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Preparation of Nano-sized Indium Tin Oxide (ITO) Powders and Their Sintering Behavior

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Abstract In order to fabricate a high density sintered body of ITO, nano-sized ITO powders were synthesized by coprecipitation methods. Aqueous solutions of indium and tin salts were mixed and coprecipitated by changing their pH. Coprecipitated ITO powders possessed 20-30 nm crystallite size and a relatively high BET value (35 m^2/g), however, aggregation of particles were occurred. Therefore, a novel recrystallization technique was applied in order to eliminate the aggregates. The recrystallized ITO material consists of a little bit larger needlelike crystals, 20 nm × 80 nm, and it possesses a higher BET value (57 m^2/g) compared to the plain coprecipitated material (35 m^2/g). Metastable phase formation and higher content of aggregated particles were observed in the coprecipitated materials. Densification was 95% to 98% complete after 5 hour sintering at 1500°C for the recrystallized powders while densities of the coprecipitated powders were below 75%.

Key words : Indium Tin Oxide, Coprecipitation, Sintering behavour, Recrystallization

1. Introduction

The simultaneous occurrence of high electrical conductivity and high optical transparency in the visible region is possible in wide-band-gap oxides[1,2]. These conditions are obtained in oxides of indium, tin, zinc, cadmium and their alloys in thin film form, prepared by a number of deposition techniques. Creating electron degeneracy by introducing non-stoichiometry and/or appropriate dopants can significantly improve the optoelectrical properties of these materials. Indium-tin oxide(ITO), which contains 5-10 wt. % of tin oxide as a dopant, has been a most widely used transparent conductor in display applications due to its superior electrical and optical properties and good etching characteristics.

For transparent electrodes in liquid-crystal display devices, close tolerances of the flatness of the electrodes are essential, and can be achieved by the low-temperature vacuum-deposition processes(sputtering, evaporation). When used as a sputtering target, the ITO sintered body should be as close as possible to maximum theoretical density, for two reasons[3]. First, the use of a high density sintered body maximizes its useful life as a sputtering target. A second reason is that the increase in density maximizes thermal conductivity, and this is very effective in preventing cracks which could result in a non-uniform deposition of the ITO.

In order to manufacture a high density ITO sintered body, various processes have been utilized; hot-pressing, HIP and liquid phase sintering. However, these methods have incurred a high manufacturing cost and deterioration in film properties, thus better manufacturing methods have been demanded. In this study, a preparation method of producing fine, reactive and unaggregated ITO powders has been investigated and characteristics of the powders synthesized by the new method are compared with those of powders prepared by the

conventional coprecipitation process.

2. Experimental Procedure

Aqueous solutions of indium nitrate and tin chloride were prepared by dissolving $In(NO_3)_3 \cdot xH_2O$(>99.99% purity, Kojundo Chemical, Tokyo, Japan) and $SnCl_4 \cdot yH_2O$(>99.9% purity, Kojundo Chemical). The values of x and y were around 6 and 2. The solutions whose concentration ranged from 0.1 N to 5 N were mixed at a ratio of 88 : 12 and aqueous solution of 5 N ammonium hydroxide was added as a precipitation reagent. The final pH was adjusted to 10 by adding excess ammonium hydroxide solution. The coprecipitated gels were filtered and rinsed three times with deionized water to eliminate the unreacted ions. Another series of preparations were made by the same procedure and the precipitated gels were recrystallized to change the crystal morphology[4]. The filtered gels were dried at 80°C and calcined at various temperatures. The dried gels and the calcined powders were analyzed by TGA, DTA, XRD, and BET. Thermogravimetric(TGA) and differential thermal analysis(DTA) studies were carried out at a heating rate of $10°C \cdot min^{-1}$. For the calcined powders, cold isostatic pressing at 200 MPa yielded cylindrical pellets of approximate dimensions $\Phi 12.5\,mm \times 10\,mm$ and these pellets were sintered for 5 hours at 1500°C. The densities of sintered pellets were measured according to the Archimedes principle.

3. Results And Discussion

For brevity, ITO is used in the proceeding text to identify indium-tin oxide($In_2O_3 : SnO_2 = 90 : 10$ in wt. %) and IT(OH) is corresponding to the hydroxide precursor gel.

Fig. 1 shows TGA/DTA data for the coprecipitated and the recrystallized IT(OH) precursor gels. Both gels possess two endothermic peaks below 300°C. The endotherms at 60°C are associated with adsorbed water and those at 270°C are due to water of crystallization. However, the endotherm at 380°C is only detected from the coprecipitated precursor gel. This peak is related with the evaporation of NH_4Cl. Therefore, it can be argued that the recrystallization process is effective in minimizing the impurity ions.

