Preparation of In_2O_3 Fine Powders and Their Two-Step Sintering

Hiroshi YAMAMURA, Yasutomo TAKAHASHI and Katsuyoshi KAKINUMA

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama-shi 221-8686

In_2O_3 微粉末の合成とその2段階焼結

山村 博・高橋靖知・柿沼克良

神奈川大学工学部応用化学科, 221-8686 横浜市神奈川区六角橋 3-27-1

Fine powders of In_2O_3 were obtained by thermal decomposition of the precipitates, which were prepared by an oxalate method in ethanol solution. The sinterability of the powders was improved considerably, compared with that of commercial powders. The maximum density reached 82% of the theoretical value by sintering at 1450°C. Furthermore, the relative density increased as high as 90.9% by a new two-step sintering process, which includes a presintering step at a relatively low temperature and a final sintering step at 1450°C under atmospheric condition. The electrical resistivity of sintered In_2O_3 was strongly dependent on the relative density and increased in proportion to the measurement temperature, showing metallic conduction behavior. The temperature coefficient (α) in the linear relationship was ascribed to an electron scattering effect due to porosities. The residual resistivity (ρ_r) of 0.0038 $\Omega \cdot \text{cm}$, which was estimated by extrapolation to 0 K, agreed with the value reported for the single crystal grown from vapor phase.

[Received June 25, 2001; Accepted September 26, 2001]

Key-words: Two-step sintering, Electrical conductivity, Relative density, Oxalate, Fine powder

1. Introduction

Indium oxides (In_2O_3) are widely used in electro-optic applications because of their high level of transparency in the visible light range and high electronic conductivity. In particular, as Sn-doped In_2O_3 (ITO) thin films have been used as transparent electrodes of liquid crystal devices and other display devices, many papers concerning the thin films have been reported. On the other hand, there are only a few reports about the sintered bulk sample of pure In_2O_3 because of the difficulty in sintering. Although a sintered ITO sample with above 90% relative density has been reported on, the details of the powder preparation process have not been clarified.^{1,2)} De Wit³⁾ pointed out that the reported electrical conductivity data were widely scattered due to the preparation conditions, impurities, grain boundaries and different densities. Sasaki et al.⁴⁾ reported in their study of the In_2O_3 - ZrO_2 system that the electrical resistivity of pure In_2O_3 was estimated to be 0.25 $\Omega \cdot \text{cm}$ at room temperature, which was much larger than the value of the single crystal reported by Behr et al.,⁵⁾ though they also reported that the densities of all samples were more than 94% of the theoretical density. Son et al.⁶⁾ reported that the sintered In_2O_3 with full density was obtained by firing at 1500°C under pressure (5 MPa) after presintering at 1000–1130°C, while no electrical conductivity data were found in their paper. Recently, Muraoka et al.⁷⁾ succeeded in obtaining sintered ITO with high density by doping 2.0 mass% Bi_2O_3 .

In order to obtain a highly sintered In_2O_3 sample, which shows an intrinsic bulk property, we tried to prepare fine powders of In_2O_3 by an oxalate method in an ethanol solution,^{8,9)} by means of which fine powders of Pb(La) (Zr, Ti) O_3 (PZT, PLZT) have been successfully prepared, and to sinter the In_2O_3 fine powders by a pressureless two-step sintering method.

2. Experimental procedures

2.1 Preparation of fine powders

In_2O_3 powders were prepared by the oxalate method in an ethanol solution. For comparison, a commercial In_2O_3 powder

(Furuuchi Chemicals, 99.99%) was also used. $\text{In}(\text{NO}_3)_3$ (High Purity Chemicals., 99.99%) was used as the starting reagent. Aqueous solutions of $\text{In}(\text{NO}_3)_3$ with various concentrations (0.3–0.8 mol/l) were slowly titrated into the ethanol solutions of oxalic acid at room temperature at a constant rate. The oxalic acid amounts used were 1.5 times the stoichiometric amounts. The final pH value of the solution was 2.3. After the solution containing the precipitates was stirred at room temperature for 1 h, it was suction-filtered. The precipitates separated were washed several times by ethanol, dried at 110°C, and finally fired at various temperatures between 600 and 800°C for 2 h in air.

