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Sintering of tin-doped indium oxide (Indium-Tin-Oxide, ITO) with Bi_2O_3 additive

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Tin-doped indium oxide (Indium-Tin-Oxide, ITO) is known as a poorly sinterable material. Densification of ITO powders with relatively large particle size (1–2 μm) was enhanced remarkably by the additive (Bi_2O_3) whose melting point is lower than the sintering temperature. The maximum bulk density of 6.75 g/cm^3 (relative density; 95%) was obtained when pressurelessly sintered in air at 1500 °C for 5 hours using the starting material containing 2.0 mass % Bi_2O_3, while the density was approximately equal to the green density when sintered using the starting material without Bi_2O_3. Increase of electrical resistivity caused by the additive was suppressed successfully when a small amount of Bi_2O_3 (1.0 mass %) was added and heated at 1500 °C. The bismuth was eliminated from the sintered body to achieve the low resistivity (8.1×10^{-4} ohm · cm) which was approximately equal to that of the pure ITO. © *1998 Kluwer Academic Publishers*

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1. Introduction

Thin films of tin-doped indium oxide (Indium-Tin-Oxide) are transparent in the visible range and electrically conductive. The ITO films are widely used as transparent electrodes for liquid crystal displays and other display devices. The films are often deposited by the sputtering method using a sintered body called a target. Since ITO is poorly sinterable, the relative density is typically between 62 and 65% [1] when pressurelessly-sintered in air without any special techniques. Reported high densities (90% [2], 93% [3] and 98% [4]) were estimated to be obtained with special know-how such as powder processing not mentioned in the literature. Dense targets were reported to be advantageous for producing the films with excellent properties at high deposition rate with high process stability. De Wit *et al.* [5] examined sintering additives (MgO, ZrO_2 or CeO_2) for densification of In_2O_3 in air; relative density of 93% was obtained with 1 mol % MgO.

Nate and Kishi [6] reported high density (99%) by sintering in oxygen atmosphere. In the oxidizing atmospheres, formation of the volatile species, In_2O and SnO, is suppressed to enhance the densification. Recent reports on high densities are supposed to be achieved in the oxygen-rich atmosphere except when the sintering atmosphere is specified. Addition of TiO_2, ZrO_2 and SiO_2 to ITO powders by Nadaud *et al.* [7, 8] was also conducted in an oxygen atmosphere; relative density of ≧99% was achieved by TiO_2 addition at 1380 °C for 5 hours. However, sintering at high temperature in an oxidizing atmosphere is basically dangerous, so that a complicated and expensive furnace system is required.

In the present work, densification of ITO in air atmosphere was attempted using a minimum amount of additive with low melting point. No report was found for the sintering of ITO using the additive by which formation of liquid phase was expected. The expected advantage of this technique is less dependence on particle sizes and the powder processing. The additive is expected to disappear, for example, by evaporation after the completion of densification so that the disadvantage (lowering the electrical conductivity or visible transparency of the films) caused by the additive should be minimized when used as a sputtering target. In order to examine the above hypothesis, Bi_2O_3 (melting point: 820 °C [9]) was selected as a model additive.

2. Experimental

The powders were supplied from Kojundo Chemical Lab., Co., Ltd. The ITO powders (99.9%, $In_2O_3 : SnO_2 = 95 : 5$ mass %) with relatively large particle size (∼3 μm) were used intentionally in the present work. The ITO powders were blended with Bi_2O_3 powders (99.99%) in the required ratios (Bi_2O_3 : 0.5, 1 or 2 mass %) before mixing in deionized water for 2 hours using a plastic mill and alumina

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balls (10 mm ϕ). The dried mixture was formed with a press under 20 MPa. The green bodies were packed on a Pt container or alumina plate, which was placed in an electric furnace of the resistance heating type ($MoSi_2$ heating elements). The green bodies were sintered pressurelessly under the given conditions in air atmosphere at 1000 to 1500 °C for 5 hours. The heating rate was 10 °C/min. After sintering, the sintered bodies were furnace-cooled under air.

