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EVOLUTION OF WATER VAPOR FROM INDIUM–TIN–OXIDE THIN FILMS FABRICATED BY VARIOUS DEPOSITION PROCESSES

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Abstract

Tin-doped In_2O_3 (indium–tin–oxide) transparent conducting films are widely used as electrodes of liquid crystal displays and low-E windows. In the present study, a systematic TDS study was undertaken for ITO films fabricated by various deposition processes; such as PVD, dip coating and spray deposition. Water vapor was the main gas evolved from the films; gas evolution from the silicon substrate was negligible. The evolution proceeded via two steps at approximately 373 and 473–623 K. The amount of the evolved water was in the order: (dip-coated film)>(PVD films)>(spray-deposited film). This order was identical to that of the film's resistivities.

Keywords: grain size, indium–tin–oxide, thermal desorption spectroscopy, thin films, water vapor

Introduction

Tin-doped In_2O_3 (indium–tin–oxide, ITO) transparent conducting films are widely used as electrodes of liquid crystal displays. These ITO films are mainly manufactured by physical vapor deposition (PVD) such as the magnetron sputtering process [1] so that many investigations have focused on the films deposited by the PVD process. Transparent conducting films are also expected to be used as low-E windows, which reduces the energy consumption of air conditioning units by shielding infrared radiation from the sun. For this purpose, the PVD process is rather unsatisfactory since the transparent conducting films must be less-expensively deposited onto large-area glass substrates. The chemical process such as dip coating [2–10] does not satisfy the film quality; the lowest resistivity ($2.1\cdot10^{-4}$ ohm cm [7]) at present seems much higher. Spray deposition [11, 12] seems to be promising since a lower resistiv-

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ity ($7.7 \cdot 10^{-5}$ ohm cm [12]) using an extremely inexpensive setup was recently achieved. Based on these results, it is important to understand the difference either quantitatively or semi-quantitatively between the various ITO films. Some of the present authors reported that thermal analysis (thermal desorption spectroscopy, TDS) was effective for evaluating the influence of the preparation conditions (film thickness and heating temperature) of ITO films fabricated by the dip coating process.

Conventional thermal analyses such as TG-DTA or DSC are applicable to thin films in some cases [13–18], but in other cases, their sensitivities are insufficient to detect a thermal change in a minute amount of the specimens. The high sensitivity of mass spectroscopy is advantageous for the thermal analysis of thin films. The authors focused on TDS, which should be categorized as a kind of evolved gas analysis (EGA). In order to analyze thin films, it is essential to maintain a high vacuum (low background pressure) in the analysis chamber and to precisely measure the specimen temperature.

In the present study, a systematic TDS study was undertaken for ITO films fabricated by various deposition processes, such as PVD (magnetron sputtering, vacuum evaporation, ion-plating), dip coating and spray pyrolysis. The films (thickness, ~250 nm) fabricated on a silicon substrate were heated to 1073 K in a high vacuum in order to monitor the evolved gases by mass spectroscopy. A comparison was mainly made between the two extreme examples (dip-coated film and spray-deposited film) regarding the nanostructure (grain size, density or porosity) and the water evolution.

Experimental

Fabrication of ITO films

The fabrication of the ITO film (Sn/(In+Sn), ~5 at%) was reported elsewhere [5, 19] in detail. A silicon wafer was used as the substrate instead of glass for the radiation heating in the TDS apparatus. The coating and the heating were repeated three or ten times to increase the film thickness to approximately 75 nm (for FE-SEM) or 250 nm (for TDS), respectively. The film thickness was determined by X-ray fluorescence analysis (energy dispersive type, fundamental parameter method) using a JEOL JSX-3200. The nanostructures of the films were observed by FE-SEM (Hitachi S-5200). The substrates with the film were cut into 10×10 mm sections for the TDS measurements. The as-received substrate and the substrate without the film after heating were also prepared to examine the gas evolution from the substrate.