2.2 Sintering procedures and characterization of samples

In_2O_3 powders thus obtained were compacted into pellets by pressing uniaxially at 5 MPa, and pressing again isostatically at 200 MPa. The pellets were sintered at various temperatures of 1200–1500°C for 10 h in air. The maximum relative density obtained was at most 83.4% when the pellets were sintered at 1450°C. In order to increase the density, a pressureless two-step sintering process was first introduced in the present study. As the first step, the compact was presintered at temperatures in the range of 700–1100°C for 10 h at a heating rate of 10°C/min, and then it was pressed again isostatically at 200 MPa after cooling to room temperature. As the second step, the presintered samples were sintered again at various temperatures in the range of 1200–1450°C for 10 h in air, by changing the heating rate from 1 to 10°C/min. The highest density was obtained at the sintering temperature of 1450°C with the heating rate of 10°C/min.

Particle size distribution was measured by a sedimentation method (Shimadzu, SA-CP3). Sodium hexa-metaphosphate aqueous solution (0.2 mass%) was used as a dispersant. The powder morphology of both the oxalates and the heat-treated samples as well as the microstructure of the sintered materials were observed using a secondary electron microscope (SEM; JEOL, JSM-5200). X-ray diffractometry (Rigaku, RAD-A) with monochromated Cu K α radiation

was used for the identification of the samples and the determination of their lattice constant. The theoretical density was estimated using the lattice parameter. The observed density of the sintered materials was determined by the Archimedes method, using deionized water.

The electrical conductivity of the sintered samples was mainly measured by a dc four-probe method in the temperature range from RT to 900°C in air. The isothermal conductivity was measured at temperatures below 900°C in air. Platinum paste as an electrode was applied to both sides of the sample by firing at 1000°C for 15 min in air. The geometrical dimensions of the sintered bar for the dc method were 4 mm × 4 mm and ~30 mm length. The electrical conductivity was estimated from the slope of the linear relationship between applied currents in two (plus and minus) directions and the corresponding voltages for cancellation of the Seebeck effect due to the temperature distribution in the furnace and confirmation of an ohmic contact.

3. Results and discussion

The indium oxalate powders were prepared from an indium nitrite aqueous solution of various concentrations by the oxalate method in ethanol solution. Thermal decomposition of the dried oxalate was completed at about 400°C in thermogravimetry (TG). The weight loss of 52.0% observed in the thermal analysis was larger than the theoretical value (43.8%) calculated from a chemical composition of $\text{In}_2(\text{C}_2\text{O}_4)_3$. The difference between the observed and calculated weightlosses would be ascribed to the presence of hydrated water in the oxalates. The X-ray diffraction (XRD) analysis revealed that the powder obtained by thermal decomposition at 1000°C was a cubic phase of In_2O_3 with the lattice constant of 1.012 nm, which agreed well with the JCPDS value of 1.0118 nm.¹⁰⁾ Average particle sizes of the In_2O_3 powders were strongly affected by the concentration of the $\text{In}(\text{NO}_3)_3$ solution and the calcination temperature. Figure 1 shows the average particle sizes of In_2O_3 powders calcined at 600, 700 and 800°C as a function of the $\text{In}(\text{NO}_3)_3$ concentration. In the case of the 0.2 mol/l solution, anomalously large particles were prepared. Above 0.2 mol/l, the In_2O_3 particle size decreased as the concentration of $\text{In}(\text{NO}_3)_3$ increased, then increased above 0.7 mol/l solution. The SEM observation revealed that the large particles, obtained from the 0.7 and 0.8 mol/l solution, were largely agglomerated. The calcination at higher temperatures increased the particle size. The In_2O_3 powders that were obtained by firing the oxalates from 0.3 mol/l solution at 700°C for 2 h were used for the sintering experiments because the powder, of which D_{50} sizes were under 1 μm and the size distribution was the narrowest, could be well dispersed. On the other hand, the commercial In_2O_3 powders have a 2.5 μm average particle size and broad particle-size distribution.

