

Preparation and characterization of fine indium tin oxide powders by a hydrothermal treatment and postannealing method

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Indium tin oxide powder with an In to Sn mole ratio of 95:5 was successfully prepared from a coprecipitated In–Sn hydroxide gel by hydrothermal processing followed by calcination at relatively low temperatures (~500 °C). Hydrothermal treatment of the In–Sn coprecipitated gel at 300 °C for 24 h led to the formation of a single phase of tin-doped indium oxyhydroxide (InOOH:Sn). Under hydrothermal conditions the oxyhydroxide phase appeared well crystallized with particles ~80 nm in size. Calcination of the oxyhydroxide phase above 450 °C in air yielded a substitutional-vacancy-type solid solution of $\text{In}_2\text{Sn}_{1-x}\text{O}_{5-y}$.

I. INTRODUCTION

Sn-doped In_2O_3 (or ITO) is an advanced ceramic material with many electronic and optical applications due to its high electrical conductivity (up to $10^4 \Omega^{-1} \text{cm}^{-1}$) and transparency to light.¹ ITO thin films are used in transparent electrodes for display devices, transparent coatings for solar energy heat mirrors, and windows films in *n-p* heterojunction solar cells, etc.

The thin films are commonly prepared by the magnetron sputtering, which utilizes dense tin doped indium oxide targets.² Few works have been reported on the preparation of ITO targets.^{3–6} The sputtering efficiency and properties of the sputtered films are mainly dependent on the characteristics of sputtering targets.³ To optimize the efficiency, the targets should be as dense as possible, but densification of ITO is rather difficult due to rapid vaporization of In_2O_3 above 1200 °C.⁷ An oxidizing atmosphere allows high densification by sintering at 1600 °C, whereas a neutral atmosphere (Nitrogen or Argon) leads to poor densification.⁴ The preparation of the ITO targets is normally achieved using conventional solid-state reaction routes requiring the high-temperature (above 1200 °C) reaction of In_2O_3 and SnO_2 under an O_2 atmosphere.⁶

We believe that the characteristics of the starting powder strongly influence the properties of the final ITO target. In practice, small spherical particles may improve the high density. The direct calcination of the coprecipitated In–Sn hydrated gel failed to form pure ITO powders.⁸ The aim of this study is to make very fine crystalline Sn-doped In_2O_3 powder with controlled stoichiometry at low temperatures to use as the starting material for fabricating dense ITO targets. Therefore, hydrothermal techniques were used to obtain the tin-doped indium oxyhydroxide phase from the coprecipitated In–Sn amorphous gel. Various experimental conditions have been tested to optimize the crystallinity of the hydrothermally produced powders. Postannealing of this powder leads to the production of fine ITO powders. No literature data are available on the hydrothermal synthesis of Sn doped Indium oxide powder.

II. EXPERIMENTAL PROCEDURE

The required amounts of starting materials of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and SnCl_2 (both 99.99% pure, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were dissolved in distilled water separately. A mole ratio of In/(In + Sn) 0.95 was maintained. In order to obtain complete dissolution, one drop of concentrated HCl was added to the SnCl_2 solution. The two solutions were then mixed at room temperature using a magnetic stirrer. The concentrations of In and Sn in the mother solution were also controlled in the ranges of 0.1–5 M and 0.002–0.1 M, re-

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spectively. Then the solution was added drop-wise (2 ml/min) to 5 M NH_4OH (500 ml, excess) solution (Wako Pure Chemical Industries, Ltd., Osaka, Japan) while stirring. A light yellow color gel precipitate was obtained. The reaction mixture soaked at 80 °C for 10 h while stirring. The precipitate was then filtered and thoroughly washed with distilled water until it was free from Cl^- and NH_4^+ . The co-precipitated gel was air-dried. The gel was next hydrothermally treated at 300 °C for 24 h using a microautoclave (inner volume 20 cm^3), with a Hastelloy C corrosion resisted liner. The fill ratio of the solution volume against the inner volume of the autoclave was 60%. The pH of the media was controlled using ammonia solution. After the hydrothermal treatments the powders were filtered and washed with distilled water, then dried at 50 °C under vacuum. The powder was calcined at 500–1000 °C for 4 h in air in order to obtain the ITO powder. X-ray diffraction (XRD) measurements (Rigaku, Rotaflex, Tokyo, Japan) of the coprecipitated gel and its hydrothermal and calcined products were carried out for phase identification. The lattice parameters of both the hydrothermally treated Sn doped and undoped samples were obtained by XRD. National Bureau of Standards (NBS)-Si powder was used as an internal standard for calibration. The powder diffraction patterns of from $2\theta = 20^\circ$ to 70° were recorded with a scan speed of $0.01^\circ 2\theta/\text{min}$. The unit cell parameters observed were subjected to a least-square refinement. The ^{119}Sn Mössbauer spectra (Wissel GmbH, Germany, used inconstant acceleration mode) of hydrothermally produced and calcined powders (700 °C for 4 h) were performed at room temperature in order to study the environment of tin in the ITO powders. ^{119}Sn in CdSnO_3 was used as a γ -ray source and the specimen powder was used as an absorber. Mössbauer spectra were measured by transmission geometry. The relative velocity between the source and absorber was calibrated using the α -Fe spectrum of ^{57}Fe at room temperature. The isomer shift is relative to BaSnO_3 . Spectra obtained were

