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THERMALLY INDUCED CHANGES IN AMORPHOUS INDIUM-TIN-OXIDE THIN FILMS

Gas evolution and crystallization

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Amorphous indium–tin–oxide (ITO) transparent conducting film (15 at% Sn; thickness, 150–190 nm) was deposited on silicon wafer at room temperature by RF magnetron sputtering for temperature programmed desorption (TPD) in vacuum. The thermal crystallization was accompanied by evolution of water vapor (the main gas), argon and carbon dioxide. The total amount of evolved water vapor (H_2O [mol]/(In [mol]+Sn [mol])>0.2) was one or two orders of magnitude more than that from the nanocrystalline ITO films reported in our previous papers. The thermal change of amorphous ITO film was remarkably affected by the position of the substrate. An abrupt gas evolution was characteristic of the amorphous ITO films deposited on the position near the target center. The evolution temperature (548–563 K) was higher than the gas evolution temperature from the crystalline films. The far from center positioned films crystallized at higher temperature with relatively slower evolution of the gases.

Keywords: *amorphous ITO films, argon, carbon dioxide, TPD, water vapor*

Introduction

Indium–tin–oxide (ITO) transparent conducting films have been widely applied in the field of anti-static electricity shielding coating, heat reflecting mirrors, solar cells, liquid crystal displays (LCDs) and organic light emitting devices (OLEDs) due to their unique combination of electrical and optical properties [1]. The problems due to gas inclusions in the ITO films become even more significant for vacuum micro-electronic devices, because the operational life is directly related to the amount of residual gases present in the vacuum envelope [2, 3]. Thus, one needs to know the type of trapped gas and the process temperatures necessary to remove these gases from the films. Temperature programmed desorption (TPD) using a mass spectrometer is an excellent technique for analyzing the minute amounts of gas species evolved from the film samples and for characterizing the bonding strength of the species with the surface of the solid. Our previous work [4, 5] found that the amount of the evolved water vapor from the crystalline ITO films is dependent on the deposition process such as spray CVD (chemical vapor deposition), sputtering, ion-plating, electron-beam heating vacuum evaporation or dip coating and the post-deposition annealing conditions such as temperature and time. The amount of evolved water vapor was related to the total surface area of the crystal grains; much amount of water evolution from porous films was ascribed to the surface of the open pores. The evolutions at the peak temperature of approximately 373–393 K belonged to physically adsorbed water. These, at temperatures higher than 473 K, were attributed to chemically adsorbed water or thermal decomposition of indium hydroxide formed on the surface of the crystal grains. Although polycrystalline films are used because of their high conductivity and transmittance, amorphous films have recently become increasingly important since they can be deposited at room temperature on heat-sensitive flexible organic substrates and organic light emitting layers [6–9]. Nishimura *et al*. [10] and Ando *et al*. [11] reported evolution of water vapor from partly-crystallized amorphous ITO films which was sputter-deposited in water vapor atmosphere introduced intentionally and discussed the crystallization process during the post-deposition annealing at various temperatures in atmospheric pressure of nitrogen atmosphere for 1 h. The present study reports the evolution of water vapor as well as other gases from the fully amorphous ITO films sputter-deposited without intentional introduction of water vapor and discusses the crystallization process occurring simultaneously during the heating process of a TPD mea-

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surement. The present results will be more deeply discussed than in the proceedings of a NATAS symposium [12] and also compared with the results of Nishimura *et al.* [10] and Ando *et al.* [11].

Experimental

Deposition of ITO films

An amorphous ITO thin film was deposited by RF magnetron sputtering downwardly onto the room temperature substrate placed at the bottom of the water-cooled vacuum chamber (ANELVA model SPF-332H). The background pressure of the system was $1\cdot10^{-3}$ Pa evacuated by an oil diffusion pump with a liquid-nitrogen trap. The film was deposited in argon atmosphere (pressure, 1.0 Pa; purity, 99.999%; flow rate, 19 mL min^{-1}) with sputtering power of 30 W. The target (3-inch diameter, 80 mass% In_2O_3–20 mass% SnO_2) to substrate distance was approximately 60 mm. The target surface was selectively sputtered due to the magnetic field to form an erosion ring (diameter, 35 mm). A silicon wafer substrate (50×100 mm^2) was heated at 823 K in air for 30 min prior to the film deposition in order to clean the surface. The substrate after the deposition was cut into small pieces (10×10 mm^2). The two pieces were categorized as being 'near-center' or 'far-center' position with distances from the center 0 and 18 or 32 and 38 mm, respectively.

