

解 説

ITO 薄膜合成プロセス最適化への熱分析の応用

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Application of Thermal Analysis to Optimization of Preparation Process of Indium-Tin-Oxide Thin Films

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The present article introduces that thermal analysis of thin films are possible and useful. Thermal change of crystalline and amorphous indium-tin-oxide (ITO) transparent conducting films was investigated by temperature programmed desorption (TPD) and high-temperature X-ray diffraction (HT-XRD). Water vapor was the main gas released from the all films. Porous crystalline films released more water vapor than those from the dense ones. The thermal crystallization of amorphous films accompanied fast release of large amount of water vapor, which was attributed to disappearance of In-OH and Sn-OH bonds. The in-situ measurement of the crystallization process by HT-XRD analysis revealed that the thermal crystallization could be suppressed by the optimization of water vapor pressure during the sputter-deposition.

Keywords: ITO thin films; Gas evolution; Thermal crystallization

1. Introduction

Thin films of indium-tin-oxide (ITO) are widely used as electrodes in electro-optical devices such as organic light-emitting devices, liquid crystal displays, and solar cells because they are transparent as well as electrically conductive.¹⁻⁵⁾

Although much effort has been devoted to increasing the electrical conductivity and optical transmittance of ITO thin films, little attention has been paid to the gas evolutions and thermal change of ITO films. The problems due to gases in ITO films are especially severe for vacuum micro-electronic devices, because the operational lifetime

of such a device is limited by the residual gases present in its vacuum envelope.^{6,7)} One thus needs to know which gases are trapped in the films and the process temperatures needed to release them. On the other hand, gases adsorbed on the surface of the films or implanted into them are also important parts of the film microstructure.

This paper shows thermal analysis is useful tool for the characterization and the stability evaluation of thin films. Temperature-programmed desorption (TPD) with a mass spectrometer and high-temperature X-ray diffraction analysis (HT-XRD) were used for thermal change of polycrystalline and amorphous ITO films.

2. Temperature Programmed Desorption (TPD) and High-Temperature X-ray Diffraction Analysis (HT-XRD)

TPD is an excellent technique for analyzing adsorbed gases on the films surfaces and for analyzing the species that release from the components of films. Apparatus involves heating a sample and simultaneously detecting the residual gas in the vacuum by means of a mass analyzer. As the temperature rises, certain absorbed species will have enough energy to escape and will be detected as a rise in pressure for a certain mass. As the temperature rises still further the amount of the species on the surface will reduce causing the pressure to drop again. This results in a peak in the pressure versus time plot. The temperature of the peak maximum provides information on the binding energy of the bound species.

HT-XRD is another useful tool for studying, monitoring or investigating crystal state of the films during thermal treatments in controlled atmospheres. The advantages of such a technique over the conventional practice, where samples are heat treated in a separate oven and then analyzed by XRD include: consistency of sample placement; preservation of high temperature structures to facilitate observation of meta-stable phases that are unstable upon exposure to outside atmosphere or during cooling.

3. Released Water Vapor from Crystalline ITO Films

Seki *et al.*⁸⁾ and Sawada *et al.*⁹⁾ investigated the gases released from polycrystalline ITO films prepared by various deposition processes such as spray CVD (chemical vapor deposition), sputtering, electron-beam

evaporation, and dip coating. The TPD results indicated water vapor to be the main gas released. The amount of water vapor was quantitatively determined as described by Hirashita and Uchiyama;¹⁰⁾ the hydrogen implanted silicon wafer was used as the calibration standard. The substrate without the film was measured to confirm that the gases evolution from the substrate were negligible. The amount of water vapor released as well as the film resistivity (**Fig.1**) was greatest for the dip-coated film and least for the spray CVD film. The release proceeded in two steps: one at ≈ 373 K tentatively attributed to physically desorption; the other at $473 \sim 623$ K tentatively attributed to chemically desorption or thermal decomposition of indium hydroxide that had formed on the surface of the crystal grains. The micro-structures of a dip-coated film and a spray CVD film are shown in **Fig.2**. The film deposited by spray CVD is denser and looks like a well-sintered piece. The dip-coated film is more porous and that is probably why it absorbed more water. The density of the crystalline films can