Figure 2 shows typical shrinkage curves of both the present powder and the commercial powder obtained by dilatometry. The compacted sample bar was heated at a heating rate of 10°C/min in air. Shrinkage of the present powder began at 700°C and was completed at 1100°C, which was about 300°C lower than that of the commercial powder. Furthermore, the shrinkage was two times larger than that of the commercial powder. These results show that the In_2O_3 powder prepared by the oxalate method can be sintered more easily than the commercial one. The sintering experiments were carried out at various temperatures in the range of 1100–1500°C for 10 h in air. The density of the sample increased as the sintering temperature increased and the maximum density reached 82% of the theoretical value by sintering at 1450°C. However, the density abruptly decreased when the powder was sintered at 1500°C. On the other hand, in case of the commercial In_2O_3 powder, the

Fig. 1. Average particle size of In_2O_3 powders calcined at 600, 700 and 800°C as a function of $\text{In}(\text{NO}_3)_3$ concentration. Temperatures are calcination temperatures of the oxalates.

Fig. 2. Shrinkage curves of In_2O_3 . (a) present sample, (b) commercial powder.

relative density was 56.4% when it was sintered at 1450°C for 10 h in air. Figure 3 shows a typical SEM micrograph of the sintered In_2O_3 with a relative density of 82%. The microstructure of the sintered specimens is composed of dense grains connected with the grown necks, accompanied by large pores. Because the shrinkage began at 800°C, as shown in Fig. 2, the compact was presintered at 800°C under atmospheric condition. After cooling to room temperature, it was rubber-pressed hydrostatically again under 200 MPa in order to destroy the neck contact which was formed in the presintering process and to obtain a high green density by the particle rearrangement. The final sintering was

Fig. 3. SEM micrograph of the sintered In_2O_3 with a relative density of 82%.

Fig. 4. SEM micrograph of the In_2O_3 with a relative density of 90.9%, which was sintered by two-step sintering.

carried out at 1450°C for 10 h in air. By this two-step sintering, the maximum relative density could reach as high as 90.9%. The observed SEM picture of the sintered materials is shown in Fig. 4, where the average grain size was estimated to be $\sim 3\mu\text{m}$ and the anomalous neck growth was relatively suppressed, although there were some pores still remaining. The densities decreased with increasing the presintering temperature above 800°C . It is emphasized that the present In_2O_3 powder showed high sinterability through the two-step sintering process in air, while Son et al.⁶⁾ obtained higher density materials by application of the hot-pressing technique in the second step.

The electrical resistivity (ρ) of the sintered samples with various densities increased with the increase of the measurement temperature, showing a metallic conduction behavior. This may be contradictory because In_2O_3 is known as an n-type semiconductor. However, it is known that the metallic conduction can occur due to the presence of a Fermi level in the conduction band, which is called as a "degenerated state," when carrier density is above 10^{18} cm^{-3} . Although the electrical conductivity of semiconductive materials is usually discussed by means of Arrhenius plots, it would be better for the ρ values to be plotted as a function of temperature in the present study because the In_2O_3 sintered material showed metallic conduction. As a result, the resistivity changed linearly in proportion to the absolute temperature (K), as shown in Fig. 5. Accordingly, ρ can be represented

Fig. 5. Electrical resistivity of sintered In_2O_3 as a function of temperature. Percentages denote the relative density.

Fig. 6. Residual resistivity (ρ_r) as a function of the relative density.

by Eq. (1).

$$\rho = \rho_r + \alpha T \quad (1)$$

where ρ_r and α denote the electrical resistivity at 0 K (residual resistivity) and the temperature coefficient of the resistivity, respectively. It was found that the In_2O_3 sintered sample with lower density had higher resistivity and higher α value.