The density measurement of the sintered body was performed by the Archimedean method. The sintered bodies were cut into $2 \times 2 \times 10$ mm pieces for the electrical resistivity measurement by the four-point method (probe distance; approximately 1 mm) with silver paste. The composition of the sintered bodies was determined by X-ray fluorescence (XRF) analysis (Philps, type PW-1480) using Mo radiation (60 kV, 40 mA) and a LiF (200) crystal. The crystalline phases in the sintered bodies were identified by powder X-ray diffraction (XRD) (Rigaku, type RINT-2500V) using a Cu radiation (40 kV, 300 mA) and a graphite monochlometer. Remarkable darkening observed at the bottom of the sintered bodies suggested the lowering down of the liquid phase. Therefore, the sampling was performed at the approximate center of the sintered body for the electric resistivity measurement and the XRF and XRD analyses.

3. Results and discussion

3.1. Mass loss and composition

The mass losses for the samples are shown in Fig. 1. The mass loss increased with increasing Bi_2O_3 content and sintering temperature. The mass loss of ITO without Bi_2O_3 addition was explained by evaporation of indium and tin as the volatile compounds In_2O and SnO respectively. In the case of the Bi_2O_3-added pellets, the mass loss at relatively low temperature (1300 °C) correlated approximately with the amount of the Bi_2O_3 addition supporting the vaporization of Bi_2O_3. At the higher temperature (1400 and 1500 °C), evaporation of ITO was predominant, since the mass loss exceeded the added mass of Bi_2O_3. It should be noted that a small amount of Bi_2O_3 addition suppressed the evaporation of ITO; the mass loss of the pellet without Bi_2O_3 exceeded that with 0.5 mass % Bi_2O_3 at 1400 and 1500 °C. The suppression by the Bi_2O_3 addition was also observed for the pellets with more addition of Bi_2O_3 at 1500 °C; the mass loss of the pellet without Bi_2O_3 addition was approximately equal to those with more addition (1.0 and 2.0 mass %) of Bi_2O_3. The latter measurements included the mass loss due to the evaporation of Bi_2O_3 so that the evaporation of ITO itself was smaller than the former.

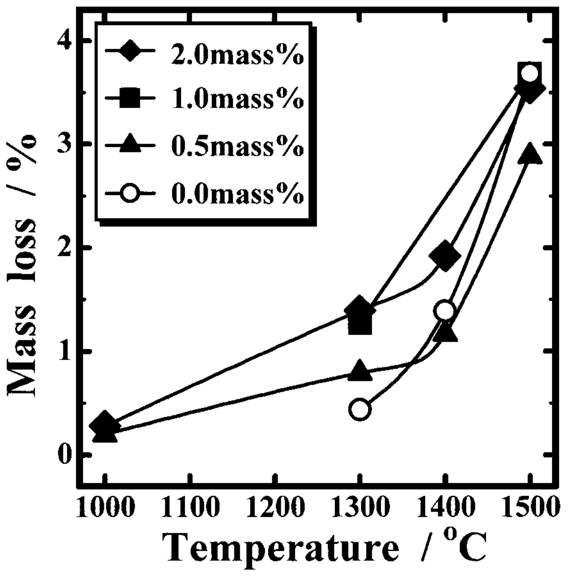

Figure 1 Mass loss for the pellets. ●, ▲, ■ and ◆; ITO with 0.0, 0.5, 1.0 and 2.0 mass % Bi_2O_3 addition, respectively.

The contents of bismuth and tin (indicated as Bi_2O_3 and SnO_2 mass %) are shown in Figs 2 and 3, respectively. The decrease of bismuth at high temperature (Fig. 2) can be explained by the evaporation of Bi_2O_3 and/or melt down of the liquid phase containing

