Effects of Heat Treatment Methods in Indium-Tin-Oxide Films by DC Magnetron Sputter of Powder Target

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ITO (Indium-tin-oxide) thin films were deposited on glass substrates by a dc magnetron sputtering system using ITO powder target. The methods of heat treatment are important factor to obtain high quality ITO films with low electrical resistivity and good optical transmittance. Therefore, both methods of the substrate temperature and post-deposition annealing temperature have been compared on the film structural, electrical and optical properties. A preferred orientation shifts from (411) to (222) peak at annealing temperature of 200 °C. Minimum resistivity of ITO film is approximately 8.7×10^{-4} Ωcm at substrate temperature of 450 °C. Optical transmittances at post annealing temperature above 200 °C are 90 %. As a result, the minimum value of annealing temperature that is required for the re-crystallization of as-deposited ITO thin films is 200 °C.

Keywords : ITO, DC magnetron sputtering, Substrate temperature, Post-annealing temperature, Powder target.

1. INTRODUCTION

Transparent and conducting ITO films have found many applications such as transparent electrode, antireflection coating, heat reflecting mirrors, electro-magnetic shield coating, display devices, and opto-electronic and photo-voltaic devices [1-3]. Therefore, ITO films are being widely investigated, in order to optimize low electrical resistivity and good optical transmittance.

High quality ITO thin films have been prepared by various deposition methods such as electron beam evaporation (EB), thermal evaporation, chemical vapor deposition (CVD), pulsed laser ablation, sol-gel process, dc magnetron sputtering, rf magnetron sputtering and electron cyclotron resonance (ECR), etc. [4-13] Among these deposition methods, dc magnetron sputtering is widely used for ITO films deposition. Desirable features of dc magnetron sputtering are accurate control of the film thickness, good film uniformity and easy fabrication of the ITO target. The methods of heat treatment are important factor because it is common practice in many of the device fabrication processes and significant for the stability and reproducibility of the entire process.

In this paper, ITO thin films have been prepared on glass substrates by a dc magnetron sputtering method of powder target. The effects of the substrate temperature and post deposition annealing temperature in dc magnetron sputtered ITO films have been discussed on the structural, electrical and optical properties.

2. EXPERIMENT

ITO thin films were deposited on glass substrates by a dc magnetron sputtering system (Leybold, AG-L560) of ITO powder target, mounting in sputter-up type configuration. The sputtering target consists of 90 wt% In_2O_3 and 10 wt% SnO_2 powders. The mixed powders followed by alumina ball milling in a polyethylene container for 5 hr. and filled in a copper holder of 2 inch. The substrates were ultrasonically cleaned for 5 min using methanol as a solvent, and blown dry in N_2 gas. High purity argon (99.99 %) was introduced as a sputtering gas. The target surface should be cleaned necessarily before every sputtering run. Therefore, the target was pre-sputtered in argon atmosphere for about 10 min in order to remove the oxidizing surface and impurity layer that may have formed during exposure to air. The substrate temperature was applied during the film deposition or the post-deposition annealing temperature was performed subsequently for as-deposited ITO films. The substrate temperature and annealing temperature ranging from room temperature to 500 °C were used in order to investigate a good compromise between electrical resistivity and optical transmittance.

Film thickness measurements were carried out using a α-step 500 surface profilometer manufactured by Tensor. Optical transmittance and reflectance measurements of ITO films were performed using a UNICAM 8700 spectrophotometer made by Phillips, in the visible and infrared range. Electrical resistivity measurements were measured with a standard 4-point probe (CMT-SR 1000, Chang-Min Co.) and Hall measurement system (Lake-

Table I. The sputtering conditions of ITO thin films for dc magnetron sputtering procedure.