The thickness and composition of ITO films were measured by X-ray fluorescence analysis (EDX, fundamental parameter method [13]; JEOL model JSX-3200) and shown in Fig. 1. The thickness of the film (150–190 nm) decreases slightly with the distance from the center. The composition (average; 15 at.% Sn as indicated by the Sn/(In+Sn) atomic ratio) agreed with that of the target (15 at.% Sn) and was independent of the position.

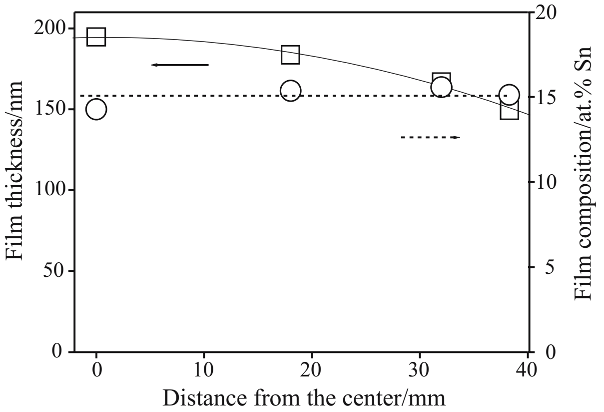

Fig. 1 Thickness and composition of the amorphous ITO film

Temperature programmed desorption

The TPD apparatus (ESCO model EDM-WA1000S/W) was evacuated to approximately $1.0\cdot10^{-7}$ Pa by a turbo molecular pump. The specimen (10×10 mm^2) 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 silicon substrate to heat at the heating rate of 20 K min^{-1}. The surface temperature of the film was monitored and controlled by an upper thermocouple, which was pressed onto the surface of the thin film as executed in our previous measurements [4, 5]. Gases evolved from the specimen were measured with a quadruple mass analyzer having an ionization voltage of 70 V. The mass fragments of *m*/*z* 2, 15, 16, 17, 18, 28, 32, 35, 40 and 44 were monitored. The amount of water vapor was quantitatively determined as described by Hirashita and Uchiyama [14]; the hydrogen implanted silicon wafer was used as the calibration standard. The substrate without the film was measured to confirm that the gas evolution from the substrate was negligible.

X-ray diffraction

The crystal state of the ITO films was evaluated by X-ray diffractometer (Rigaku model RINT 2500) with graphite-monochromated CuK_α radiation (λ=1.5405 Å). A line-shaped X-ray source was operated at 40 kV and 300 mA and the data were collected in the range of 2θ=10 to 60° with an interval of 0.01° and a scan speed of 2° min^{-1}. Four pieces of the substrate with the equivalent positions (same distance from the center) were quenched from the various temperatures during the TPD measurements in order to check the simultaneous occurrence of the crystallization and the gas evolution during the heating in vacuum.

Results and discussion

Gas evolution

The TPD curve of evolved water vapor is shown in Fig. 2 for a typical amorphous ITO film deposited on the near-center position (distance from the center, 18 mm). Simultaneous detection of strong signals (*m*/*z* 17 and 18) indicated that water vapor was the main gas evolved from the film. Other major species (*m*/*z* 40 and 44) are shown in Fig. 3. The *m*/*z* 40 should be attributed to argon, which was implanted into the film during the sputtering deposition. The *m*/*z* 44 should be attributed to mainly carbon dioxide, whith an accompanying peak at *m*/*z* 28 (not shown in the Fig. 3). The second *m*/*z* 44 peak appeared at approx. 640 K and was exceptional since it was found only on this piece and it was not accompanied by *m*/*z* 28 peak at all. This might be caused

