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EVOLUTION OF WATER VAPOR FROM INDIUM–TIN-OXIDE TRANSPARENT CONDUCTING FILMS FABRICATED BY DIP COATING PROCESS

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Abstract

Tin-doped indium oxide In_2O_3 (indium–tin-oxide) transparent conducting films were fabricated on silicon substrates by a dip coating process. The thermal analysis of the ITO films was executed by temperature-programmed desorption (TPD) or thermal desorption spectroscopy (TDS) in high vacuum. Gas evolution from the ITO film mainly consisted of water vapor. The total amount of evolved water vapor increased on increasing the film thickness from approx. 25 to 250 nm and decreased by increasing the preparation temperature from 365 to 600°C and by annealing at the same temperature for extra 10 h. The evolution occurred via two steps; the peak temperatures for 250 nm thick films were approx. 100–120 and 205–215°C. The 25 nm thick films evolved water vapor at much higher temperatures; a shoulder at approx. 150–165°C and a peak at approx. 242°C were observed. The evolution temperatures increased by increasing the preparation and the annealing temperatures except in case of the second peak of the 25 nm thick films. The evolution of water vapor at high temperature was tentatively attributed to thermal decomposition of indium hydroxide, $In(OH)_3$, formed on the surface of the nm-sized ITO particles.

Keywords: EGA, indium oxide, TDS, TPD, thin films

Introduction

Thermal analyses such as TG-DTA-MS are effective to understand the thermal change of the precursory materials of ceramic thin films via CVD process [1, 2]. Conventional TG-DTA or DSC is applicable to thin films in some cases [3–8]. However,

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the sensitivities are insufficient in most cases. Attentions have been paid to mass spectroscopy because of its high sensitivity. In this respect, the authors focused on temperature-programmed desorption (TPD) or thermal desorption spectroscopy (TDS), which should be categorized as a kind of evolved gas analysis (EGA).

Tin-doped In_2O_3 (indium–tin-oxide) transparent conducting films are widely used as electrodes of all flat panel displays and touch panels, shielding infrared radiation and electromagnetic waves etc. The authors reported previously the results of TPD [9]; water vapor was the main gas evolved from ITO films and the evolution proceeded via two steps (at ~100 and 200–250°C). The evolved amount was in the order of (dip-coated films [10])>(PVD films)>(spray-CVD films [11]). In the present work, the dip-coated films were investigated by TPD in detail; influence of the film thickness and preparation condition (heating temperature and heating time) is investigated.

Experimental

ITO films

Fabrication of the ITO films (Sn/(In+Sn), approx. 5 at.%) were reported elsewhere [10, 12]. A silicon wafer was used as the substrate instead of the glass. The substrates were dip-coated using ethanol solution containing indium(III) diacetate monohydroxide $In(OH)(O_2CCH_3)_2$, tin(II) dichloride, $SnCl_2\cdot 2H_2O$, and 2-aminoethanol (monoethanol amine), $H_2NC_2H_4OH$. Although the films were coated simultaneously on both sides of the substrate during the dipping, the coating on either side was wiped with acetone in the present work. The coated substrate was heated at 365 or 600°C in air for 30 min during which oxide film (thickness, approx. 25 nm) was fabricated. The coating and the heating were repeated ten times in order to fabricate thicker films (thickness, 250 nm) which we call 'ten-layer films' although the boundary between the layers was not detected by high-resolution FE-SEM observation. The film thickness was determined by X-ray fluorescence analysis (energy dispersive type, fundamental parameter method) using a JEOL JSX-3200. In order to enhance the crystal growth and grain growth, some oxide films were heat-treated at 365 or 600°C for extra 10 h in air, which we call 'annealing' in the present paper. The film-deposited substrates were cut into 10×10 mm sections for the TPD measurement. The blank test was executed using the as-received substrate and the annealed substrate without the film.

Temperature-programmed desorption

A schematic illustration of the TPD apparatus (ESCO EMD-WA1000S) is shown in Fig. 1. The system was evacuated to $\sim 1.0\times 10^{-7}$ Pa by a turbo molecular pump. The specimen (film-deposited silicon wafer) was placed on a quartz stage directly using a manipulator system. Radiation from a halogen lamp was guided via a quartz rod and the quartz stage to the uncoated surface of the Si substrate.