XRD patterns shown in Fig. 2 and Fig. 3 indicate that IT(OH) and an amorphous phase are formed in the coprecipitated gels while only the IT(OH) phase exists in the recrystallized gels. The crystal structure evolving from these gels are quite different. After heat treatment for

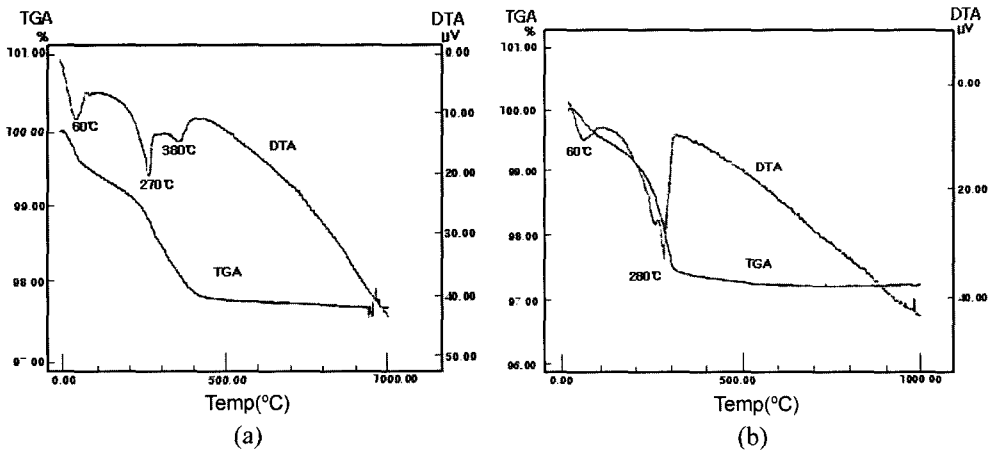

Fig. 1. TGA/DTA data for (a) the coprecipitated IT(OH) precursor gel and (b) the recrystallized IT(OH) precursor gel.

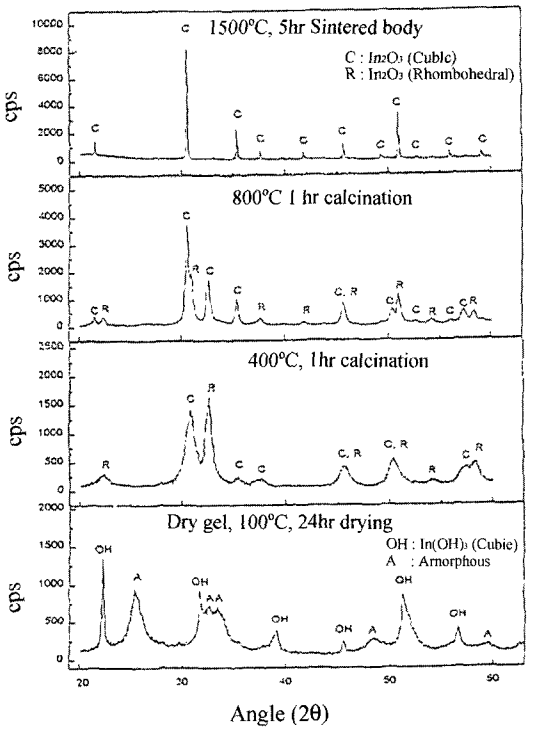

Fig. 2. XRD pattern of a coprecipitated gel shows that IT(OH) phase and an amorphous phase are formed.

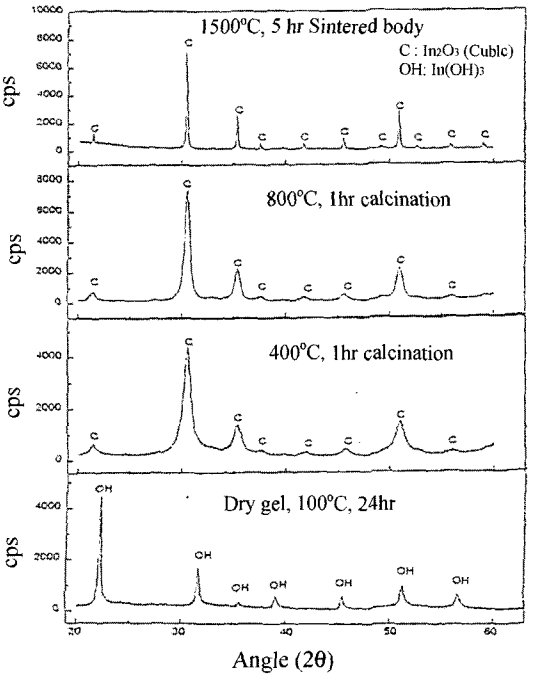

Fig. 3. XRD pattern of a novel recrystallized gel shows that IT(OH) phase is the only phase formed

1 hour at 400°C, the coprecipitated gels transformed to the cubic and rhombohedral phases, however, powder prepared from the recrystallized gels contains a cubic single phase. The rhombohedral phase is quite stable and it remains in the powder calcined as high as 800°C. However, after sintering this phase disappears and seems to be transformed into the cubic phase as shown in Fig. 3(d). The rhombohedral ITO phase is a high pressure ITO phase, thus it is a metastable phase. Since a fast rate crystallization process has been applied in the coprecipitation process, little time is allowed for the diffusion of constituents. Therefore, metastable phase formation is unevitable in the coprecipitated precursor gels.