The ITO film (~5.0 at%Sn) was spray-deposited on the silicon wafer in air at 573–623 K. The spraying was done 250 times with a sprayer (a cosmetic atomizer PV14033-00; Shoubi-Do, Co., Ltd.) using an ethanol solution (ethanol, 99.5%, 500 mL) containing indium(III) chloride (99.99%, 12.8 g), $InCl_3 \cdot 2.7H_2O$, and tin(II) chloride (99.9%, 0.51 g), $SnCl_2 \cdot 0.86H_2O$. A 250 nm-thick film was obtained. The

film thickness was determined by X-ray fluorescence analysis using a JEOL JSX-3200.

The sputter-deposited and electron-beam-deposited ITO films (~250 nm thicknesses) on the silicon wafer were prepared at 573 and 613 K, respectively.

Thermal desorption spectroscopy

An ESCO EMD-WA1000S was used for the thermal desorption spectroscopy. The system was evacuated to ~$1.0 \cdot 10^{-7}$ Pa using a turbo molecular pump. The specimen (film-coated substrate) was directly placed on a quartz stage using a manipulator system. Light from a halogen lamp was guided via a quartz rod and the quartz stage to the uncoated surface of the substrate, which selectively absorbed the light. The stage temperature was monitored by a thermocouple inserted in the quartz stage to control the heating rate at 30 K min^{-1} (323–1073 K). Another thermocouple was pressed on the film surface. The surface temperature approximately agreed with the stage temperature up to approximately 473 K, but deviated at the higher temperature; for example, the surface temperature was approximately 673 when the stage temperature was 773 K at a heating rate of 30 K min^{-1}. Gas evolved from the specimen was measured with a quadruple mass analyzer having an ionization voltage of 70 V. The mass fragments of 2, 12, 16, 17, 18, 28, 35 and 44 *m*/*z* were monitored. The amount of water vapor was quantitatively determined as described by Hirashita and Uchiyama [20]; a hydrogen-implanted silicone wafer was used as the calibration standard. The total amount of water molecules from 333 to 1053 K was also determined.

Results and discussion

Chemically-deposited films

The typical thermal desorption spectra of the dip-coated ITO film are shown in Figs 1 and 2. The main gas evolved from the specimen was determined to be water vapor because of the simultaneous detection of mass fragments 18 and 17 *m*/*z* corresponding

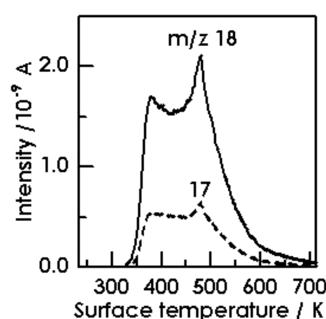

Fig. 1 Thermal desorption spectra of mass fragments of 17 and 18 *m*/*z* for a typical ITO film prepared by the dip coating process. Film thickness, ~250 nm; prepared by heating in air at 873 K for 30 min

to H_2O^+ and OH^+, respectively, as shown in Fig. 1; their intensity ratio agreed with that of water. The result for the as-received substrate without the film is indicated for

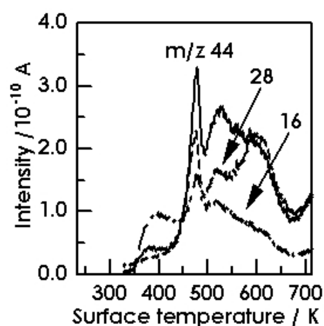

Fig. 2 Thermal desorption spectra of mass fragments of 16, 28 and 44 *m/z* for a typical ITO film prepared by the dip coating process. Film thickness and the preparation conditions are as described in the caption of Fig. 1

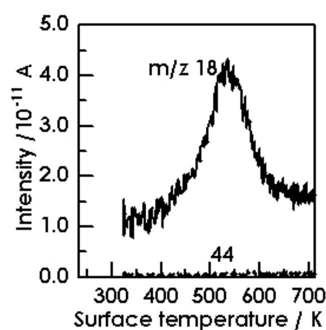

Fig. 3 Thermal desorption spectra of mass fragments of 18 and 44 *m/z* for an as-received Si wafer. Wafer thickness, 0.6 mm; without annealing