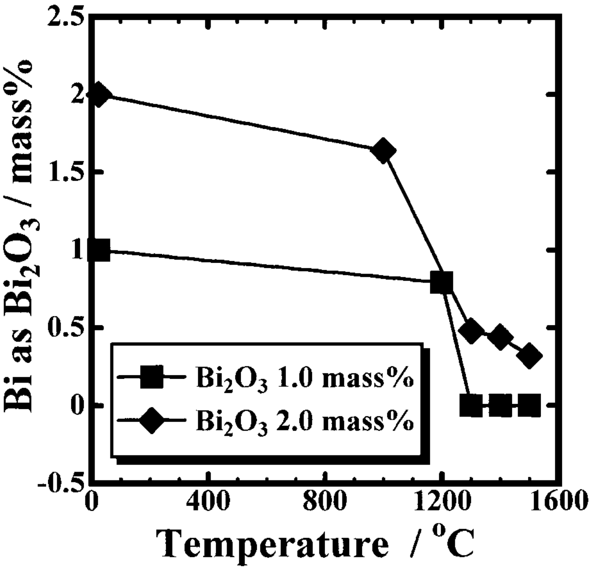

Figure 2 The bismuth contents for the pellets determined by XRF analysis. ■ and ◆; ITO with 1.0 and 2.0 mass % Bi_2O_3 addition, respectively.

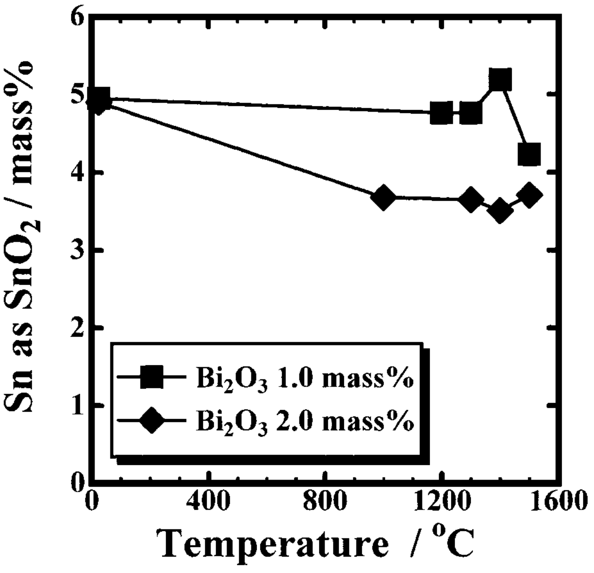

Figure 3 The tin contents for the pellets determined by XRF analysis. The figure captions are identical with those of Fig. 2.

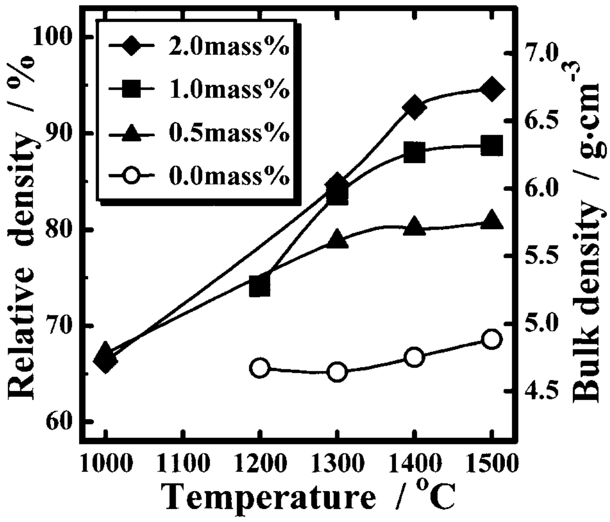

Figure 4 Densities of the sintered pellets. The figure captions are identical with those of Fig. 1.

