Original Paper

Growth Mechanism of Indium-Tin-Oxide Transparent Conducting Films Prepared by Spray CVD

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The authors previously reported on highly conducting ITO films (lowest resistivity: 7.7×10^{-5} ohm·cm) prepared by spraying an ethanol solution of indium (III) chloride and tin (II) chloride (approximately 7 at.% Sn as indicated by Sn/(In+Sn) atomic ratio) using a perfume atomizer and a laboratory hotplate heated to approximately 350 °C (Y. Sawada, *Mater. Sci. Forum*, **2003**, *437/438*, 23.). The present study focused on the growth mechanism of ITO films with the same composition (approximately 7 at.% Sn) as the previous work. A film deposited on a Si wafer was observed using high-resolution field-emission scanning electron microscopy (FE-SEM). The nanostructure of the exposed and fractured surface was investigated to understand the growth mechanism. The film was dense and without pores. The film consisted of large, densely packed grains whose crystals were highly oriented in the 100 direction. The film growth was initiated by nucleation of the oxide particles (diameter is a few nm) to form an island-like structure, followed by selective deposition on the exposed substrate surface and terminated by selective growth of the 100-oriented crystal grains to form columnar structures.

Key Words: *ITO Films*, *Chemical Vapor Deposition*, *Transparent Conducting Films*

1. Introduction

Tin-doped indium oxide (In_2O_3), which is called indium-tin-oxide, is a typical transparent conducting material. Thin films of ITO are widely used as transparent electrodes for all flat panel displays including liquid crystal displays (LCDs), plasma display panels (PDPs), organic light-emitting diodes (OLEDs), various kinds of solar cells and low-E windows, for example[1-8]. The ITO films are deposited mainly by magnetron sputtering using an expensive vacuum system. Deposition of low-resistivity films requires dense ceramic targets that must be sintered at a high temperature (> 1400 °C) in an oxygen atmosphere in a special furnace. Therefore, large-area deposition is difficult and very costly. The target must be replaced after only a limited portion has been engraved during the sputtering operation. Moreover, a lot of sputtered materials are deposited on the inner wall of the deposition chamber. On the other hand, there was a report that the CVD process can prepare low-resistivity ITO thin films comparatively easy. However, the problem with that process is that the deposition temperature becomes higher. The authors previously reported an easy and inexpensive process to deposit ITO films by spray chemical vapor deposition (CVD)[9,10]. The X-ray diffraction spectra of these films agreed with that of indium oxide (cubic bixbyite structure). The deposition temperature in the CVD process was comparatively low because droplets prepared by the atomizer were small, and the carrier gas was not used.

The lowest resistivities of as-deposited and annealed films were 1.2×10^{-4} and 7.7×10^{-5} ohm·cm[10], respectively. The as-deposited resistivity was compatible with those of films deposited by magnetron sputtering. Fukano and Motohiro executed the same spray CVD process and reported on the reproducibility of the process[11]. The annealed resistivity agreed with the lowest value (7.7×10^{-5} ohm·cm) reported by Ohta et al., who prepared single-crystal ITO films on an yttrium-stabilized zirconia (YSZ) single-crystal substrate by pulsed laser deposition (PLD)[12]. Thus, our original spray CVD process has the feature that low-resistivity ITO thin films can be prepared by a high cost performance. Large columnar grains were densely packed in these ITO films deposited by our original spray CVD. It is thought that ITO films deposited by our original spray CVD process obtains a low-resistivity because there is no hollow portion that the carrier electron does not generate and high carrier mobility is obtained because the crystal particles are densely packed. It is thought that crystal particles of ITO films should be large and dense to obtain ITO films with a low resistivity[10].

The authors prepared OLEDs that used ITO thin films (3.7×10^{-4} ohm·cm) deposited by our original spray CVD process for the anode[13,14]. The luminescence characteristic was equal to that of commercial ITO film (2.1×10^{-4} ohm·cm) deposited by a sputtering process. Therefore, the ITO films deposited at atmospheric pressure by our original spray CVD can be used as transparent electrodes.

Nanostructures of ITO films deposited by physical methods (physical vapor deposition (PVD))[15-28] including magnetron sputtering were investigated primarily. Mayer reported a poorly resolved SEM image having large grains to exhibit the nanostructure of ITO films deposited by CVD[29]. However, they only reported the final stage of the growth of the films. In this

study, the growth mechanism of ITO films deposited by spray CVD was investigated systematically using a field emission scanning electron microscope (FE-SEM) from the initial stage of deposition to understand the growth process of an excellent nanostructure. The industrial meaning of this process is that it can be used as an indicator to achieve deposition of low-resistivity ITO transparent conducting films on a plastic substrate, for example. This process leads to the establishment of the technology that prepares low-resistivity thin films with reproducibility if the growth mechanism of the films is understood.