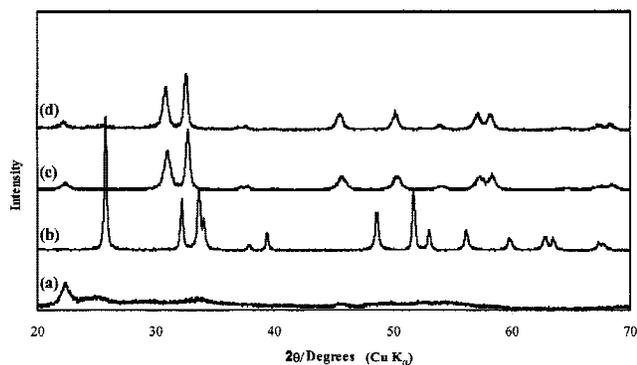


FIG. 1. XRD patterns of (a) the In-Sn coprecipitated gel powder (b) after hydrothermal treatment at 300 °C for 24 h and after calcination in air for 2 h at (c) 500 °C, and (d) 700 °C.

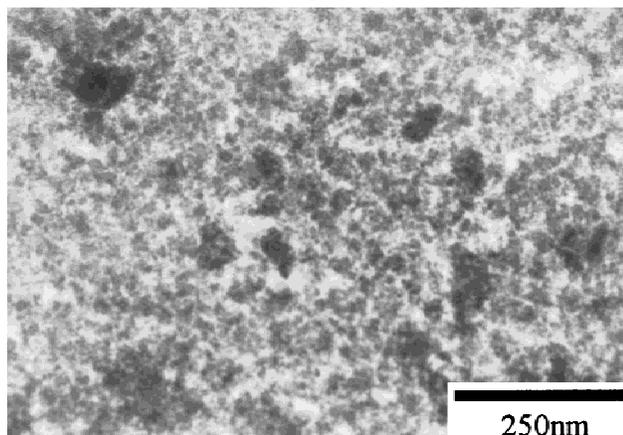
analyzed by a least square fit to the Lorentz function. Thermogravimetric differential thermal analysis (TG-DTA; SEIKO-SSC-5200H, Seiko Instruments Inc., Tokyo, Japan) of the hydrothermally treated powder was carried out from 25 to 1000 °C in air in order to study the precursor decomposition and the phase changes. The test cell contained 10 mg of sample, while the standard cell contained 10 mg of $\alpha\text{-Al}_2\text{O}_3$. The heating rate was 20 °C/min. Morphological characterization of the prepared powders was performed using transmission electron microscopy (TEM; Hitachi H-800, Tokyo, Japan) at 200 kV. The samples were supported on carbon-coated 100 mesh copper grids. A portion of each powder was dissolved in 1 M HCl and analyzed by inductively coupled plasma atomic emission spectrometer (ICPS-SPS 7000A-SII Seiko Instruments Inc., Tokyo, Japan).