The appearance of metastable phase after precipitation and crystallization is not uncommon[5-9]. This anomaly has been widely noted in oxides prepared at low temperature. The existence of a nonequilibrium phase may be attributed to "kinetics." It is often assumed that crystallization at low temperature leads to metastable phase via a topotactic mechanism because of limited atomic mobility. For mixed-metal oxide systems, it can also be argued that the formation of a nonequilibrium structure containing a random distribution of the cations is a direct consequence of its kinetically limited crystallization from an atomically-mixed precursor. This hypothesis seems to be supported by the experimental studies that have been conducted on a variety of doped-zirconia systems[5-9]. The thermal analysis and XRD results on the coprecipitated precursor suggest that this hypothesis is relevant for the ITO materials synthesized from liquid precursors[9]. Therefore, it is very likely that kinetically limited crystallization effects are dominant in the formation of the nonequilibrium(metastable) IT(OH) phase.

The morphology of ITO powders obtained by coprecipitation of aqueous salt solutions are mostly equiaxed, and aggregates are observed. The recrystallization treatment changed the crystal morphology from equiaxed to needlelike or plate form. No aggregates or agglomerated clusters are found in the powders obtained from the recrystallized ITO precursor. It is probably due to removal of the amorphous phase in the coprecipitated gels which could react with IT(OH) to form aggregates during subsequent heat treatment.

Fig. 4 shows that the recrystallization treatment is very effective in enhancing the sintered density of ITO materials. Maximum sintered density of the coprecipitated ITO powders was 75% of the theoretical density(7.15 cm^3/g). In contrast, 98% of theoretical density is achieved from a recrystallized ITO powder. The sizes of fine equiaxed particles were in the range of 20-30 nm. This is finer than the recrystallized needlelike particles whose particle size was 20 nm in width and 80 nm in length. In general, fine ceramic powders possess better sinterability than coarse powders owing to their larger surface area. Therefore, it is obvious that there are other factors affecting sinterbility of ITO materials. It appears from BET data that the coprecipitated powders have smaller surface area compared to the recrystallized materials(35 m^2/g vs. 57 m^2/g). As shown in the thermal analysis result the coprecipitated powders possess higher impurity content. The coprecipitated powders contain a significant amount of aggregates and their size is as large as 300 nm. This particles could induce inhomogenity during sintering and retard densification of the ITO powders. Therefore, it can be assumed that enhancement in the sintering density of the recrystallized materials is due to elimination of the aggregates and removal of the unreacted ions. Another factor to be considered is difference in the crystal structure of the ITO materials. The coprecipitated powders possess the rhombohedral phase and this may inhibit achieving the high density because the diffusivity or surface energy of the rhombohedral particles is lower than that of the cubic phase.

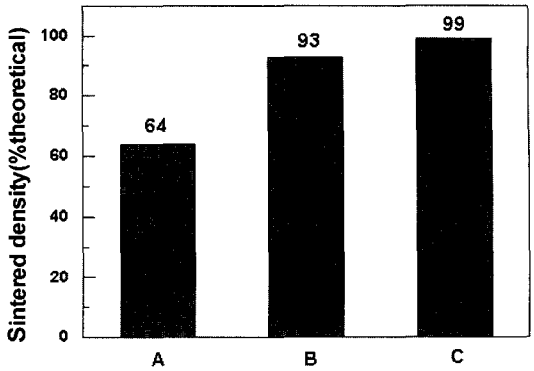

Fig. 4. Sintered densities of ITO powders.

4. Conclusions

The influence of the novel recrystallization treatment on synthesis of the ITO powders from liquid precursors has been investigated by TGA/DTA and XRD.

Improvement in the sintered density of ITO powders were achieved by a recrystallization treatment. It is believed that the increase in the sintered density of the recrystallized ITO materials is due to the less aggregate forming tendency and the less impurity ion content.

The observed phenomena are consistent with similar effects produced by low temperature synthesis of ceramic precursors. It is clear from the present results that the solution precursor route has a enormous potential for manufacturing of high density and impurity free ITO materials.

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