d XPS spectra in the deposited films, tin(II) of the precursors was oxidized to tin(IV) in the aqueous solutions.

Using this technique, SnO_2 coatings were successfully deposited on cotton fibers. The organic fibers were removed by combustion at 500 °C for 3 h in air using a conventional electric furnace after drying the deposited samples. The heating rate was 5 °C min^{-1}. After removing the organic fibers used as a substrate, the deposited SnO_2 was obtained as hollow fibers. The morphology of the samples observed using a scanning electron microscope (SEM, Hitachi S-2150) was shown in Figure 2. Since the shape of the SnO_2 fibers was reflected by the original structure, the deposition occurred through heterogeneous nucleation on the cotton surface. The precursor solutions supersaturated with SnO_2 directly produce the crystal nuclei on the surface. Since relatively dense coatings were obtained on the fibers, the morphology of the fibers is not deformed during the calcination. Thus, the shape of the ceramic textiles can be definitely controlled by this technique.

According to an XRD pattern, the hollow fibers are identified to crystalline SnO_2 having a rutile structure. Since the weak peaks assigned to SnO_2 were observed on the XRD patterns for the as-deposited samples, it is confirmed that the deposition of SnO_2 was induced after oxidation of tin(II) in the aqueous solution. The crystallinity increased with the calcination above 300 °C. Doping of antimony slightly affected the crystallinity of SnO_2 films.

The composition was measured by XPS using the hollow

Copyright © 2000 The Chemical Society of Japan

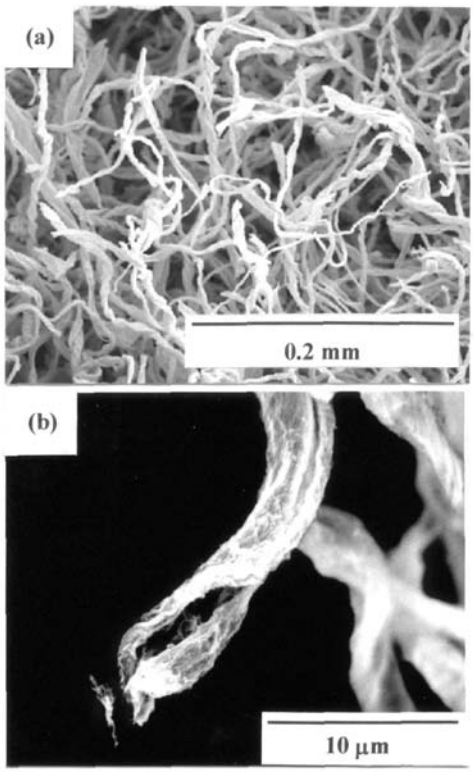

Figure 2. Micrographs of SnO_2 fibers obtained with (a) optical microscope and (b) scanning electron microscope.

fibers and samples deposited on a glass substrate at the same conditions as for cotton fibers. Antimony was detected in the fibers and the films deposited in the solutions containing SbF_3. The Sb/Sn molar ratio in the deposited samples was almost the half of that in the precursor solutions. The difference of the molar ratio between the deposited films and the precursor solutions is ascribed to the reactivity of SnF_2 and SbF_3. Oxidation and hydrolysis of SnF_2 is assumed to be faster than those of SbF_3. However, further investigation is needed to clarify the detail of the deposition mechanism. Since a trace amount of carbon was detected on the hollow fibers, organic compounds were almost removed by the calcination.

The resistivity of the samples deposited on glass slides was measured by the four probe method using a Loresta MP MCP-T350. The films was used for the estimation of the resistivity because hollow fibers were not suitable for the exact estimation. The resistivity of the films heated below 300 °C was higher than the detection limit (10^2 ohm cm) regardless of the antimony content. On the other hand, the resistivity of the films fired above 300 °C depended on the Sb/Sn molar ratio. The minimum value (3.5×10^{-3} ohm cm) was obtained by calcination at 600 °C at Sb/Sn = 0.15 (solution). The high resistivity of the untreated samples is attributed to low crystallinity, the valence of antimony or residual fluorine atoms on the surface. This result indicates that SnO_2 composing the fibers exhibit sufficiently high electrical conductivity. Thus, antimony-doped SnO_2 hollow fibers are applicable to the usage for electrical conductive polymer composites. Moreover, highly tailored catalysts and gas sensors could be prepared by this technique because the shape of the ceramic fibers is easily controlled by the organic templates.

In conclusion, tin oxide hollow fibers with and without antimony doping were prepared from aqueous solutions of tin(II) fluoride and antimony(III) fluoride using organic fibers as a template. The shape of the fibers exactly reflects the original structure of the organic template. The resistivity of the deposited tin oxide was estimated to be in the order of 10^{-3} ohm cm.

References

1 J. S. Maudes and T. Rodriguez, *Thin Solid Films*, **69**, 183 (1980).
2 R. Pommier, C. Gril, and J. Marucchi, *Thin Solid Films*, **77**, 91 (1981).
3 J. Kane, H. P. Schweizer, and W. Kern, *J. Electrochem. Soc.*, **123**, 270 (1976).
4 R. N. Ghoshtagore, *J. Electrochem. Soc.*, **125**, 110 (1978).
5 T. Muranoi and M. Furukoshi, *Thin Solid Films*, **48**, 309 (1978).
6 E. Leja, T. Pisarkiewicz, and A. Kolodziej, *Thin Solid Films*, **67**, 45 (1980).
7 K. Tsugeki, T. Yoshikawa, H. Maeda, K. Kusakabe, and S. Morooka, *J. Am. Ceram. Soc.*, **76**, 3061 (1993).
8 H. Nagayama, H. Honda, and H. Kawahara, *J. Electrochem. Soc.*, **135,** 2013 (1988).
9 S. Deki, Y. Aoi, O. Hiroi, and A. Kajinami, *Chem. Lett.*, **1996**, 433.
10 L. Baskaran, J. Song, Y. L. Liu, G. L. Chen, and J. Graff. *J. Am. Ceram. Soc.*, **81**, 401 (1998).
11 K. Shimizu, H. Imai, H. Hirashima, and K. Tsukuma, *Thin Solid Films*, **351**, 220 (1999).
12 S. Deki, Y. Aoi, and A. Kajinami, *J. Mater. Sci.*, **32,** 4269 (1997).
13 K. Tsukuma, T. Akiyama, and H. Imai, *J. Non-Cryst. Solids*, **210,** 48 (1997).
14 H. Imai, K. Shimizu, M. Matsuda, and H. Hirashima, *J. Mater. Chem.*, **9,** 2971 (1999).