III. RESULTS AND DISCUSSION

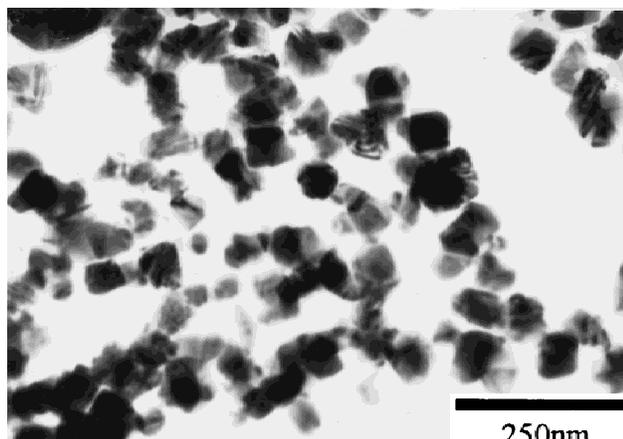
Separate coprecipitation experiments showed that precipitation of $\text{In}(\text{OH})_3$ and $\text{Sn}(\text{OH})_2$ occurs above the pH values of 5 and 2.2, respectively. During aging in an aqueous media, In^{3+} and Sn^{2+} cations combined with OH^- to form $\text{In}(\text{OH})_3$ and $\text{Sn}(\text{OH})_2$ and formed hydrous gel type precipitates. Therefore, a homogenous gel is formed the coprecipitation method. The coprecipitated gel particles show very poor crystallinity as shown in the XRD pattern in Fig. 1(a). The XRD pattern shows broad low intensity peaks that were also observed in the pure $\text{In}(\text{OH})_3$ gel. The evolution in the intrinsic microstructure of the gel powder was studied TEM. Observations show [see Fig. 2(a)] highly aggregated particles approximately 15 nm in size. The absence of well-defined rings in the electron diffraction pattern (not shown in the figure) confirms that the particles are substantially amorphous.

Under hydrothermal conditions the reactant was converted to a well-crystallized powder. The XRD pattern of the hydrothermally treated powder is shown in Fig. 1(b). The narrow peaks of the XRD pattern indicate that the treated powder has well-crystallized fine particles. The powder was identified as single-phase tin-doped indium oxyhydroxide with lattice parameters $a = 5.2561 \pm 0001 \text{ \AA}$, $b = 4.5788 \pm 0001 \text{ \AA}$, and $c = 3.2702 \pm 0001 \text{ \AA}$, (cell volume $78.70 \pm 0.01 \text{ \AA}^3$) the crystal structure is a long range ordered orthorhombic system similar to InOOH .⁹ No additional phases are observed. A similar phase of InOOH was observed¹⁰ under hydrothermal conditions at 300–400 °C with very high pressures (>80 atm) and long treatment times (100 h) with the lattice parameters of $a = 5.26 \pm 0.01 \text{ \AA}$, $b = 4.56 \pm 0.01 \text{ \AA}$, and $c = 3.27 \pm 0.01 \text{ \AA}$. The lattice parameters of pure InOOH phase in this study were determined as $a = 5.2698 \pm 0.0001 \text{ \AA}$, $b = 4.5702 \pm 0.0001 \text{ \AA}$, and $c = 3.2755 \pm 0.0001 \text{ \AA}$ (cell volume $78.70 \pm 0.01 \text{ \AA}^3$), re-

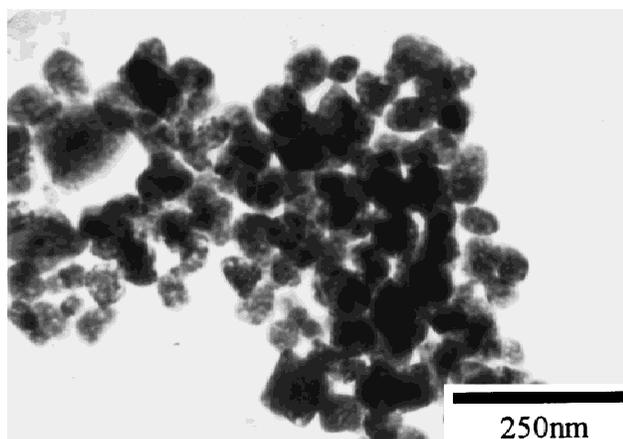
spectively, and very similar to the above reported values. The cell volume of the tin-doped indium oxyhydroxide powders decreases from pure InOOH phase values due to the difference in the ionic radii ($r_{\text{In}^{3+}} = 0.80 \text{ \AA}$ and $r_{\text{Sn}^{4+}} = 0.69 \text{ \AA}$).¹¹



(a)



(b)

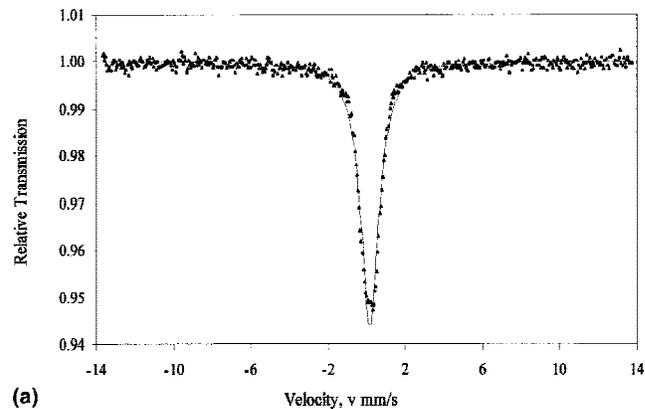


(c)