The stage temperature was monitored by a thermocouple inserted in the quartz stage to control the heating rate at 30°C min^{-1}. Another thermocouple was pressed on

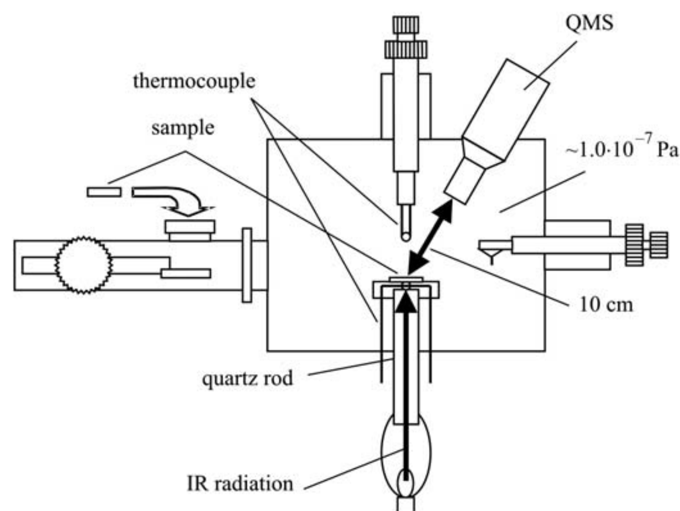

Fig. 1 Schematic illustration of the TPD apparatus

the film surface. The surface temperature agreed approximately with the stage temperature up to 200°C and deviated at higher temperature; the surface temperature was 400°C when the stage temperature was approximately 500°C.

Gas evolved from the specimen was analyzed with a quadruple mass analyzer (QMS) with an ionization voltage of 70 V. The mass fragments of 2, 15, 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 [13]; a hydrogen-implanted Si wafer was used as a calibration standard.

Results and discussion

Amount of the evolved water vapor

The main gas evolved from the specimen was water vapor as described previously [9]. The detections of mass fragments 18 and 17 *m/z* corresponding to H_2O^+ and OH^+, respectively, are synchronized; their intensity ratio agreed with that of water. Water vapor evolved at between approximately 100 and 400°C. Gas evolution from the substrate was negligible.

The amount of the evolved water vapor as a function of the ITO film thickness is shown in Fig. 2. In this figure, the amount of water vapor was plotted tentatively as a thickness of water layer assuming that the water molecules exist as a liquid layer. The maximum amount of water (assumed layer thickness, 30 nm) in the present case was evolved from relatively thick (thickness, 250 nm) ITO films prepared by repeating ten times the dip coating and heating at relatively low temperature (365°C).

Amount of water increased by increasing the thickness of the ITO films; this suggested that the origin of water was attributed to the interior of the ITO films. High

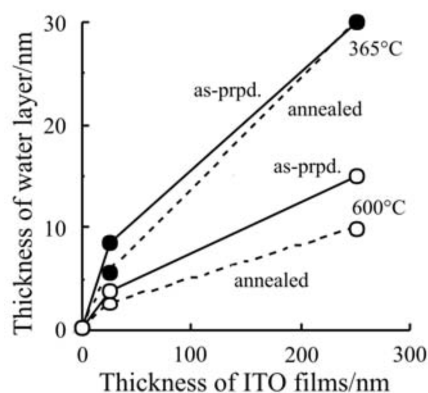

Fig. 2 Amount of water vapor evolved from ITO films as a function of the film thickness. The film thickness of water was tentatively plotted assuming that a layer of liquid water formed. Solid line, as-prepared at the indicated temperature; broken line, annealed after the preparation at the same temperature for extra 10 h

resolution FE-SEM observation of the fractured films in the previous paper [9] supported this hypothesis; the films fabricated by dip coating were porous and composed of nm-sized grains. The amount of water was lowered by increasing the preparation temperature from 365 to 600°C and by annealing for extra 10 h. This should be understood mainly by the grain growth (decrease of the total surface area) of the ITO crystals. The amount of water was exceptionally unchanged after the annealing in case of the film (thickness, 250 nm) prepared at 365°C; this should be interpreted as no grain growth occurred due to the low preparation temperature. On comparing the amount of evolved water per thickness of ITO film, the very thin films (thickness, 25 nm), which we call monolayer films, evolved more water than ‘ten-layer’ films (thickness, 250 nm). The excess amount of water suggested a different origin in case of the monolayer films.

250 nm thick films

Figures 3 and 4 show TPD spectra of water vapor (mass fragment *m/z* 18) evolved from the ‘ten-layer’ ITO films (film thickness, 250 nm) prepared at 365 and 600°C, respectively. The solid line indicates the result of the as-prepared ITO films. The broken line indicates the result of the ITO film prepared and annealed at the same temperature for extra 10 h. The evolution of water vapor proceeded via two steps (peak temperature, approx. 100–120 and 205–215°C; the authors attributed tentatively in the previous paper [9] to physically absorbed water for the first step and to chemically absorbed water or decomposition of indium hydroxide formed on the surface of the oxide for the second step, respectively. In case of the films prepared at 600°C (Fig. 4), annealing i.e. a prolonged heating time increased the peak temperatures from 106 to 122°C in the first step and 206 to 215°C in the second step. In case of the films prepared at lower temperature (365°C), as indicated in Fig. 3, the peak temperature in the first step (103°C)