Sputtering conditions	Values
DC power	10 ~ 80 [W]
Base pressure	2×10^{-6} [Torr]
Working pressure	2.2 ~ 19 [mTorr]
T-S distance	6 [cm]
Target material	90 In_2O_3-10SnO_2 powder
Thickness	200 [nm]
Sub. rotation speed	6 [r.p.m.]
Sub. temperature	RT ~ 500 [°C]
Annealing Temp.	RT ~ 500 [°C]

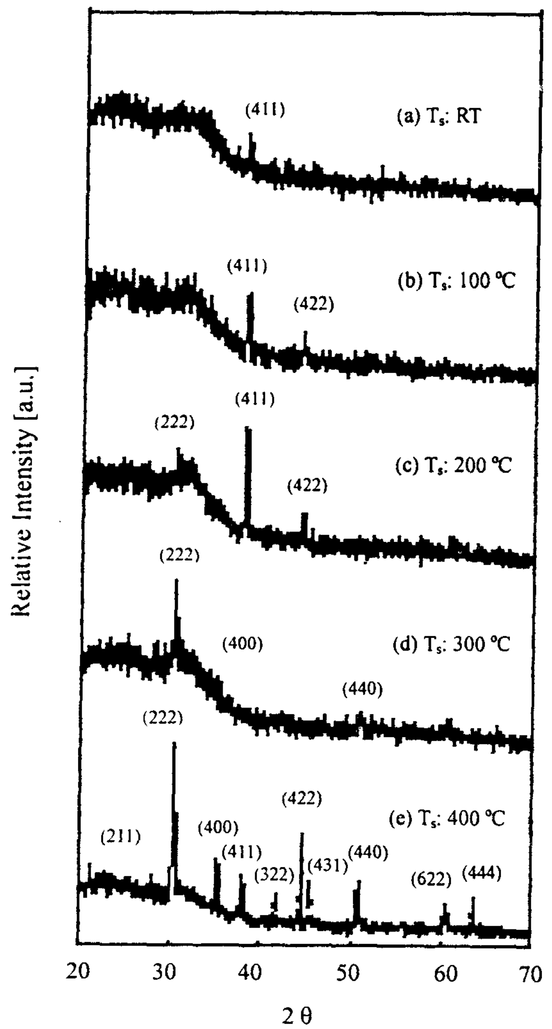

Fig. 1. X-ray diffraction patterns of ITO thin films with a variety of substrate temperature.

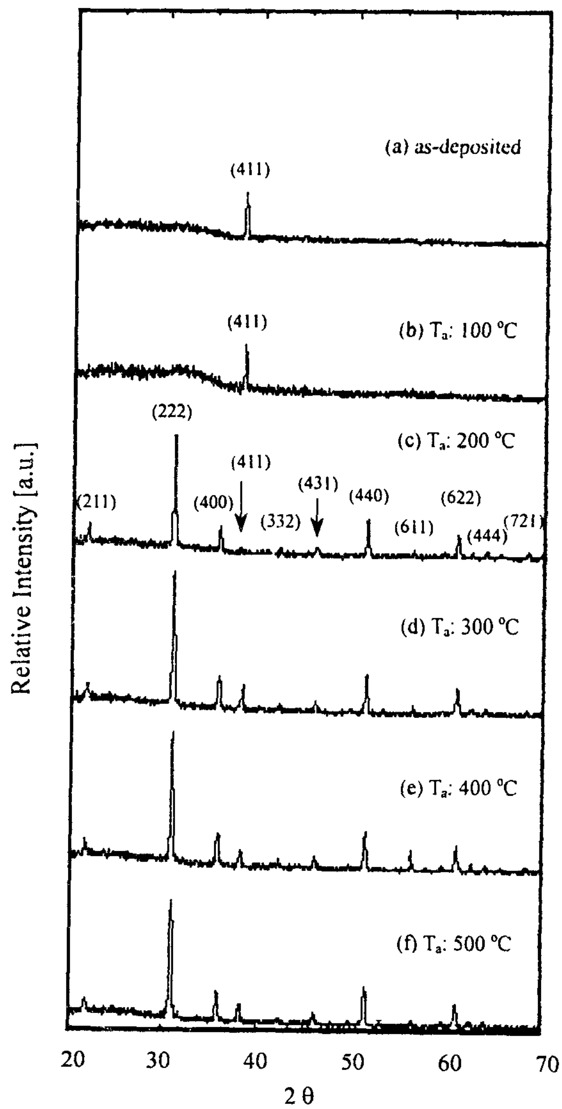

Fig. 2. X-ray diffraction patterns of ITO thin films with change of post-annealing temperature.

shore EMA-CS electromagnet system and Keithley measurement system with 7065 Hall Card).