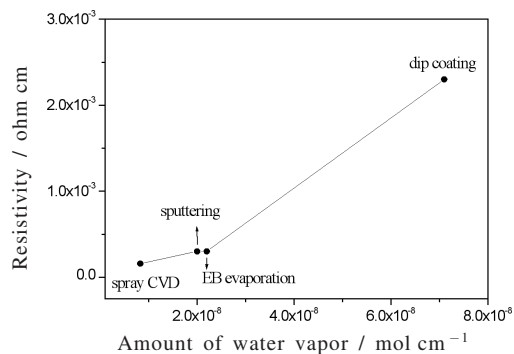


Fig.1 Resistivity and the amount of water vapor released from crystalline ITO films.

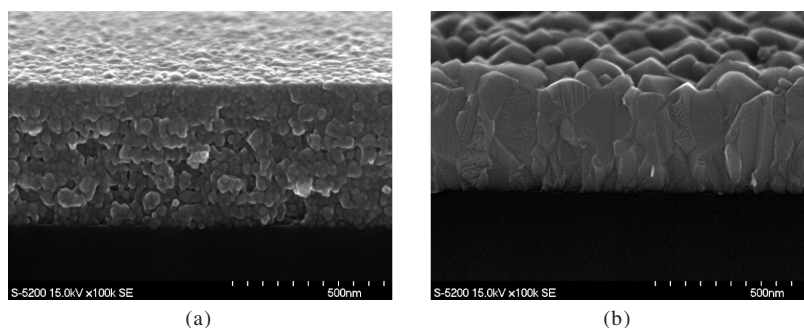


Fig.2 Micro-structure of crystalline ITO films fabricated by (a) dip coating and (b) spray CVD.

thus be roughly estimated from the amount of the released water vapor.

4. Gases Released from Amorphous ITO Films

Although polycrystalline films are used because of their high conductivity and transmittance, amorphous ITO films have recently become increasingly important because they can be deposited at room temperature on heat-sensitive flexible organic substrates and organic light-emitting layers.¹¹⁻¹⁴⁾ Wang et al. have deposited amorphous ITO film (15at.% Sn) on silicon wafers at room temperature by RF magnetron sputtering without intended introduction of water vapor into the chamber. The release of water vapor and other gases from those films as well as the crystallization process occurring during the heating process of a TPD measurement is reported.¹⁵⁾

Fig.3 shows TPD curves of m/z 18 and 40. Water vapor was also the main gas released from the amorphous ITO film. The m/z 40 should be attributed to argon, which was implanted into the film during the sputtering deposition. Simultaneous release of water vapor and argon abruptly occurred at the peak temperature of 548 K. It should be emphasized that this temperature was much higher than those observed (approx. 473 ~ 493 K) for the desorption of water molecules chemically-adsorbed on the surface of a porous film composed of ITO nanocrystals.⁸⁾ It should be also emphasized that the relative amounts of water vapor (2.17×10^{-7} mol cm⁻²) released from this amorphous ITO film was higher by one or two orders of magnitude than those released from the crystalline films.

5. Formation of In-OH and Sn-OH Bonds in the Amorphous ITO Films

Shigesato *et al.*¹⁶⁾ found In-OH bonds by XPS (X-ray photoelectron spectroscopy) at the interface between amorphous ITO film sputter-deposited in an atmosphere containing water vapor and the SiO₂ overcoat fabricated on the glass substrate. Water vapor was released at high temperatures by TPD from the partly-crystallized amorphous ITO film sputter-deposited in an atmosphere containing water vapor which is attributed to the hydrogen incorporated in the ITO film.^{17,18)} Nishide et al. reported TPD for HfO₂ and TiO₂ films prepared by sol-gel process

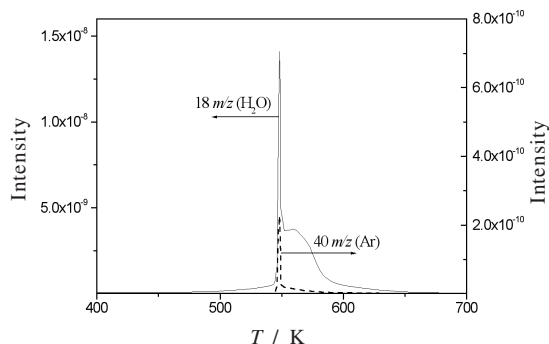
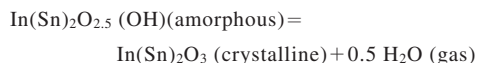


