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# FORMATION PROCESS OF INDIUM OXIDE TRANSPARENT CONDUCTING FILMS VIA THERMAL DECOMPOSITION
## Nanostructure observation of dip-coated films during electron-beam irradiation

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Indium 2-ethylhexanoate monohydroxide, $In(OH)(O_2CCH(CH_2CH_3)(CH_2)_3CH_3)_2$, is a precursory material to fabricate $In_2O_3$-based transparent conducting films by dip-coating process. Formation process of indium oxide transparent conducting films was investigated using an ultra-low acceleration voltage FE-SEM. The nanostructure change of the precursory layer was observed during the electron beam irradiation in vacuum. A flat and homogeneous surface of the as-coated layer changed to porous and net-work like nanostructure after 80 s; the pore diameter increased and the pore distance decreased although the number of pores remained unchanged. These processes were interpreted as the preliminary step to form porous films composed of nm-sized inter-linked oxide particles as reported in the previous papers by the authors.

***Keywords:*** *dip coating, indium-tin-oxide, nanostructure, thermal decomposition, transparent conducting films*

## Introduction

Indium oxide, $In_2O_3$, is often doped with tin to form so-called ITO (indium-tin-oxide) transparent conducting films. The ITO films are used for transparent electrodes for flat panel displays (liquid crystal display, organic light emitting display and touch panels, etc.) and solar cells, shielding of electromagnetic waves and infrared radiation for buildings and automobiles etc. The ITO films are often fabricated via thermal decomposition of the coated precursory materials such as indium 2-etylhexanoate monohydroxide, $In(OH)(O_2CCH(CH_2CH_3)(CH_2)_3CH_3)_2$ [1, 2] whose TG-DTA-MS was reported by the present authors [3]. Xu *et al*. [4], Ching and Hill [5] and Tsuchiya *et al*. [6] reported a similar precursory material (indium 2-etylhexanoate, $In(O_2CCH(CH_2CH_3)(CH_2)_3CH_3))_3$) whose thermal decomposition was investigated by Gallagher *et al*. [7] using TG and the present authors [8] using DSC.

The above-mentioned results of thermal analyses indicated only the overall thermal change of the precursory materials. Nanostructures of ceramics, especially thin films are important to understand the properties and determined strongly by the thermal decomposition process of the precursory materials. Observation of the morphology is the basis of science and film fabrication technology. In the present study, in situ observation of the as-coated layer of the precursory material was attempted by field-emission type scanning electron microscope (FE-SEM). Recent progress of FE-SEM enables observation of the nm-sized region with low damage of the specimen. However, evaporation, thermal decomposition and melting of the specimens sometimes occur by the electron beam irradiation, since the heating is concentrated to the nm-sized portion even though reducing the acceleration voltage and the beam current. Therefore, in the present study, the electron beam was used for heating the layer of the precursory material and observation of the nanostructure change of the layer to clarify the formation process of indium oxide transparent conducting films in vacuum. However, measurement and estimation of the sample temperature are extremely difficult and abandoned in the present study.

## Experimental

Glass substrates (Corning#7059 or silica glass, $25\times40\times0.8$ mm$^3$) were washed ultrasonically with a detergent (Semicoclean 56, Furuuchi Chemical Co.) for 10 min, rinsed several times with pure water, picked up quickly from boiling acetone, and finally exposed to ultraviolet irradiation (excimer lamp; wave length, 172 nm) for 5 min in nitrogen flow. Indium

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2-ethylhexanoate monohydroxide (8 mass%) solutions were supplied from Asahi Denka Kogyo and used as the coating solution. Doping of tin was intentionally avoided in order to clarify the mechanism using a simple starting material. The film thickness was controlled by the viscosity of the coating solutions; relatively thick and thin films were deposited, respectively, using the high viscosity solution (approx. 50 mPa s; xylene:ethanol:butylacetate=9:1:1) and the low viscosity solution (approx. 6–21 mPa s; xylene:ethanol=3:1). The dip coating was performed only once by pulling the glass substrate out of the solution at the rate of 20 cm min$^{-1}$ and dried in air for several days. Some coatings were exposed to UV-irradiation (excimer: 172 nm) for 5 min in nitrogen flow for attempting the photochemical decomposition of the precursory material at room temperature. The thickness for the as-coated layers were measured using energy-dispersive X-ray fluorescence analyzer (JEOL JSX-3200, Rh, 30 kV) and fundamental parameter method assuming that the layer is composed of $In_2O_3$ (density, 7.0 g cm$^{-1}$). The layers were observed using an ultra-low acceleration voltage FE-SEM (model LEO ULTRA 55, Carl Zeiss) with acceleration voltage of 0.1–30 kV and beam current of 200 pA.