2. Experimental details

Indium (III) chloride, $InCl_3 \cdot 3.5H_2O$ (purity: 99.99 %) and tin (II) chloride, $SnCl_2 \cdot 2H_2O$ (purity: 99.9 %), were dissolved in ethanol (purity: 99.5 %) and stirred for 12 h. The total concentration of metal ions in the solution was fixed at ~0.1 $mol \cdot l^{-1}$. The solution composition was fixed at 7 at.% Sn, at which the lowest resistivity was obtained. A 100-oriented Si wafer (25 × 25 × 0.7 mm^3) was used as a substrate for the FE-SEM observation to avoid charge-up caused by the electron beam radiation. Using a glass substrate for observation of the initial stage of the film growth (island-like structure) or for that of the fractured surface was not possible. The solution was manually sprayed intermittently in air using an inexpensive atomizer designed for cosmetic purposes. A small amount of the solution (approximately 0.15 ml) was repeatedly sprayed. A Si wafer substrate was heated on a laboratory hot plate (Corning PC-400) to ~350 °C. The substrate temperature was monitored by a thermocouple that was attached to the upper surface of the substrate. Spraying in the air was conducted 1, 2, 3, 6, 12, 25, 50, 100 and 200 times. The substrate temperature was reduced by ~5 °C due to the heat of evaporation. Therefore, the spraying operation was conducted after the temperature recovery.

The film deposited on the Si wafer was observed using high-resolution FE-SEM (Hitachi S-5200) with a typical acceleration voltage of 15-20 kV. The observed grain size agreed with the crystallite size determined according to the peak width of the X-ray diffraction (model RINT-2500V, Rigaku) using a copper target (40 kV, 300 mA) and a graphite monochromator.

3. Results and Discussion

An FE-SEM image of the film surface that was sprayed 1, 2, 3, 6, 12, 25, 50, 100 and 200 times is shown in Fig.1. The substrate surface was still exposed until the 25th spray; in other words, no continuous film was formed, but there were many nuclei, i.e., small isolated grains a few nanometers in size (island-like structures). Through aggregation of smaller surrounding grains, sizes of the grains increased. With successive sprays, the film eventually covered the substrate with densely filled grains. A cross section of the film that was sprayed 1, 2, 3, 6, 12, 25, 50, 100 and 200 times is shown in Fig.2. No remarkable change was seen in the grain size in the vertical direction during the first 12th sprays. However, the grain size along the vertical direction increased during the 25 to

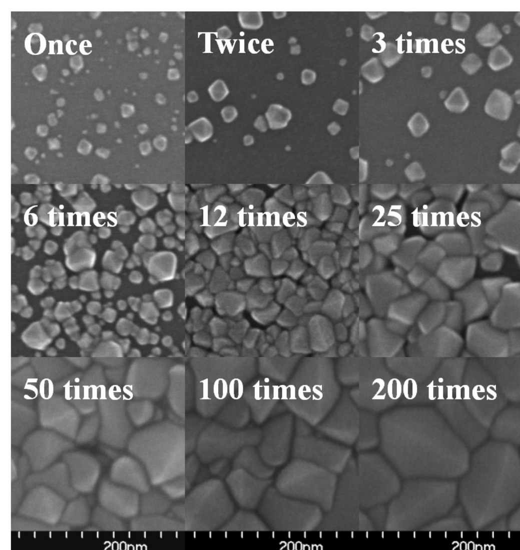

Fig.1 FE-SEM image of surface morphology of ITO film deposited on Si substrate after 1, 2, 3, 6, 12, 25, 50, 100, and 200th sprays.

200th spray. The crystals of the ITO film grew in the vertical direction to form a dense columnar structure. Thus, the grain growth proceeded first horizontally, then vertically. The vertical grain size as a function of the number of sprays is shown in Fig.3. The vertical grain size was rather constant until the surface of the substrate was completely covered at approximately the 12th spray and increased in proportion to the number of sprays. The surface morphology of the ITO films deposited on a glass substrate was the same as those deposited on a Si substrate. The surface of the Si was estimated to be covered with a natural oxide (SiO_2), i.e., silica glass. The fractured surface of sufficiently thick ITO films deposited on glass substrates had approximately the same nanostructure as those deposited on Si substrates. The resistivity of ITO film sprayed 200 times on the Si substrate agreed with that deposited on the glass substrate. These results support the assumption that a Si substrate would be suitable for examining the growth mechanism of ITO films on a glass substrate.