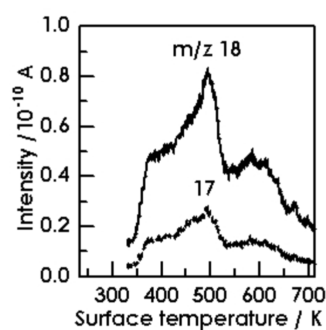

Fig. 4 Thermal desorption spectra of mass fragments of 17 and 18 *m/z* for a typical ITO film prepared by the spray process. Film thickness ~250 nm

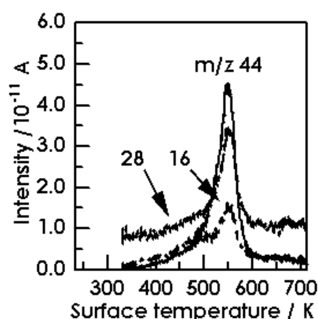

Fig. 5 Thermal desorption spectra of mass fragments of 16, 28 and 44 *m*/*z* for a typical ITO film prepared by the spray process. Film thickness and the preparation conditions are as described in the caption of Fig. 4

reference in Fig. 3; the evolution from the substrate was negligible. A lower evolution of water vapor (not shown in the figure) was observed for a substrate without the film after heating. The evolution of water vapor terminated at approximately 673 K. Two peaks were observed at surface temperatures of approximately 373 and 473 K, which we call the first and second peaks, respectively. The origin of the water vapor will be discussed later. Mass fragments of 16, 28 and 44 *m*/*z* are indicated in Fig. 2. The evolution of carbon dioxide was observed at 473 and 523–673 K, which will be discussed in a future report.

The typical thermal desorption spectra of the spray-deposited ITO film are shown in Figs 4 and 5. The main gas evolved from the specimen was determined to be water vapor as shown in Fig. 4. In Figs 1 and 4, the amount of water vapor for the spray-deposited film was drastically less than that for the dip-coated film. A shoulder and a peak were observed at surface temperatures of approximately 373 and 473 K, respectively, and similar to that of the dip-coated film. The mass fragments of 16, 28 and 44 *m*/*z* are indicated in Fig. 5. The evolution of carbon dioxide was observed at 523–573 K, probably due to the

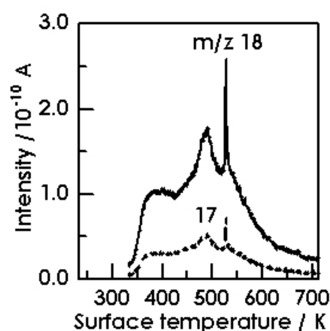

Fig. 6 Thermal desorption spectra of mass fragments of 17 and 18 *m*/*z* for a typical ITO film prepared by the sputtering process. Film thickness, ~250 nm; prepared at 573 K

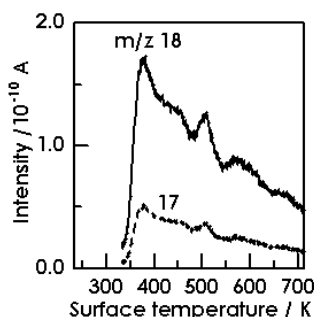

Fig. 7 Thermal desorption spectra of mass fragments of 17 and 18 *m/z* for a typical ITO film prepared by the electron beam process. Film thickness, ~250 nm; prepared at 613 K

combustion of contamination on the film surface. The low intensity ($<2\cdot10^{-12}$ A) of the mass fragment of 35 *m/z* (Cl^+) from the dip-coated and spray-deposited ITO films suggested the complete oxidation of tin(II) chloride.

