



Phase Transformation Behavior of Nanocrystalline ITO Powders during Heat-Treatment: Oxygen Partial Pressure Effect

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Abstract. Nanocrystalline indium tin oxide (ITO) powders with different tin contents ranging from 0 to 8 at% were prepared by a coprecipitation process. A mixture of rhombohedral and cubic structured nanocrystalline ITO powders was obtained, and the amount of the rhombohedral ITO increased as the content of Sn increased. During heat-treatment the rhombohedral ITO was transformed to cubic around 900°C. The phase transformation behavior of the powders was examined as a function of oxygen partial pressure. When the rhombohedral ITO powder was heat-treated in a low oxygen partial pressure (nitrogen gas) atmosphere the phase transformation was accelerated and this acceleration can be attributed to the formation of oxygen vacancies that accelerate atomic transport in the rhombohedral ITO.

Keywords: phase transformation, nanocrystalline powder, ITO, oxygen partial pressure

1. Introduction

Recent research has concentrated on the preparation of homogeneous nano-sized powders because of their high driving force of densification [1]. During nano powder fabrication processes in chemical routes precursors are usually pyrolyzed to an inorganic material at as low a temperature as possible to form a crystallization in order to prevent particle coarsening. In this case, because long-range diffusion is kinetically limited during crystallization, metastable phases often crystallize depending on the precursors [2–4]. Otherwise, the extremely small curvature radius of nano particles induces high capillary force on the particles, which often forms high-pressure phases in nano powders [4]. When the metastable and/or high-pressure phases are exposed to higher temperatures, phase transformations to the stable phases have been observed [2–4]. After the phase transformation a vermicular structure development was observed because the phase transformation accompanied a signif-

icant coarsening of the particles in the microstructure [2, 3].

In our previous study [4], rhombohedral nanocrystalline indium tin oxide (ITO) powders, which is the high pressure phase, was produced. During heat-treatment in air it transformed into a stable phase of cubic ITO, and the phase transformation induced enormous particle growth which had a bad effect on densification and this was explained by the Hedvall effect. Meanwhile, it was known that various thermodynamic variables such as cation [5] and anion dopant [6], particle size [7], reaction atmosphere [8] are the functions of phase transformation. However, there has been no systematic study on the phase transformation behavior in nanocrystalline ceramics. In particular, the variables on the phase transformation from nanocrystalline rhombohedral ITO to cubic ITO have not been subject to investigation.

In this study, the effect of oxygen partial pressure on the rhombohedral-cubic phase transformation in nanocrystalline ITO, which was

manufactured through a coprecipitation method, was examined.

2. Experimental

Nanocrystalline ITO powders were prepared by a coprecipitation method. Indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot 5.7\text{H}_2\text{O}$, 99.99%) and tin chloride hydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 99.9%) were used as starting materials. Indium and tin solutions were prepared by dissolving the starting materials individually in doubly deionized water and the concentration of the solutions was adjusted to 2N. The mixed solutions corresponding to the composition with various In/Sn ratio of which the Sn concentration of 0, 4 and 8 at% was prepared and NH_4OH was added to a continuously stirred bath of the mixed solution until the pH reached 9.5. After the coprecipitation at 15°C , the precipitates were immediately washed several times with doubly deionized water to remove residual Cl^- and NO_3^- ions, and the precipitates were dried at 85°C . The dried precipitates were then calcined at 600°C for 1 h in air. As a result, nanocrystalline ITO powders were obtained and the size of particles was in the range of 20–26 nm regardless of the Sn content [9]. In/Sn atomic ratios of powders were also analyzed by an X-ray fluorescence spectrometer (XRF, Model PW 2400, Philips, Eindhoven, The Netherlands) and the ratios were well matched to the target compositions.