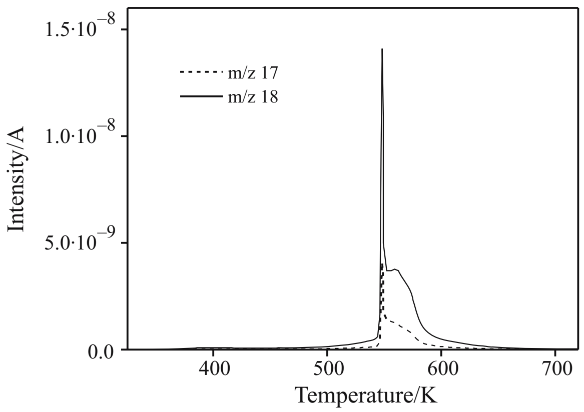

Fig. 2 TPD curves of water vapor (*m*/*z* 17 and 18) evolved from an amorphous ITO film deposited at the near-center position. Distance from the center, 18 mm; film thickness, 180 nm; film composition, 15 at.% Sn

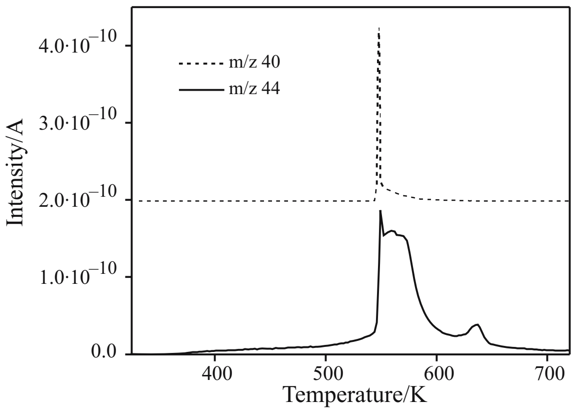

Fig. 3 TPD curves of argon (*m*/*z* 40) and carbon dioxide (*m*/*z* 44) evolved from a typical amorphous ITO film deposited at the near-center position. The TPD measurement was executed simultaneously with that indicated in Fig. 2

by the surface contamination although the characterization of the compound was impossible. Simultaneous evolution of water vapor, argon and carbon dioxide abruptly occurred at the peak temperature of 548 K. This temperature was much higher than those observed (approx. 473–493 K) for the water molecules chemically-adsorbed on the surface of the porous film composed of ITO nanocrystals [4]. The amorphous film was compared with the crystalline ones deposited by various methods in Table 1. The relative amounts of water vapor (H_2O [mol]/(In [mol] +Sn [mol]=0.24) evolved from the present amorphous ITO film was higher by one or two orders of magnitude than those from the crystalline films.

Crystallization

Figure 4 shows the X-ray diffraction spectra of the as-deposited and quenched ITO films (near-center position; distance 18 mm). The as-deposited films and the quenched ones at 533 K (before the abrupt gas evolution) showed completely amorphous XRD profiles without any trace of the XRD peaks unlike reported by Nishimura *et al.* [10] and Ando *et al.* [11] for their partly-crystallized films. The films quenched at higher temperatures (553 and 773 K) showed the cubic In_2O_3 structure. The XRD spectra (not shown) of the far-center position (distance 32 mm) were also amorphous and crystalline when quenched before and after the gas evolution, respectively. These spectra illustrate the fact that crystallization of the amorphous ITO film took place simultaneously with the abrupt gas evolution.

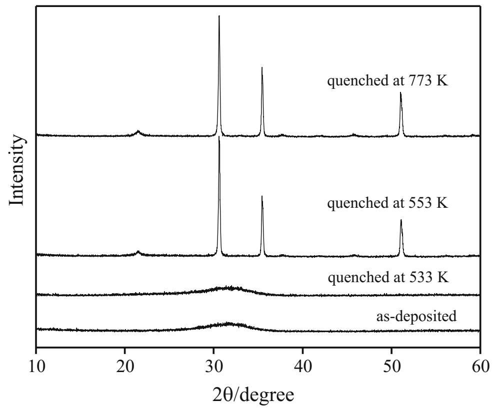

Fig. 4 XRD spectra of the near-center position ITO film as-deposited and quenched at different temperatures. The specimen quenched from 773 K was that measured in Figs 2 and 3. Other specimens were deposited at the equivalent positions (distance from the center, 18 mm)

Table 1 Amount of evolved water vapor from amorphous and crystalline ITO films

Deposition process	Substrate temperature/K	Structure of the thin film	Film thickness/nm	Amount of evolved water/mol cm^{-2}	$[H_2O/(In+Sn)]$/ mol mol^{-1}
Spray CVD	623	crystal	250	8.03E-9	0.006
Sputtering	573	crystal	250	6.90E-8	0.015
EB evaporation	613	crystal	250	2.09E-8	0.016
Dip coating	873	crystal	250	1.93E-8	0.054
Sputtering*	room temperature	amorphous	180	2.17E-7	0.241

*present study

Influence of the substrate position on the thermal change

Figures 5 and 6 show the TPD curves of water vapor (*m*/*z* 18) and argon (*m*/*z* 40), respectively, evolved from the amorphous ITO films deposited at various distances from the center. The spectra can be categorized as near-center positions (0 and 18 mm) and far-center ones (32 and 38 mm).