## Results and discussion

Figure 1 shows a typical surface morphology of the as-coated precursor layers without UV-irradiation (oxide thickness; 525 nm). The surface was flat and homogeneous at the beginning of the SEM observation with the acceleration of 230 V. After 80 s of electron beam irradiation, porous and network nanostructure was formed. Number of the pores unchanged during the irradiation. The real-time observation of the nanostructure change was successfully recorded by the digital movie. Dependence of the pore diameter on the EB irradiation time is shown in Fig. 2; the size of a predetermined pore was measured at every second. Pore diameter increased by the irradiation time although the data scattered due to the smooth edge of the pore. The pore distance between the predetermined two pores (width of the residual trunk-like portion) on the irradiation time is shown in Fig. 3. The distance decreased by the irradiation.

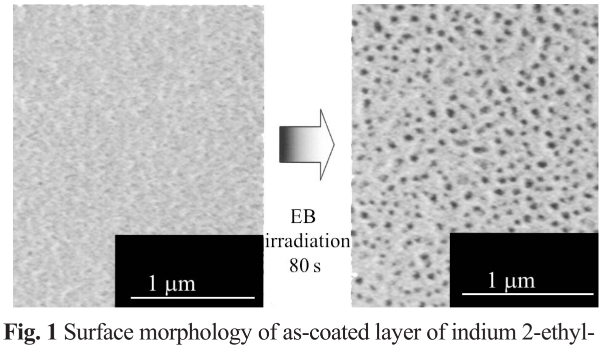

**Fig. 1** Surface morphology of as-coated layer of indium 2-ethylhexanoate monohydroxide (oxide thickness; 525 nm)

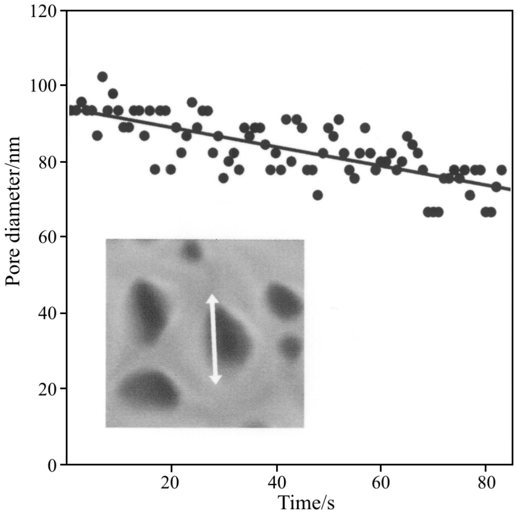

**Fig. 2** Dependence of the pore diameter on the EB irradiation time

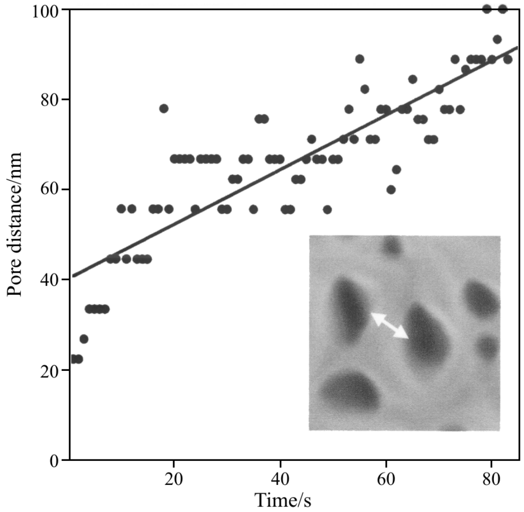

**Fig. 3** Dependence of the pore distance on the EB irradiation time

Figure 4 shows, for reference, the ITO films fabricated by dip coating using a similar precursory material, indium diacetate monohydroxide [9, 10]. The resulting oxide film was porous and many particles were connected to form a network structure. The surface nanostructure was independent of the film thickness which is proportional to the number of coating; in this case, a 30 nm oxide layer was deposited by a dip coating and the heating. These photos suggest that the nanostructure after the EB irradiation shown in Fig. 1 is interpreted as the preliminary step to form porous films composed of nm-sized inter-linked oxide particles as reported in our previous papers [9, 10].