Fig.3 TPD curves of water vapor (m/z 18) and argon (m/z 40) released from an amorphous ITO film.

and concluded that the water vapor released in a vacuum at high temperatures (520 and 498 K) should be attributed to the breakage of Hf-OH and Ti-OH bonds.^{19,20)} These results support the hypothesis that the water vapor released from an amorphous ITO film at a high temperature is attributed to the breakage of In-OH and/or Sn-OH bonds rather than to the release of adsorbed water molecules. The formation of In-OH and Sn-OH would be accelerated by the glow discharge of the sputtering process because the bonding hydrogen could be generated by electron-impact dissociation of water molecule.²¹⁾

Amount of water released from the amorphous ITO films indicated by the ratio $\text{H}_2\text{O} [\text{mol}] / (\text{In} [\text{mol}] + \text{Sn} [\text{mol}])$ was approximately 0.24. The simultaneous crystallization and release of water vapor can be tentatively described as follows:



This suggests that amorphous indium tin oxide is not the oxide (In(Sn)₂O₃) but rather the oxyhydroxide (In(Sn)₂O_{2.5}(OH) or In(Sn)₄O₅(OH)₂). This is analogous to amorphous silicon, which is not pure silicon but composed of both silicon and hydrogen. Non-destructive analysis of the In-OH and/or Sn-OH by some spectroscopic method will be a future subject to clarify the nature of amorphous ITO films.

6. Thermal Crystallization of Amorphous ITO Films

The X-ray diffraction spectra of the quenched ITO films¹⁵⁾ are shown in **Fig.4**. The films quenched

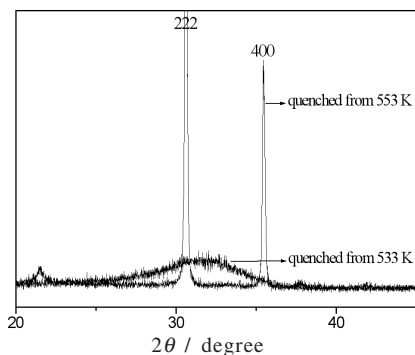


Fig.4 XRD spectra of ITO films quenched from 533 and 553 K.

from 533 K (before the abrupt release of gas) has completely amorphous XRD profiles without any trace of peaks, whereas the profiles of films quenched from 553 K (after the abrupt release of gas) show that those films had the cubic In_2O_3 structure. These spectra are consistent with the crystallization of the amorphous ITO film coinciding with the abrupt release of water vapor from that film.

Nishimura *et al.*¹⁷⁾ and Ando *et al.*^{18,22)} also inferred their TPD results and their observations after post-deposition annealing at various temperatures under nitrogen for 1 hour that crystallization and the release of water vapor occurred simultaneously. Moreover, they found that water addition enhanced the nucleation of crystallites but suppressed their growth. The shape of TPD curve for water vapor shown in **Fig.3** can be explained by crystallite nucleation releasing water abruptly and grain growth releasing water continuously.

7. The Effect of Water Vapor Introduced during the Sputter-Deposition on the Thermal Crystallization Process

To understand the role of water vapor on the thermal crystallization process, amorphous ITO films deposited on silicon wafers under water vapor partial pressures between 0 and 6×10^{-5} Torr were detected by HT-XRD.²³⁾ Peak intensity changes for 222 during the thermal crystallization process are shown in **Fig.5**. For all films except the partly crystalline film deposited at a water vapor pressure of 6×10^{-5} Torr, the initial thermal crystallization temperature increased as the water vapor partial pressure increased. The peak intensities for 222

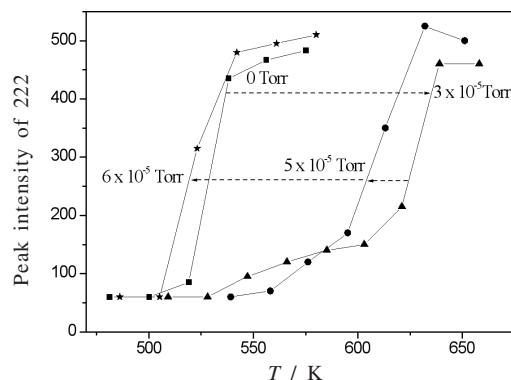


Fig.5 Peak intensity of 222 during thermal crystallization. Direction of arrow represents the change of thermal crystallization temperature.

increased rapidly at lower temperature when the film was deposited without water, which suggests that the thermal crystallization happened easily. For films deposited under water vapor pressures of 3×10^{-5} Torr, the peak intensity of 222 increased slowly within a wide temperature range (approx. 50 ~ 80 K) at the beginning of the crystallization process and then increased rapidly at high temperatures.