The ITO powders were formed into cylindrical pellets by cold isostatic pressing (CIP) with a pressure of 300 MPa. The pellets were inserted into a tube furnace and heat-treated at $900\text{--}1000^\circ\text{C}$ for 1 h with a heating rate of $5^\circ\text{C}/\text{min}$ in different oxygen partial pressure. Oxygen (99.99%) and nitrogen gas (99.99%) were used as the atmospheric gas. The crystal structures of the powders were identified by an X-ray diffractometer (M03XHF, Mac Science) using $\text{Cu-K}\alpha$ radiation. The volume fraction of cubic and rhombohedral In_2O_3 was determined by measuring the integrated intensity of cubic (222) and rhombohedral (110) peaks. The microstructure of the fractured surface of the samples was observed by using a scanning electron microscope (JEOL 5400). The surface areas of the heat-treated powders were analyzed by using a BET (Micromeritics Instrument, ASAP2010).

3. Results and Discussion

Figure 1(A) shows the X-ray diffraction patterns of the precipitates and their calcined powders. In the case of the precipitates (Fig. 1(A) a, b)), broad peaks at positions corresponding to the $\text{In}(\text{OH})_3$ [10] and InOOH [11] were observed. After calcining at 600°C for 1 h (Fig. 1(A) c, d), the hydroxide precipitates yielded a mixture of cubic and rhombohedral ITO.

According to the previous study [4], we found that the precipitate of InOOH transforms to $\text{In}(\text{OH})_3$ as the aging time increases, which signifies that the metastable InOOH develops at first then transforms to $\text{In}(\text{OH})_3$ during the aging process. On the other hand it is observed in Fig. 1(B) that the amount of InOOH also increased when the content of Sn increased. In Fig. 1(B), the amount of the rhombohedral ITO, which was determined by measuring the integrated intensity of X-ray diffraction increased from 8 to 60% as the Sn concentration increased from 0 to 8 at%. As a result, we

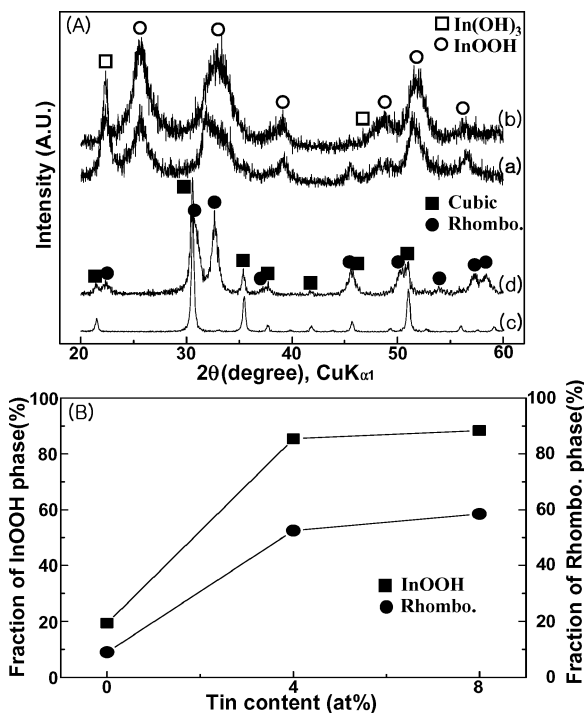


Fig. 1. (A) X-ray diffraction patterns of the precipitates with (a) 0 and (b) 8 at% Sn and its calcined powder with (c) 0 and (d) 8 at% Sn. (B) The amount of InOOH and rhombohedral ITO as a function of the Sn content.