3. RESULT AND DISCUSSIONS

3.1. XRD patterns

Fig. 1 shows XRD patterns with a variety of substrate temperature for the sputtering deposition of ITO thin films. As the substrate temperature is not applied on ITO film, the weak (411) peak of In_2O_3 is observed. As the substrate temperature increases from room temperature to 100 °C, the strength of (411) peak increases, and (422) and (222) peaks of In_2O_3 other than (411) peak appears slightly. But the (422) peak on ITO thin films has been largely observed under the conditions of high sputtering power and pressure. When the substrate temperature of 300 °C is applied, the above mentioned (411) and (422) peaks are disappeared gradually, and the (222) peak is strongly increased. As well as (400) and (440) peaks on which have not observed at low substrate temperature appear. With much more increasing temperature, the strengths of (222), (400) and (440) peaks are increased sharply. Furthermore, new peaks of (211), (332), (622), and (444) planes are observed, and the weak (411) and (422) peaks on which are observed often at low temperature appear again at the temperature of 400 °C as the shown in Fig. 1(e).

From the above results, ITO films are grown as a preferred orientation of (411) peak at low temperature or without substrate temperature. However, it is observed that the preferred orientation is changed from (411) to (222) peak at the boundary of 300 °C temperature. In the case of more than 400 °C, ITO films consist of several peaks.

Fig. 2 presents XRD patterns with a variety of annealing temperature on ITO thin films at atmosphere. ITO films are prepared by sputtering deposition at room temperature without substrate temperature. The XRD pattern on ITO films prepared at annealing temperature of less than 100 °C exhibits only the (411) peak of In_2O_3, almost same to that without annealing temperature, and identifies with the result of substrate temperature at low temperature as is evident in Fig. 1 (a) and (b). As a result, it is estimated that the substrate temperature and annealing temperature less than 100 °C have not influence upon the crystal structure of ITO films. However, the strength of (411) peak reduces at the annealing temperature of 200 °C as shown in Fig. 2 (c) and, in contrast, the (222) peak increases obviously. It means that ITO films deposited at room temperature are re-crystallized by the annealing heat treatment of 200 °C and are grown as a preferred orientation of (222) peak. In addition, several peaks such as (211), (400), (431), (440) and (622) is observed, exhibiting mainly at high substrate temperature. As shown for XRD pattern in Fig. 2 (d), the (222) peak at 300 °C increases sharply. With much more increase of annealing temperature, any great change in (222) and other peaks is not discovered, as shown in Fig. 2 (c)~(f). From the above results, it may be recognized that the minimum annealing temperature that is required for the re-crystallization of as-deposited ITO thin films is 200 °C.

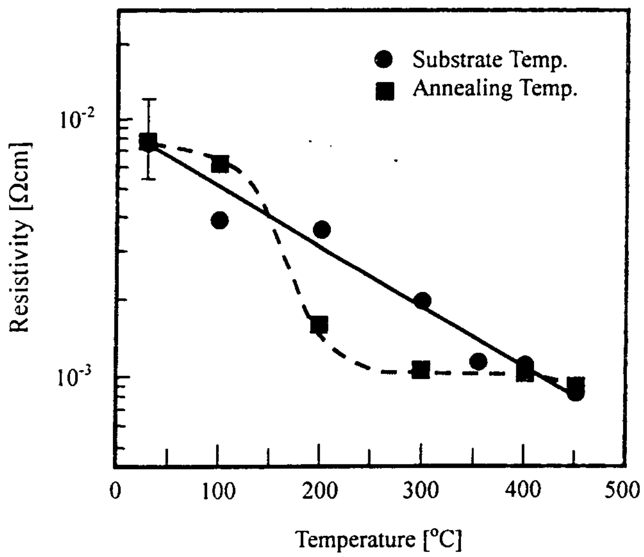

Fig.3. Electrical resistivity of ITO films with the heat treatment methods between substrate temperature and annealing temperature.