Physically-deposited films

The typical thermal desorption spectra of PVD films, i.e., sputtering-deposited and electron-beam-deposited ITO films, are shown in Figs 6 and 7, respectively. The amount of the evolved water vapor for the PVD films was less than that for the dip-coated one. The spectra for the sputtering-deposited film in Fig. 6 were similar to those for the dip-coated film, except for the third sharp peak at ~523 K. It should be interpreted that the third peak was derived from the decomposition of indium hydroxide on the film surface. Figure 7 shows the thermal desorption spectra for the electron-beam-deposited film. These spectra were not similar to the other films in this paper. There were two peaks; the first stronger peak and the second weaker peak at surface temperatures of ~373 and 473 K, respectively.

The amount of evolved water vapor

The number of desorbed water molecules is shown in Table 1. The evolution from the Si substrates, as-received and annealed, were negligible. The amount at the evolved water was in the order; (dip-coated films) > (PVD films) > (spray-deposited films). This order was identical with that of the film resistivities. The evolution proceeded via two steps (or three steps in the case of sputtering-deposited film) at ~373 and 473–623 K, which were tentatively attributed to physically desorbed water, and chemically desorbed water or the decomposition of indium hydroxide formed on the surface of the grains, respectively. The amount of the evolved water vapor for a sputtering-deposited film was approximately equal to that for the electron-beam-deposited one. Their amounts of evolved water vapor were less than the values from the dip-coated films. In Fig. 8, the nanostructure of a dip-coated film was porous hence a larger amount of adsorbed water was expected.

Table 1 Number of desorbed water molecules

Deposition processes		Substrate temperature/K	Number of desorbed water molecules/10^{15} cm^{-2}	Film resistivity/ 10^{-4} ohm cm
Reference	Si substrate	298	1	–
Chemical processes	dip coating	873	43	23
	spray pyrolysis	573–623	5	1.6
Physical processes	sputtering	573	12	2–4
	electron beam	613	13	2–4

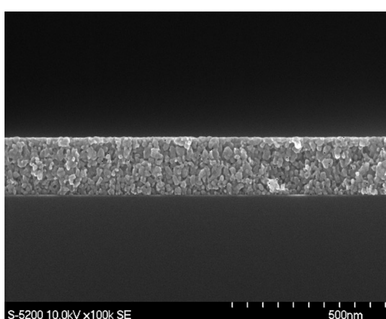

Fig. 8 Nanostructure of the ITO film fabricated by the dip coating process. Prepared on Si wafer using the solution of 5 at%Sn by heating in air at 873 K for 30 min

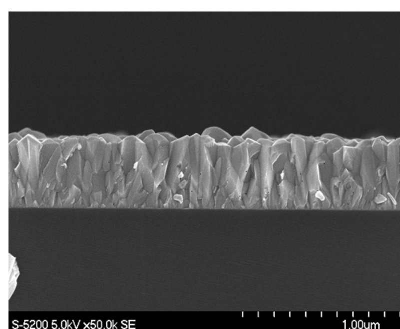

Fig. 9 Nanostructure of the ITO film fabricated by the spray pyrolysis process. Prepared on Si wafer using the solution of 5 at%Sn by heating in air at 573–623 K

The thickness determined from the present figure is larger than that determined by XRF; this should be attributed to the porous nature of the film. The grain size of the dip-coated film was ~20 nm. A spray-deposited film desorbed a small number of water molecules. The nanostructure of the spray-deposited film is shown in Fig. 9. In this figure, the ITO film seems to have a high density and looks like a sintered species. It is assumed that most of the desorbed water from the spray-deposited film was adsorbed water on the ITO

film surface. The resistivity of a spray-deposited film was lower than that of a dip-coated film as shown in Table 1.

Conclusions

Water vapor was the main gas evolved from the films; gas evolution from the substrate was negligible. The evolution proceeded via two steps (or three steps in the case of sputtering-deposited film) at ~373 and 473–623 K, which tentatively attributed to physically desorbed water, and chemically desorbed water or the decomposition of indium hydroxide formed on the surface of the grains, respectively. The amount of the evolved water was in the order: (dip-coated film) > (PVD films) > (spray-deposited film). This order was identical to that of the film's resistivities.

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