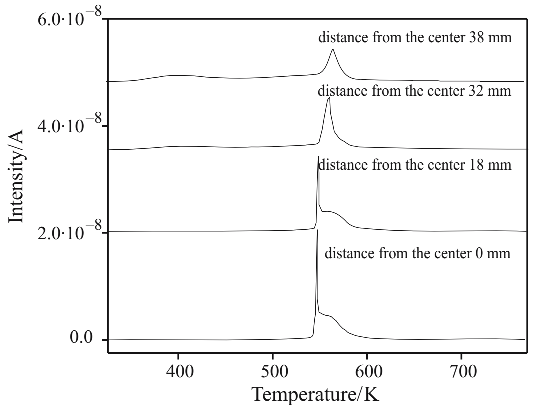

Fig. 5 TPD curves of water vapor (*m*/*z* 18) evolved from the amorphous ITO film deposited at the different positions of the substrate

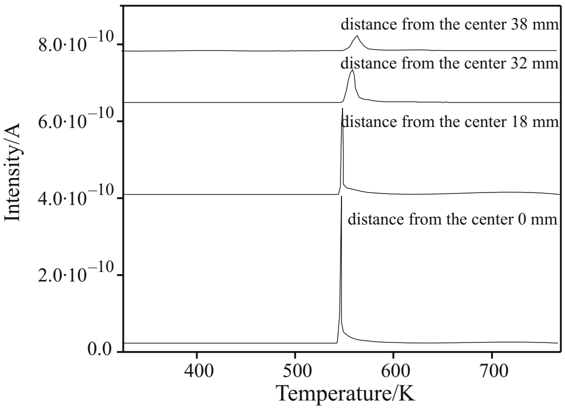

Fig. 6 TPD curves of argon (*m*/*z* 40) evolved from the amorphous ITO film deposited at different positions of the substrate

The film deposited at the far-center position evolved water vapor via two steps. The first step (peak temperature, 393 K; very low and broad peak) was attributed to a slow evolution of the physically absorbed or weakly chemisorbed water similar to those of the crystalline films [4, 5]. The second step (peak temperature, 563 K) accompanied by argon evolution and crystallization was like the near-center position ones described in Figs 2–4. However, the water vapor and argon gas evolution peaks were broad and appeared at higher temperature without shoulder.

The amount of the water vapor was calculated in Fig. 7. The ratios (H_2O [mol]/(In [mol]+Sn [mol])) were higher than 0.2. The total amount of the water vapor is approximately independent of the substrate position except for the one at 38 mm that evolved much physically-adsorbed water vapor at a low temperature. The film positions far from the center evolved more physically-adsorbed water (a broad peak) at low temperature.

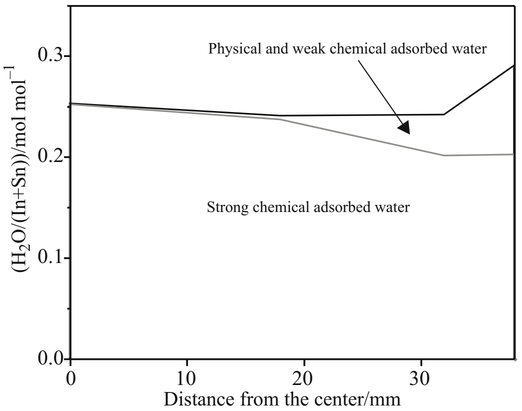

Fig. 7 Mole ratio of H_2O/(In+Sn) of the amorphous ITO film at different positions of the substrate