3.2. Electrical resistivity

The electrical resistivity of ITO thin films with the heat treatment methods between substrate temperature and annealing temperature is shown in figure. The electrical resistivity of as-deposited ITO films prepared at room temperature demonstrates relatively board values between 5.7×10^{-3} and 1.1×10^{-2} Ωcm. As the substrate temperature increases from 100 to 450 °C, the resistivity decreases more and less linearly, and the minimum value at 450 °C is approximately 8.7×10^{-4} Ωcm.

The resistivity at post-deposition annealing temperature of 100 °C is almost equal to or somewhat lower than that at room temperature. However, the resistivity curve for post-annealing method is reduced suddenly with an increase of annealing temperature, reaching a reduction of a factor of ~10 in resistivity intensity as the temperature increases from 100 to 300 °C. It is obvious that the abrupt reduction of electrical resistivity is closely related to the XRD results, presenting the shift of a preferred orientation from (411) to (222) peak as

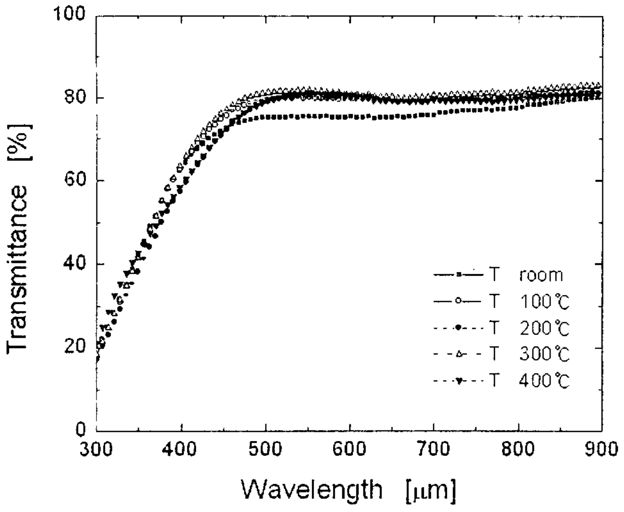

Fig. 4. Optical transmittance of ITO films as a function of substrate temperature.

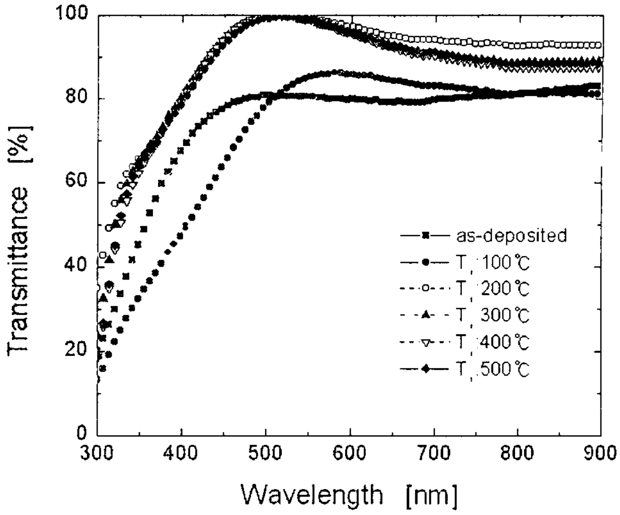

Fig. 6. Optical transmittance of ITO films as a function of post-deposition annealing temperature.