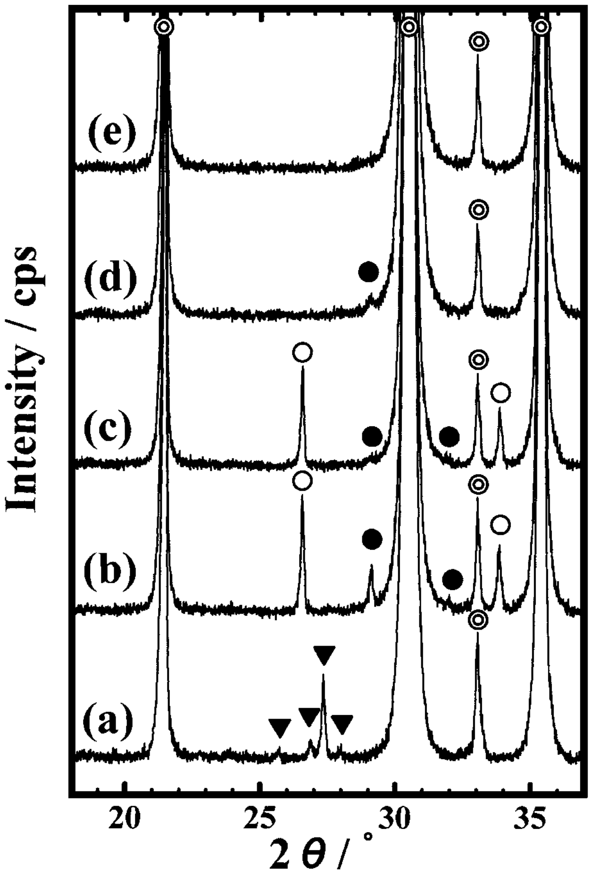

Figure 5 The X-ray diffraction spectra for the pellets. a; unheated pellet (Bi_2O_3; 1.0 mass %), b, c, d and e; heated at 1200, 1300, 1400 and 1500 °C, respectively. ◎, ▼, ○ and ●; the peaks corresponding to ITO, Bi_2O_3, SnO_2 and $Bi_2Sn_2O_7$, respectively.

bismuth. No bismuth was detected when the pellet with a small amount of Bi_2O_3 (1.0 mass %) was heated at $\geqq$1300 °C; elimination of bismuth was achieved successfully.

The contents of tin (Fig. 3) were approximately constant for the 1.0 mass % Bi_2O_3 pellets while the 2.0 mass % Bi_2O_3 pellets showed the decrease of tin at high temperature. When a sufficient amount of Bi_2O_3 was added, bismuth remained in the pellets at the high temperature to accelerate the transport of tin out of the center of the pellet.

3.2. Sintering

Fig. 4 shows the relative and bulk densities of the sintered bodies. The density of pure In_2O_3 (7.12 g/cm^3) [10] was selected as a standard for the relative density since the absolute density of ITO was unknown. In the case of the ITO samples without Bi_2O_3 addition, no densification was observed; the density (65–69%) was approximately equal to the green density (66–67%). The suppression of densification can be explained by the volatile nature of the sample; the evaporation-condensation mechanism contributes only to grain growth. The addition of Bi_2O_3 remarkably enhanced the densification. The densification was dependent on the sintering temperature and the Bi_2O_3 content. The maximum density obtained was 95% (6.75 g/cm^3) when sintered at 1500 °C using the starting material containing 2.0 mass % Bi_2O_3.

3.3. Reaction

The X-ray diffraction patterns for the pellets are shown in Fig. 5. The unheated pellet ((a) in Fig. 5) showed the strong peaks which agreed with those of In_2O_3 [10] and very weak peaks of the additive (Bi_2O_3 [11]). Absence of the peaks of SnO_2 was interpreted as complete formation of the solid solution (ITO i.e. tin-doped In_2O_3).

The sample after being heated at 1200 °C ((b) in Fig. 5) showed the peaks of SnO_2 [12] and $Bi_2Sn_2O_7$ [13] together with the strong peaks corresponding to ITO; the Bi_2O_3 disappeared. In case of the samples with no Bi_2O_3 addition (not shown in the figure), SnO_2 was not observed. These results supported the existence of liquid Bi_2O_3 into which the ITO dissolved and precipitated as ITO with less tin content, SnO_2 and $Bi_2Sn_2O_7$. The existence of SnO_2 can be understood by the large amount of tin than bismuth.

The $Bi_2Sn_2O_7$ disappeared gradually at the higher temperature. The SnO_2 was not detected for the pellets heated at $\geqq$1400 °C ((d) and (e) in Fig. 5). The disappearance of these tin-containing oxides was interpreted as evaporation of Bi_2O_3 and incorporation of tin into the In_2O_3 lattice; higher solubility of tin in In_2O_3 at higher temperature supported this hypothesis.