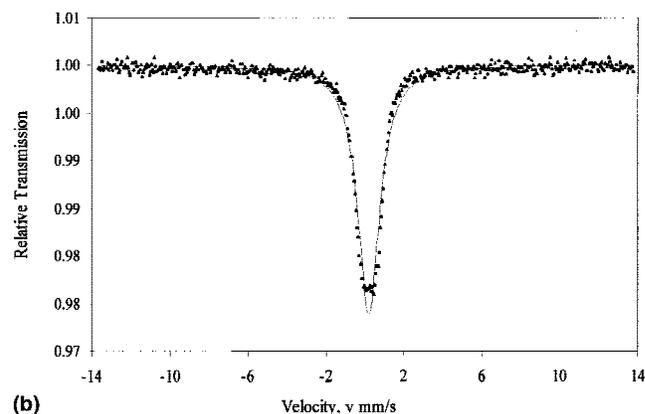
FIG. 2. TEM photographs of (a) vacuum dried coprecipitated In-Sn hydrous gel (b) after hydrothermal treatment at 300 °C for 24 h and (c) after calcination at 700 °C for 2 h.

During the hydrothermal process, the Sn^{4+} ions were generated by low temperature oxidation (between 100 to 300 °C) of Sn^{2+} , and then these ions reacted with In^{3+} to form the oxyhydroxide phase. The Mössbauer spectrum [see Fig. 3(a)] shows the oxidation state of the Sn in the hydrothermally treated powder is +4 with octahedrally coordinated oxygen, which follows the value of the isomer shift $\delta = 0 \text{ mm/sec}$. When small amounts of Sn^{4+} replace In^{3+} ions, Sn atoms enter substitutionally in the cation sublattice acting as *n*-type donors.¹²

The pH of the hydrothermal medium is also important for the crystallinity of the product. It was found that pH-9 produces the highest crystallinity whereas a high pH medium (>10) leads to poor crystallinity. The formation of InOOH phase is highly dependent on the treatment temperature and should be above 250 °C. It was also observed that the crystallinity of the hydrothermal product increases with the treatment time. This phase seems to be very stable under the hydrothermal conditions. Even long hydrothermal treatment times (300 °C for 200 h) did not change the oxyhydroxide phase. A TEM micrograph of the hydrothermally treated powder is shown in Figure 2(b). It shows that the particles have a well-faceted morphology and are isolated from each other



(a)



(b)

FIG. 3. Room-temperature Mössbauer spectra of hydrothermally produced powder (a) at 300 °C for 24 h and (b) after calcination at 700 °C for 2 h.

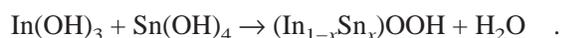
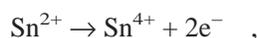
with a uniform particle size approximately 80 nm. The crystallization occurs by a dissolution and precipitation mechanism. There is no indication of any amorphous material remaining. The grain size strongly depends on the initial In and Sn concentrations in the mother solution. In order to get a uniform particle size (~80 nm) the concentrations of In and Sn in the mother solution were in the range of 0.5–0.1 M and 0.01–0.02 M, respectively. When the bulk solution had concentrations of In > 2 M and Sn > 0.04 M, uneven particle sizes were produced in range 80 to 200 nm in the hydrothermal product.

Chemical analysis showed that the mole ratio of In/(In + Sn) in the Sn-doped InOOH phase was 0.95, which is consistent with the initial mole ratio in the reaction solution. The reactions involved in the process can be expressed as follows.

In the coprecipitation process



Under hydrothermal conditions

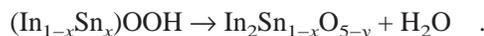


The XRD patterns of calcined (500 and 700 °C for 4 h) hydrothermally produced powders are shown in Figs. 1(c) and 1(d). Calcination of the $(\text{In}_{1-x}\text{Sn}_x)\text{OOH}$ phase, above 500 °C leads to decomposition to a substitutional-vacancy-type solid solution of $\text{In}_2\text{Sn}_{1-x}\text{O}_{5-y}$.⁸ The patterns are very similar to the reported fluorite structure type In_2SnO_5 pattern prepared by the coprecipitation method followed by post calcination.⁸ However, they failed to obtain the distinct diffraction pattern of the pure In_2SnO_5 phase. The crystallinity of the powders increased with the calcination temperature as shown in the XRD patterns [Figs. 1(c) and 1(d)]. Further heating of this phase above 1000 °C results in decomposition to the Sn-doped In_2O_3 phase which has the C-type rare-earth oxide structure with 80 atoms per unit cell.¹² However, Vorfolmееv *et al.*,⁸ obtained the initial oxide phases by decomposing In_2SnO_5 after annealing at high temperature above 1000 °C.