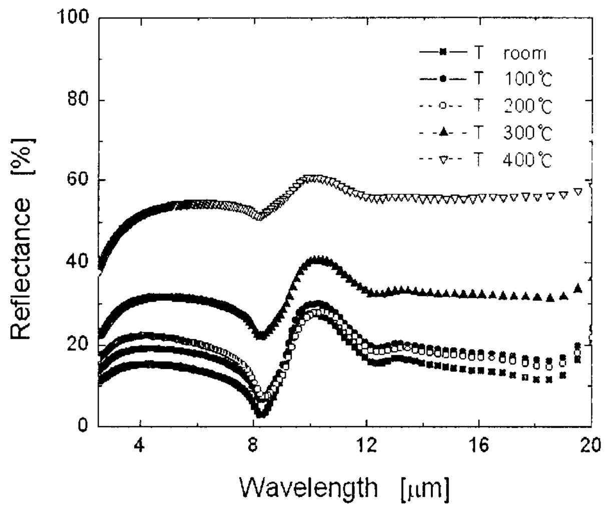

Fig. 5. Reflectance of ITO films in IR wavelength region as a function of substrate temperature.

shown in Fig. 2 (b), (c) and (d). Although the annealing temperature increases further more, any great change in resistivity of ITO films is not observed, and the minimum resistivity at the annealing temperature of 450 °C is nearly 9.1×10^{-4} Ωcm.

3.3. Optical properties

Fig. 4 shows the optical transmittance of ITO thin films in visible wavelength ranges with a variety of substrate temperature. The transmittance of as-deposited ITO film prepared at room temperature is about 75 % at the wavelength of 550 nm. The transmittances of films at substrate temperature above 100 °C are somewhat higher than that at room temperature, and exhibit above 80 % in the wavelength ranges of absorption. However, any change of optical transmittance is not monitored with an increase of substrate temperature from 100 to 400 °C. The maximum transmittance at the wavelength of 550 nm is around 85 % for ITO film at 300 °C.

Fig. 5 represents the reflectance of ITO films in IR wavelength region as a function of substrate temperature. In the case of ITO film deposited at room temperature, the reflectance is less than 20 %. But the reflectance increases in general with an increase of substrate temperature. It is observed that the reflectance is improved typically above 300 °C as shown in Fig. 5. The substrate temperature dependences of the reflectance improvement are related to the reduction of electrical resistivity as mentioned previously in Fig. 3.

The visible light transmittance of ITO films with a variety of annealing temperature is shown in Fig. 6. The transmittance of film at room temperature is 80 % at the wavelength of 550 nm. In contrast, the transmittance at 100 °C increases slightly and is as much as 85 % at 550 nm wavelength. The effects of annealing temperature on the transmittance of ITO films above 200 °C are compared certainly in this figure, and the values at the wavelength above absorption range are 90 %. It seems that the improvement of optical transmittance keeps in touch with the re-crystallization by the annealing temperature, showing the preferred orientation of XRD patterns as mentioned in Fig. 2. A preferred orientation shifts from (411) to (222) peak as a turning point of annealing temperature at 200 °C. Also, any great change in the optical transmittance does not occur although the temperature increases above 200 °C.

4. CONCLUSIONS

ITO thin films were deposited on glass substrates by dc magnetron sputtering system of powder target at different substrate temperature or post-deposition annealing temperature. The heat treatments of substrate temperature or post-deposition annealing temperature ranging from room temperature to 500 °C have been applied on ITO film in order to investigate the structural, electrical and optical properties. A preferred orientation shifts from (411) to (222) peak at annealing temperature of 200 °C. Minimum resistivity of ITO film at substrate temperature and post-annealing temperature of 450 °C is approximately 8.7×10^{-4} and 9.1×10^{-4} Ωcm, respectively. Optical transmittances at post-annealing temperature above 200 °C are 90 %. As a result, the minimum value of annealing temperature that is required for the re-crystallization of as-deposited ITO thin films is 200 °C.

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