3.4. Resistivity

Fig. 6 shows the resistivities of the sintered bodies. The decrease in resistivity of pure ITO (i.e. without Bi_2O_3 addition) at higher temperature is interpreted as formation of oxygen vacancy. The addition of Bi_2O_3 increased the resistivity, especially with a high amount of Bi_2O_3 addition (2.0 mass %). This is attributed to the bismuth containing less conductive phase between the ITO grains. In case of a small amount of Bi_2O_3 addition (1.0 mass %) at high temperature (1500 °C), the resistivity (8.1×10^{-4} ohm · cm) was approximately equal to that of the pure ITO;

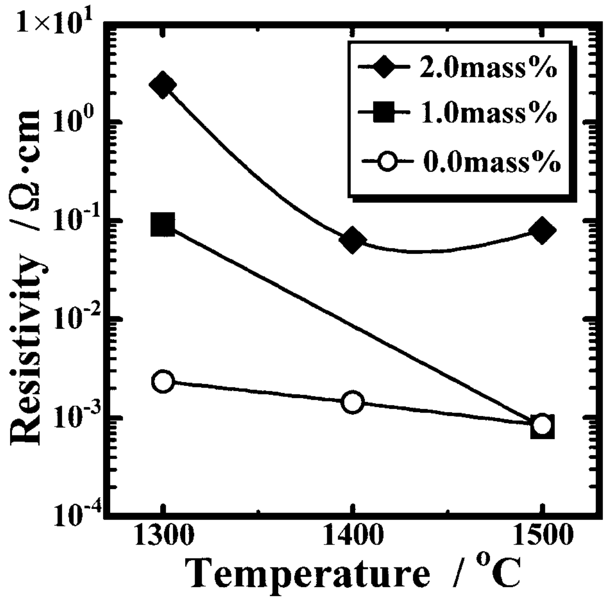

Figure 6 The resistivities of the pellets. ○, ■ and ◆; ITO with 0.0, 1.0 and 2.0 mass % Bi_2O_3 addition, respectively.

direct contact between the ITO grains was expected since no bismuth was detected by the XRF analysis.

4. Conclusion

ITO was sintered pressurelessly in the simultaneous presence of Bi_2O_3 in order to investigate the effect of a sintering aid on the sinterability of the ITO. The addition of Bi_2O_3 accelerated densification of ITO significantly. Decrease of electrical conductivity caused by the additive was suppressed when a minimum amount of Bi_2O_3 (1.0 mass %) was added and heated at 1500 °C.

References

1. J. LAMBERT BATES, C. W. GRIFFIN, D. D. MARCHANT and J. E. GARNIER, *Am. Ceram. Soc. Bull.* **65** (1986) 673–78.
2. N. OGAWA, R. YOSHIMURA, T. MOURI, T. IWAMOTO, H. BABA and S. TENMA, *J. TOSOH Res.* **34** (1990) 99–180.
3. Y. KOJIMA, *New Ceramics*, No. **12** (1992) 47–51.
4. R. YOSHIMURA, N. OGAWA and T. MOURI, *J. TOSOH Res.* **36** (1992) 153–59.
5. J. H. W. DE WIT, M. LAHEIJ and P. F. ELBERS, *Sci. Ceram.* **9** (1977) 143–50.
6. T. NATE and T. KISHI, *Hyomen-Gijyutu*, **43** (1992) 20–25.
7. N. NADAUD, M. NANOT and P. BOCH, *J. Amer. Ceram. Soc.* **77** (1994) 843–46.
8. N. NADAUD and P. BOCH, *Ceram. Internat.* **22** (1996) 207–09.
9. J. A. DEAN ED., in "Lange's Handbook of Chemistry," (McGraw-Hill, New York, 1970) p. 4–25.
10. *International Center for Diffraction Data*, 44-1087.
11. *International Center for Diffraction Data*, 41-1989.
12. *International Center for Diffraction Data*, 41-1445.
13. *International Center for Diffraction Data*, 34-1203.

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