Figure 5 shows a typical surface morphology of a thinner layer (oxide thickness; 25 nm). Fewer pores

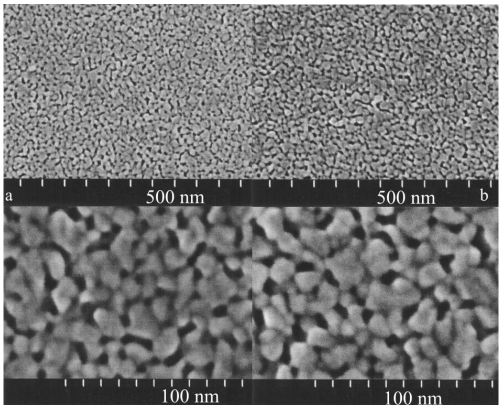

**Fig. 4** FE-SEM photos of ITO films fabricated by dip coating using a similar precursory material, indium diacetate monohydroxide (oxide thickness: a – 3 nm, b – 300 nm)

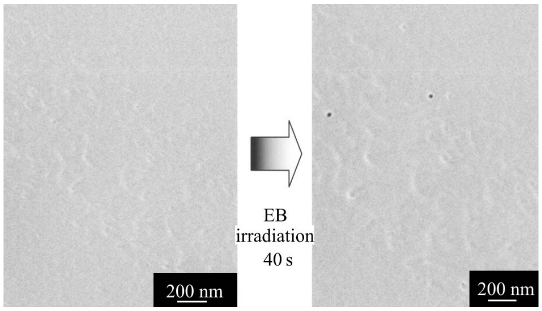

**Fig. 5** Surface morphology of a thinner as-coated layer of indium 2-ethylhexanoate monohydroxide (oxide thickness: 25 nm)

were observed. The number of pores seems to be determined by the total amount of the gases evolved from the layer of the precursory material.

Figure 6 shows a typical surface morphology of the precursor layer after UV-irradiation (oxide thickness; 587 nm). Cracks were observed from the beginning of the EB irradiation so that cracks might be caused by the UV-irradiation. Formation mechanism of cracks is tentatively attributed to volume reduction (tensile stress) of the precursory material due to the decomposition by the UV-irradiation. The EB irradiation enhanced the crack formation. Many pores appeared in the cracks during the EB irradiation. The surface was flat and unchanged during the EB irradiation. These results suggested that the decomposed gases evolved through the cracks. Figure 7 shows a thinner UV-irradiated film (oxide thickness; 100 nm). Some portion of the film was peeled off. The peeling did not occur along the interface between the coating layer and the substrate. The peeling occurred in the coating layer; the pores can be observed on the newly exposed surface of the coating layer.

Figure 8 shows the FE-SEM photos of the fractured surface of the dip coated layers. The precursory materials were observed successfully although the precursory material changed unless taking photos quickly. A surface layer was observed in the UV-irradiated coating.

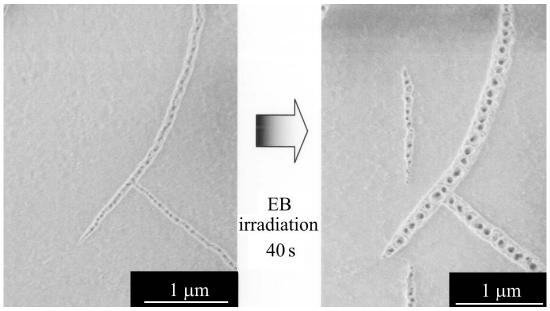

**Fig. 6** Surface morphology of the layer of indium 2-ethylhexanoate monohydroxide after UV-irradiation (oxide thickness: 587 nm)

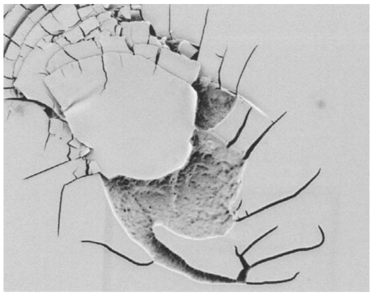

**Fig. 7** Surface morphology of a thinner layer of indium 2-ethylhexanoate monohydroxide after UV-irradiation (oxide thickness: 100 nm)

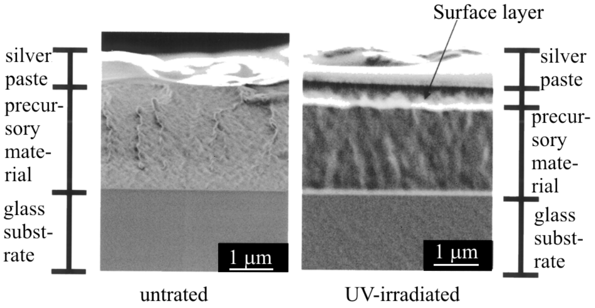

**Fig. 8** Fractured surface of the dip coated layers of the precursory material, indium 2-ethylhexanoate monohydroxide

## Conclusions

Indium 2-ethylhexanoate monohydroxide was dip-coated on glass substrates. The as-coated layers of the precursory material were observed using an ultra-low acceleration voltage FE-SEM. A flat and homogeneous surface changed to porous and network structure after electron beam irradiation. Cracks were observed for the layers prepared with UV-irradiation; the EB irradiation accelerate the crack formation and formation of pores in the cracks. Selective decomposition by electron beam radiation has a potential application to nanolithography process of dip-coated films.

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