Formation of In–OH and Sn–OH bonds

When Shigesato *et al.* executed argon ion etching for the XPS analysis of an amorphous ITO film sputter-deposited with introduction of water vapor on the SiO_2-coating of soda lime glass substrate [15], they detected at the interface an In–OH bond which was not found in the ITO films. The TPD curves (*m*/*z* 18) of the partly-crystallized amorphous ITO film sputter-deposited with water vapor introduction also showed evolution of water vapor at high temperature, which was attributed to the hydrogen incorporated with the ITO films [10, 11]. Nishide *et al.* reported TPD for HfO_2 and TiO_2 films prepared by sol–gel process and concluded that evolution of water vapor in vacuum at high temperatures (520 and 498 K) should be interpreted as the formation of Hf–OH and Ti–OH bonds [16, 17]. These results support the hypothesis that evolution of water vapor at high temperature in the present amorphous ITO film is attributed to the formation of In–OH and Sn–OH bonds rather than to adsorbed water molecules. Although no water vapor was intentionally introduced into the present sputtering system, sufficiently high partial pressure of the residual water vapor (approximately $2\cdot10^{-2}$ Pa) was estimated since the valve between the deposition chamber and the oil diffusion pump was nearly closed during the introduction of argon. Furthermore, the formation of In–OH and Sn–OH would be accelerated by the glow discharge of sputtering process since the bonding hydrogen could be generated by electron-impact dissociation of water molecule that was revealed by plasma diagnostics using optical emission spectroscopy [18]. The present substrate was placed at the bottom of the water-cooled deposition chamber to keep it at room temperature, which seemed enhance the formation of –OH during the sputtering.

Amount of water evolved from the amorphous ITO films was approximately 0.24 as indicated by the ratio H_2O [mol]/(In [mol]+Sn [mol]). The simultaneous crystallization and evolution of water vapor can be tentatively described as follows:

$$\mathrm{In(Sn)_2O_{2.5}(OH)\ (amorphous)=}$$
$$\mathrm{In(Sn)_2O_3\ (crystalline)+0.5H_2O\ (gas)}$$

This suggests that amorphous indium tin oxide is not the oxide ($\mathrm{In(Sn)_2O_3}$) but rather the oxyhydroxide ($\mathrm{In(Sn)_2O_{2.5}(OH)}$ or $\mathrm{In(Sn)_4O_5(OH)_2}$) which may be roughly analogous to the well known fact that amorphous silicon is not pure silicon but contains both silicon and hydrogen.

Simultaneous occurrence of crystallization and gas evolution

Although Nishimura *et al.* [10] and Ando *et al.* [11, 19] estimated that evolution of water vapor and crystallization occurred simultaneously based on their results of TPD and the post-deposition annealing at various temperatures in atmospheric pressure of nitrogen atmosphere for 1 h, our results give more direct evidence to analyze this phenomenon by the X-ray diffraction study of the films quenched from the TPD instrument at various temperatures. These authors also found that the growth of crystallites was suppressed while the nucleation of crystallites was sharply enhanced with increasing water addition. In our case, the estimated partial pressure of water vapor ($2\cdot10^{-2}$ Pa) in the sputtering chamber is higher than the maximum value ($1.3\cdot10^{-2}$ Pa) in Ando's experiments. The shape of TPD curve for water vapor shown in Fig. 2 can be explained that first nucleation of crystallization leads to sharp water evolution and the shoulder after the rapid crystallization is attributed to the grain growth. Argon is embedded in the thin film matrix and the resulting stress [20] will be released by the evolution of argon during the crystallization.

We interpret that the near-center film suffered from strong argon bombardment to cause the strain, which accelerates the crystallization at low temperature. The rapid crystallization at low temperature is initiated from many nuclei and followed by grain growth at higher temperature. For the films located at far from the center evolution of water vapor at low-temperature (physically adsorbed water) is explained by the larger surface area of the porous film. The far-center film with less stress will crystallize at higher temperature at which the grain growth proceeds.

Conclusions

The following results were obtained from TPD and XRD for amorphous ITO thin film deposited on a silicon wafer substrate at room temperature by magnetron sputtering process: Thermal crystallization of the amorphous ITO film took place accompanying the simultaneous and abrupt evolution of water vapor, argon and carbon dioxide. The evolution temperature and the amount of water vapor were higher than those of crystalline ITO films prepared by different processes; significant amount of water vapor (H_2O [mol]/(In [mol] +Sn [mol]>0.2) evolved from the film. Thermal change of amorphous ITO films was remarkably affected by the position of the substrate.

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