The horizontal grain size at the surface vs. the number of sprays is plotted in Fig.4. The horizontal grain size increased and then saturated at 100 or 200th sprays. The number of particles or grains on the surface of the film per unit area is plotted as a function of the number of sprays in Fig.5. The number of particles (grains) first decreased, then increased slightly, and then decreased again. These are referred to as the first, second, and third stages in this paper.

In the first stage, we expected that the small oxide particles would react with chlorine or hydrochloride to form metal chlorides,

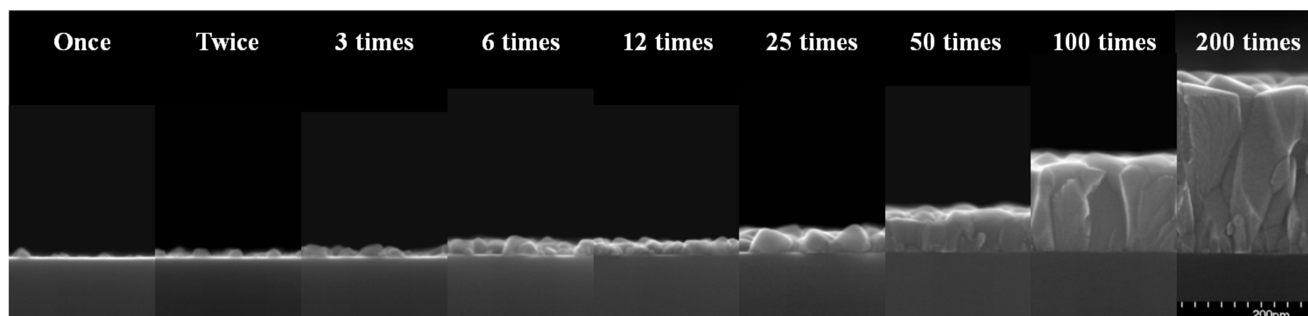

Fig.2 FE-SEM image of fractured surface of ITO film deposited on Si substrate after 1, 2, 3, 6, 12, 25, 50, 100, and 200th sprays.

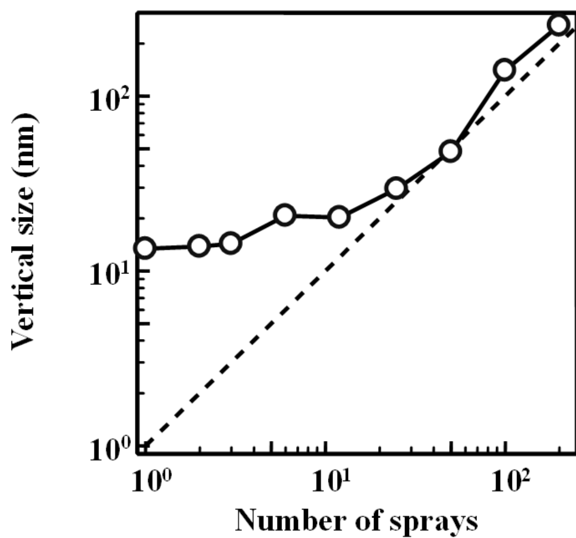

Fig.3 Vertical grain size of ITO film as a function of number of sprays.

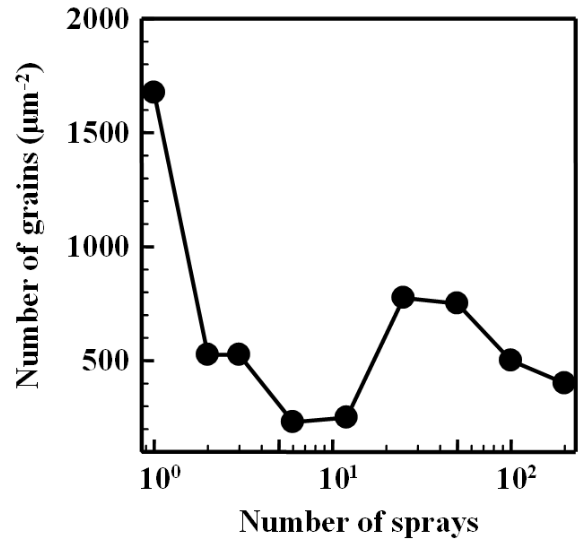

Fig.5 Number of particles or grains on ITO film surface per unit area as function of number of sprays.