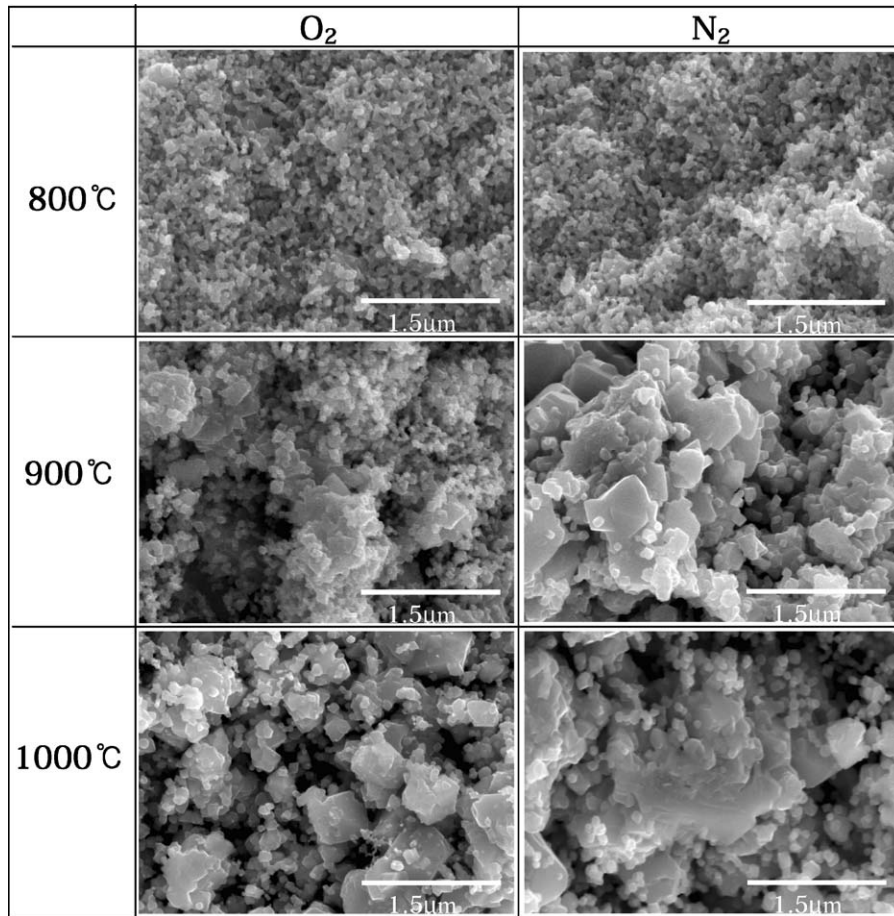


Fig. 2. SEM photographs of fracture surface of the samples with 8 at% Sn after heat-treatment at different temperatures and atmospheres.

can see a proportional relationship between the amount of InOOH in the precipitates and the amount of rhombohedral ITO after the calcinations. In₂O₃ has a polymorphism that is cubic [12] and rhombohedral [13] in structure. Rhombohedral In₂O₃ is high-pressure polymorphism of cubic In₂O₃, which is metastable in atmospheric pressure. Therefore, as observed in our previous study, it is believed that the InOOH in the precipitates transformed to the metastable rhombohedral ITO after calcination [4, 14].

In order to examine the effect of temperature and oxygen partial pressure on the phase transformation, the ITO sample with 8 at% Sn which contains a large amount of rhombohedral ITO was heat-treated at 800, 900 and 1000 °C for 1 h in an oxygen and nitrogen atmosphere. Figure 2 shows the SEM photographs of the fractured surface of the heat-treated samples. When

the samples were heat-treated at 800 °C, fairly uniform microstructures with densely packed particles were observed regardless of the oxygen partial pressure. When the heat-treatment temperature was elevated to 900 °C, which was thought to be the phase transformation temperature of ITO, an inhomogeneous microstructure with large irregular grains and large voids was observed in the microstructure. In the case of the heat-treatment at 1000 °C, most of the large grains developed. As previously mentioned, a dramatic coarsening of the nanocrystalline ceramic powders after a phase transformation was observed in (Pb, La)(Zr, Sn, Ti)O₃ [3] and Al₂O₃ system [2] as well as in our previous study [4]. Therefore, the amount of the large grains can be a measure of the phase transformation. From this point of view, the microstructures shown in Fig. 2 suggest that a sufficient phase transformation had not

proceeded at 800°C, while the phase transformation is almost accomplished at 1000°C. Because the initial powder contains about 40% of the cubic ITO, which had not experienced the phase transformation after the heat-treatment, it is thought that the small particles in the sample heat-treated at 1000°C are the cubic particles. Considering the effect of the oxygen partial pressure under the same heat-treatment temperature, larger grains were developed when the sample was heat-treated in a reducing nitrogen atmosphere. From this result, it can be certified that the lower oxygen partial pressure accelerated the phase transformation.