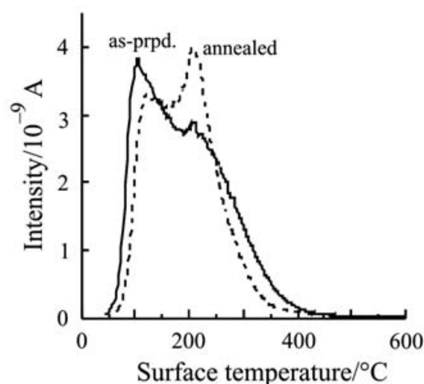

Fig. 3 TPD spectrum of water vapor evolved from 250 nm thick ITO films prepared at 365°C. Solid line, as-prepared at 365°C; broken line, prepared at 365°C and annealed at 365°C

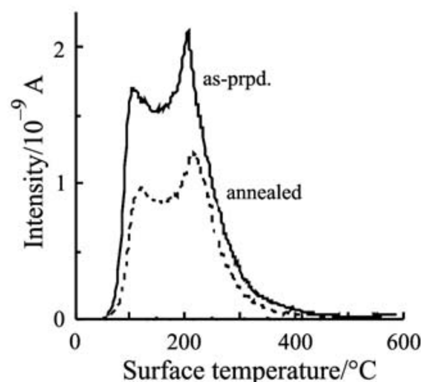

Fig. 4 TPD spectrum of water vapor evolved from 250 nm thick ITO films prepared at 600°C. Solid line, as-prepared at 600°C; broken line, prepared at 600°C and annealed at 600°C

was slightly lower than that prepared at higher temperature (600°C) and shifted drastically to higher temperature (approx. 136°C) by the annealing. Thus, the peak temperature shift to higher temperature supported the grain growth (decrease on the total surface area) as well as the decreased amount of water evolution.

25 nm thick films

Figures 5 and 6 show evolution of water vapor from the thinner (thickness, approx. 25 nm) ITO films ('monolayer films') prepared at 365 and 600°C, respectively. The evolution occurred via two steps; a shoulder (approx. 150–165°C) in the first step and a peak (approx. 242°C) in the second step were observed. It should be emphasized that these temperatures were much higher than those of the thicker films

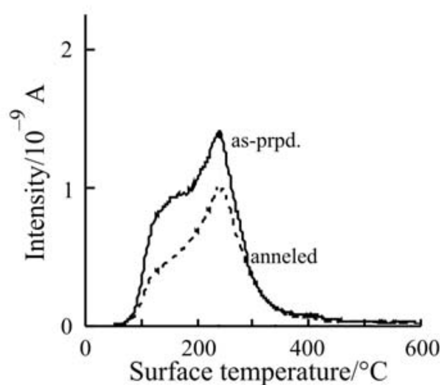

Fig. 5 TPD spectrum of water vapor evolved from the 25 nm thick ITO films prepared at 365°C. Solid line, as-prepared at 365°C; broken line, prepared at 365°C and annealed at 365°C

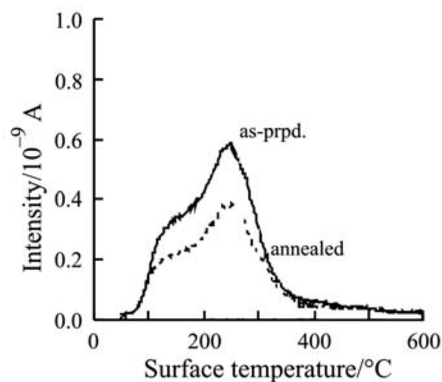

Fig. 6 TPD spectrum of water vapor evolved from the 25 nm thick ITO films prepared at 600°C. Solid line, as-prepared at 600°C; broken line, prepared at 600°C and annealed at 600°C

(thickness, 250 nm). Another important point of the present thinner films is that the peak temperature in the second step was unchanged by the preparation temperature and the annealing. The origin of water in the present case was attributed tentatively to thermal decomposition of a thin solid layer of indium hydroxide, $In(OH)_3$, formed on the surface of the ITO grains.

Conclusions

ITO films fabricated on silicon substrates by a dip coating process were investigated by TPD in vacuo. The main gas evolved from the ITO films was water vapor. The total amount of evolved water vapor increased on increasing the film thickness from approx. 25 to 250 nm. The total amount of evolved water vapor decreased by increas-

ing the preparation temperature from 365 to 600°C and by annealing at the same temperature for extra 10 h. The evolution occurred via two steps; the peak temperatures were approx. 100–120 and 205–215°C in case of the 250 nm thick films. Evolution of water vapor occurred at much higher temperatures in case of 25 nm thick films; a shoulder at approx. 150–165°C and a peak at approx. 242°C. The evolution temperatures increased by increasing the preparation temperature and the annealing except in case of the second peak of the 25 nm thick films.

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