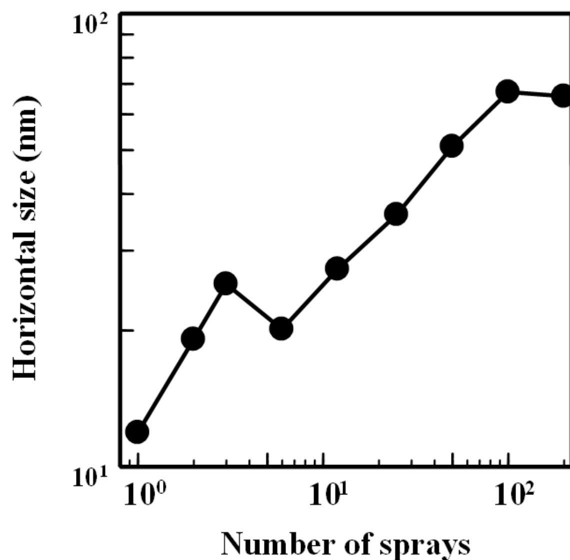

Fig.4 Horizontal grain size of ITO film as function of number of sprays.

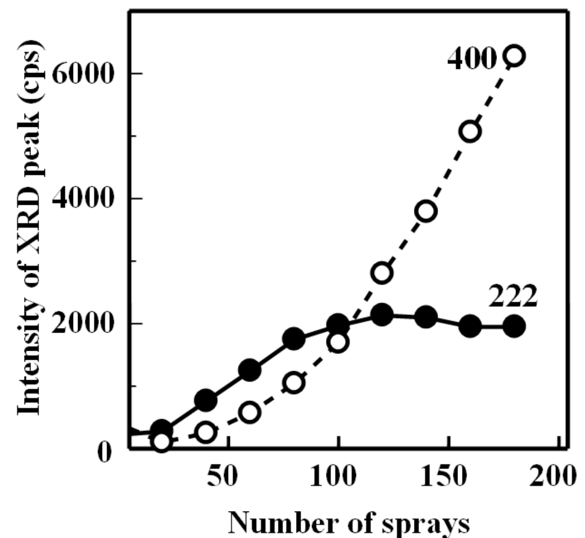

Fig.6 Intensity of 222 and 400 diffraction peaks as function of number of sprays.

which would evaporate and condense onto the surface of a larger oxide particle to precipitate the oxide. The low vapor pressure of the oxide at this temperature supported this hypothesis. During the second stage, new crystals were selectively generated on the exposed surface of the substrate between the particles to cover the substrate because the vapor of the metal chloride was expected to condense on the concave surface to decrease the surface energy. The crystals grew gradually in the horizontal direction and covered the surface of the substrate. When all surfaces of the substrate were covered, there was a shift to the third stage. The crystals and grains grew in the vertical direction. The crystals also grew horizontally to hang over the other crystals.

The relationship between the intensities of the 222 and 400 diffraction peaks and the number of sprays is shown in Fig.6. This ITO film exhibited a random orientation in the first stage. The 222 diffraction peak was stronger than the 400 diffraction peak, which was also the case of the randomly oriented fine particles and some PVD films. The intensity of the 222 peak began to saturate in the second stage. The intensity of the 400 diffraction peak increased remarkably in the third stage. This should be attributed to the selective growth of highly oriented columnar grains.

Thus, the growth mechanism of the ITO film deposited by spray CVD in this study consisted of three stages: growth of the island-like particles in the first stage, horizontal growth (selective coverage of the substrate) in the second stage, and vertical growth to form columnar structures in the third stage.

4. Conclusions

An ITO film deposited by spray CVD was evaluated by FE-SEM and X-ray diffraction to investigate the growth mechanism. The film was dense and without pores, consisting of large, densely packed grains whose crystals were highly oriented in the 100 direction. The film growth was initiated by nucleation of the oxide particles (diameter, a few nm) to form an island-like structure in the first stage, followed by selective deposition on the exposed

substrate surface in the second stage, and ending with selective growth on the 100-oriented crystals to form a columnar structure in the third stage. In the first stage, nanometer-sized isolated particles with a random crystal orientation grew horizontally. In the second stage, the surface of the substrate was covered to form a continuous film. In the third stage, the vertical growth of the crystals proceeded to form a dense columnar structure with highly oriented crystals.

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