Figure 3(A) shows the X-ray diffraction patterns of the sample heat-treatment at 900°C in different atmosphere. Compared to the X-ray diffraction of the calcined powder in Fig. 1(A-d), a great decrease in the intensity of the rhombohedral phase was observed, that is, the rhombohedral-cubic phase transformation process near 900°C was observed. Particularly, when it was compared with an O₂ atmosphere, a considerable phase transformation was proceeded when it was heat-treated in an N₂ atmosphere. Figure 3(B)

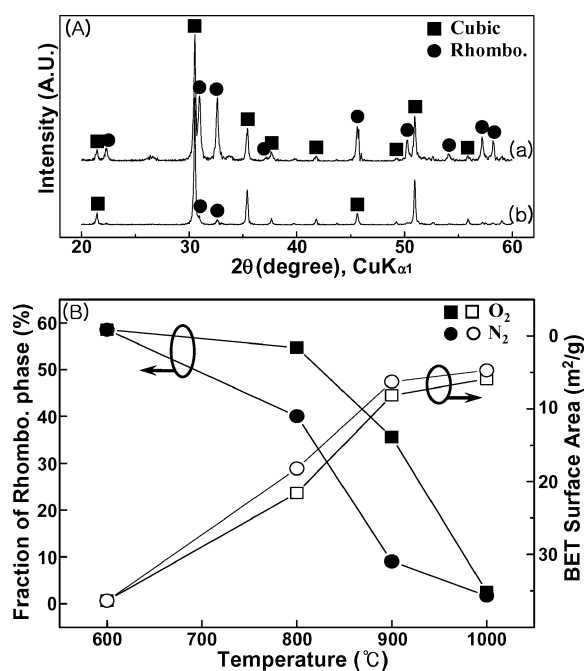


Fig. 3. (A) X-ray diffraction patterns of the samples with 8 at% Sn heat-treated at 900°C in (a) O₂ and (b) N₂ atmosphere. (B) The amount of rhombohedral ITO and BET surface area after the heat-treatment at different temperatures and atmospheres.

shows the fraction of the rhombohedral phase and BET surface area as functions of the heat-treatment temperature and the atmosphere. As the temperature increased, the rhombohedral structure, which initially made up 60% of the sample, disappeared. Eventually, almost complete rhombohedral-cubic phase transformation was achieved when the sample was heat-treated at 1000°C for 1 h. Considering the effect of the oxygen partial pressure on the phase transformation, lower oxygen partial pressure obviously enhanced the phase transformation. The surface area of calcined powder was about 36 m²/g. However, as observed in Fig. 2, the phase transformation induced an enormous grain growth which resulted in a great decrease of the surface area below 10 m²/g.

ITO has an anion-deficient fluorite derivative cubic structure (bixbyite structure). The major defect in ITO is oxygen vacancies[15]. In the bixbyite structure, oxygen vacancy plays an important role in diffusion particularly of cations of In and Sn because the empty oxygen sites play the role of diffusion channels. When the sample was heat-treated in an oxidizing atmosphere, the concentration of oxygen interstitial increased, which filled up the oxygen vacancies. In this case, it is believed that the diffusivity of ions is suppressed because the oxygen interstitials obstruct atomic movements which retard the phase transformation.

4. Conclusion

When a mixture of rhombohedral and cubic nanocrystalline ITO powders was heat-treated in oxidizing atmosphere, the rhombohedral-cubic phase transformation was retarded compared to heat-treatment in a low oxygen atmosphere. This result was explained on the basis of the crystal structure of ITO together with the defect chemistry in ITO.

Acknowledgments

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