Figure 2(c) shows a TEM micrograph of the powder calcined at 700 °C for 4 h. The crystallinity and the particle size of the powder were increased by calcination. The average particle size is ~160 nm. All particles are similar in shape; no additional phases are observed. The morphology is different from its precursor oxyhydroxide phase [Fig. 2(b)]. The room-temperature Mössbauer analysis [Fig. 3(b)] of the calcined powder again confirmed that the oxidation state of Sn in the compound is +4 in an octahedral site with isomer shift $\delta = 0$ mm/sec.

The observed Mössbauer spectrum is very similar to the In_2SnO_5 reported previously¹¹ with an isomer shift parameter of 0 mm/sec.

In order to investigate the crystallization behavior of $\text{In}_2\text{Sn}_{1-x}\text{O}_{5-y}$, TG-DTA measurements for the hydrothermally treated powder was performed in static air is shown in Fig. 4. The DTA curve shows an endothermic peak at 438 °C corresponding to a 5% weight loss observed by TG between 400–450 °C. This is ascribed to the decomposition of the $(\text{In}_{1-x}\text{Sn}_x)\text{OOH}$ to the $\text{In}_2\text{Sn}_{1-x}\text{O}_{5-y}$ phase. The endothermic peak remains unchanged, even when TG-DTA measurements were performed in an N_2 atmosphere. This confirmed that there is no additional O_2 involved during the decomposition of the Sn doped indium oxyhydroxide phase. Calcination of $(\text{In}_{1-x}\text{Sn}_x)\text{OOH}$ powders at 500 °C for 4 h under vacuum also promotes the formation of the $\text{In}_2\text{Sn}_{1-x}\text{O}_{5-y}$ phase. In the temperature range from 100 °C up to 700 °C a mass change of 5.2% was obtained from the TG curve. No gas was produced during the decomposition of the Sn doped indium oxyhydroxide phase. Chemical analysis of the calcined sample showed that the mole ratio of In/(In + Sn) was 0.95, which is unchanged from the hydrothermal product. The reaction to produce ITO powder in the calcination process can be expressed as follows:



The sintering of uniformly packed, calcined (500 °C) powder at 1450 °C for 3 h in air results to obtain a dense (~93% theoretical density) Sn-doped In_2O_3 phase ($\text{In}_{2-y}\text{Sn}_y\text{O}_3$), which has the C-type rare-earth oxide structure with fine microstructure.¹³

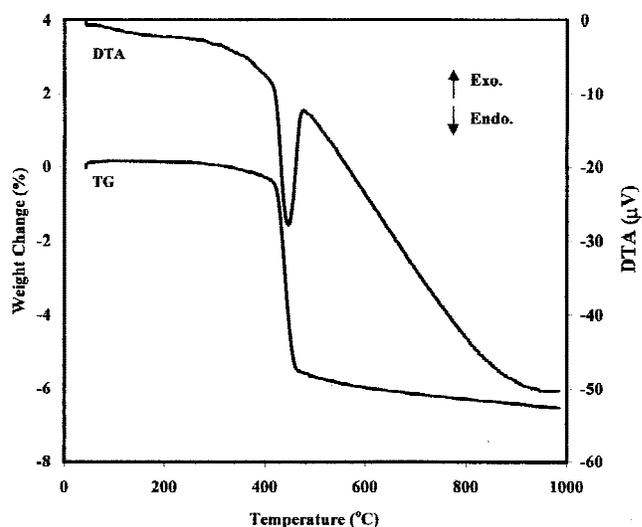


FIG. 4. TG-DTA curves of the powder hydrothermally treated at 300 °C for 24 h.

IV. CONCLUSIONS

A microcrystalline homogeneous tin-doped indium oxide has been synthesized successfully using the hydrothermal method with controlled stoichiometry. Based on x-ray diffractometry results, it can be concluded that the Sn-doped indium oxyhydroxide phase directly forms from the amorphous coprecipitated gel without any intermediate phase. Low-temperature calcination of this phase leads to decomposition to a substitutional-vacancy-type interstitial solid solution of $\text{In}_2\text{Sn}_{1-x}\text{O}_{5-y}$. This powder can be used to fabricate Sn-doped In_2O_3 targets for thin film preparation.

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