Figure 6 shows the residual resistivity (ρ_r) as a function of the relative density. The ρ_r decreased with increasing the relative density, and approached $0.0038\ \Omega \cdot \text{cm}$ by extrapolation to 100% density. The extrapolated resistivity agreed well with that of the In_2O_3 single crystal ($\sim 0.004\ \Omega \cdot \text{cm}$),

Fig. 7. Temperature coefficient (α) as a function of the relative density in the linear relationship between electrical resistivity and temperature.

which was grown by a chemical transport reaction,⁷⁾ even if many grain boundaries are included in the sintered materials. However, it would be difficult to discuss quantitatively on the basis of this agreement, because the residual resistivity was obtained by the extrapolation from a relatively high temperature. It is generally known that the ρ_r is strongly dependent on impurities, lattice distortion, pores, and grain boundaries. In the present study, the change in the ρ_r values could be ascribed to the porosity of the sintered materials, because other factors such as the impurities and lattice distortion should be almost the same in the present samples.

Additionally, Fig. 7 shows the α -value as a function of the relative density. Since the α -value of the samples with higher density became smaller and could be almost extrapolated to 0 at 100% density, it can be assumed that the α -value also corresponds to a scattering effect of electrons due to pores in the sintered materials during electron conduction.

It is known that the electrical conductivity of In_2O_3 originates from the thermal dissociation of In_2O_3 , as is described by Eq. (2).

Sasaki et al.⁴⁾ have confirmed by thermogravimetric analy-

sis that the thermal dissociation of In_2O_3 begins at 900°C and suddenly increases above 1200°C. Therefore, it can be speculated that the carrier of the electrical conductivity of In_2O_3 occurred due to the quenched state of In_2O_3 dissociated during high-temperature sintering.

4. Conclusions

Highly sinterable powders of In_2O_3 were obtained from the thermal decomposition of the oxalates, which were prepared by the oxalate method in ethanol solution. Through the sintering experiments using the In_2O_3 powders thus obtained, the following results were obtained.

(1) The sintering properties of the powders from the oxalate method were improved considerably, compared with those of the commercial powders. The maximum density reached 82% of the theoretical value at 1450°C firing.

(2) The high-density ceramics of 90.9% density of the theoretical value were obtained by two-step sintering, which includes the presintering process at relatively low temperature and the final sintering at 1450°C in air.

(3) The electrical resistivity of the sintered In_2O_3 with various densities changed linearly with absolute temperature, showing metallic conduction behavior. Both the temperature coefficient (α) in the linear relationship and the residual resistivity (ρ_r) decreased with decreasing porosity in the sintered materials. The α means the scattering effect of conduction electrons due to the pores, and the ρ_r value was 0.0038 $\Omega \cdot \text{cm}$, which agreed with the value of the single crystal grown from the vapor phase.

Acknowledgments This work is partly supported by the High Tech. Research Project at Kanagawa University funded by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

- 1) Ogawa, N., Yoshimura, R., Mouri, T., Iwamoto, T., Baba, H. and Tenma, S., *J. Tosoh Res.*, **34**, 99–180 (1990) [in Japanese].
- 2) Yoshimura, R., Ogawa, N. and Mouri, T., *J. Tosoh Res.*, **36**, 153–59 (1992) [in Japanese].
- 3) De Wit, J. H. W., *J. Solid State Chem.*, **8**, 142–49 (1974).
- 4) Sasaki, K., Seifert, H. P. and Gauckler, L. J., *J. Electrochem. Soc.*, **141**, 2759–68 (1994).
- 5) Behr, G., Werner, J., Oswald, S., Krabbes, G., Dordor, P., Elefant, D. and Pitschke, W., *Solid State Ionics*, **101–103**, 1183–87 (1997).
- 6) Son, J. W., Kim, D.Y. and Boch, P., *J. Am. Ceram. Soc.*, **81**, 2489–91 (1998).
- 7) Muraoka, M., Suzuki, M. and Sawada, Y., *J. Mater. Sci.*, **33**, 5621–24 (1998).
- 8) Yamamura, H., Tanada, M., Haneda, H., Shirasaki, S. and Moriyoshi, Y., *Ceramic Int.*, **11**, 23–26 (1985).
- 9) Yamamura, H., Haneda, H., Watanabe, A. and Shirasaki, S., *Jpn. J. Appl. Phys.*, **24**, Sup. 24–2, 433–35 (1985).
- 10) JCPDS-06-0416.