Ando *et al.*¹⁸⁾ attributed the suppressed crystal growth to the decrease in the number of oxygen vacancies and the increase in the amount of bonded hydrogen that terminates oxygen-dangling bonds. However, introducing more water during deposition (*i.e.*, depositing films under water partial pressures higher than 3×10^{-5} Torr) reduced the suppression of crystallization, which was attributed to the enhanced heterogeneity of the amorphous networks and the decrease in the surface energy available for crystallization. Thus an optimized water vapor pressure can further suppress the thermal crystallization of the film.

A quality index that indicates the preferential orientation of crystallographic planes is the relative intensity ratio $I_{400}:I_{222}$, which for a random orientation of the crystallite is 0.33. In **Fig.6** the value of this ratio is approx. 0.55 for the crystallized ITO films deposited without water vapor, thus indicating a $\langle 100 \rangle$ preferred orientation of the cubic In_2O_3 structure. The orientation of the crystallized films deposited at high water vapor partial pressures (3×10^{-5} Torr or higher), however, tended towards $\langle 111 \rangle$ orientation. The

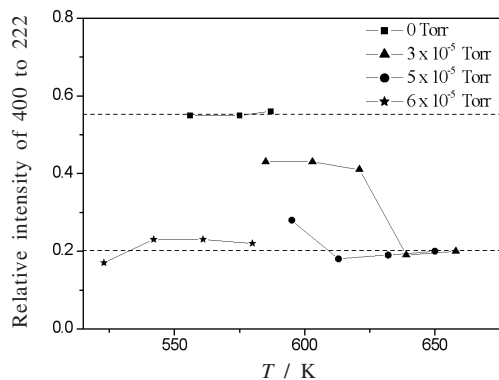


Fig.6 Relative intensity ratio of 400 to 222 during thermal crystallization.

crystallographic texture change of ITO films has been reported by Kim *et al.*²⁴⁾ and Thilakan *et al.*²⁵⁾ and explained as the crystal growth in the <100> oriented films being a stressed growth due to oxygen deficiency, whereas the growth in the <111> oriented films is related to reduced oxygen vacancies. This viewpoint can be used to explain the different preferred orientation caused by various water vapor partial pressures.

8. Conclusion

The density or porosity of the crystalline ITO films can be roughly determined by their released amount of water vapor. Thermal crystallization of the amorphous films was accompanied the abrupt release of water vapor. The amorphous films were assumed to contain In-OH and Sn-OH bonds by remarkable amount of water vapor released at high temperature. The thermal crystallization process depended on the water vapor pressure in the sputtering chamber.

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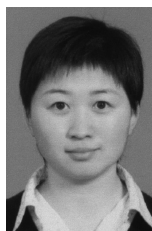
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要 旨

薄膜の熱分析が可能かつ有用な例として、多結晶およびアモルファスのスズ添加酸化インジウム (indium-tin-oxide; ITO) 透明導電膜の加熱変化を昇温脱離ガス分析法 (temperature programmed desorption; TPD) および高温 X 線回折法 (high-temperature X-ray diffraction analysis; HT-XRD) で検討した結果を解説する。ITO 膜が放出する主たるガスは水蒸気で、放出量は緻密な結晶性薄膜に比べ

て多孔質の結晶性薄膜の方が多い。アモルファス薄膜を加熱した際には水蒸気が放出された。その原因は、アモルファス薄膜中に存在する In-OH または Sn-OH 結合が結晶化の際に切断されるためと推定した。スパッタ成膜する際の水蒸気分圧を制御することによってアモルファス ITO 膜の結晶化の抑制が可能なが高温 X 線回折によって示された。



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