Crystallization Behavior of ITO Thin Films with and without External Heating during RF-Magnetron Sputtering

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Abstract

Indium tin oxide (ITO) thin films were deposited by RF-magnetron sputtering method and the crystallization behavior of the films with no external heating as a function of deposition time was examined. X-ray diffraction results indicated an amorphous state of the film when the deposition time is short about 10 min. When the deposition time was increased over 20 min development of crystallization of the films is observed.

1. Introduction

Tin-doped In_2O_3 (or indium tin oxide: denoted ITO hereafter) films are widely used in the field of optoelectronic devices such as solar cells, electroluminescence, and liquid crystal displays. Because of the relatively low resistivity and high transmissivity to visible light, the main present application of ITO film is in transparent electrodes for liquid crystal displays [1,2]. High quality ITO films have been prepared by sputtering, evaporation, chemical vapor deposition, sol-gel method, dip-coating process, and spray pyrolysis. Among these methods the magnetron sputtering is widely used in making ITO films for display devices since the method is superior in its controllability and the film obtained by this method shows good uniformity over a wide area on large size substrates.[3].

Some results have shown that it is necessary to anneal sputtered films in order crystallize and decrease their resistivity. Therefore, heating process at an elevated temperature during the film deposition or an additional post-annealing treatment at temperature around 150 °C is required [4]. In order to raise productivity, industries usually employ in-situ thermal annealing method and minimum thickness of the films is deposited in a short time. Therefore, from the academic point of view, studies on the prolonged deposition time at low processing temperature have not been conducted sufficiently.

In this study, because low temperature deposition of ITO films is highly recommended, the crystallization behavior of ITO films prepared by RF-magnetron sputtering without external heating was examined as a function of deposition time. Crystallization of films by prolonged deposition time. It was explained due to an energy transfer from kinetic energy of ions to heat energy during the ion bombardment.

2. Experimental Procedure

An ITO target was prepared by the general solid-state reaction method of oxides. High purity nanocrystalline In_2O_3 and SnO_2 powders were used as the raw materials. A mixed powder corresponding to the In_2O_3/ SnO_2 weight ratio of 90/10 was prepared. The powder was formed into 150 mm disk by cold isostatic pressing (CIP) at 300 MPa, then sintered at 1550 °C for 10 h in an oxygen atmosphere. The apparent density of the target was 96% and the dimension of the target was adjusted to 76 mm in radius and 5 mm in thickness. SiO_2 coated Corning 1737 glass was the initial background pressure of the chamber was used as the substrate 1.0×10^{-6} Torr and the working pressure was fixed to 10 mTorr by utilizing pure Ar gas. The distance between the target and the substrate was 5 cm, and RF power was kept constant at 50 W, whereas the deposition time was varied from 5 to 80 min. The deposition process was carried out at room temperature, i.e. the substrate was not heated during and after the film deposition. Film crystalline structure was investigated by X-ray diffractometer using Cu-Kα radiation. The surface morphology of the films was observed with a scanning electron microscope. Transmission electron microscope observation for the cross sectional view of the films was also conducted.

3. Results & Discussion

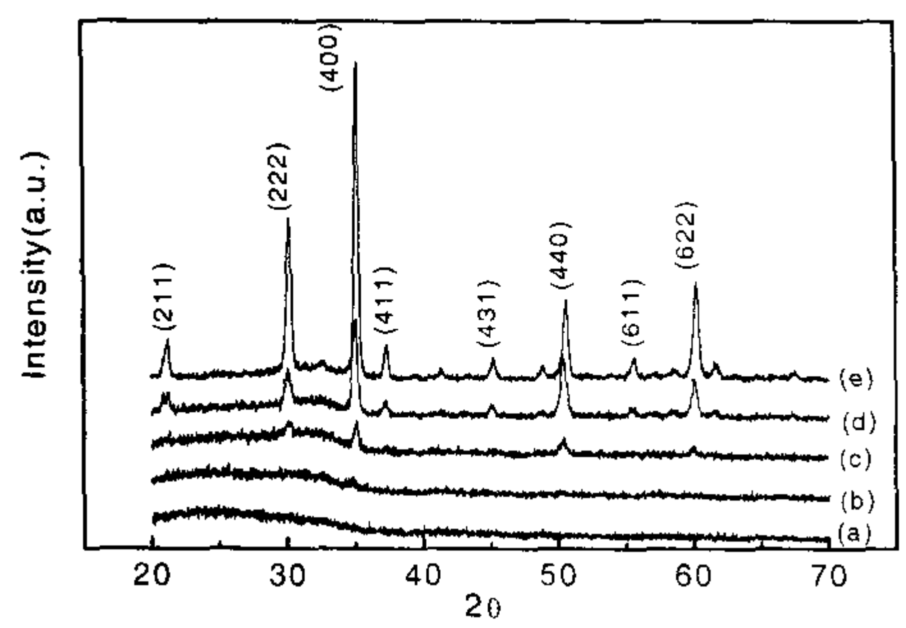

Fig.1. X-ray diffraction profiles of ITO thin films as a function of deposition time (a) 5, (b) 10, (c) 20, (d) 40 and (e) 80 min.

X-ray diffraction profiles of ITO films with different deposition time are presented in Fig. 1. The X-ray diffraction result showed that the ITO film is in amorphous state, initially at short deposition time less than 10 min as shown in Fig. 1 (a, b). Further deposition over 20 min resulted in development of the crystallization representing diffraction peaks. At 40 min of deposition, most of the typical ITO diffraction peaks of (222), (400), (440), (622) appeared and a preferential orientation of (400) plane is observed as the deposition time increased in Fig. 1 (c, d, e). The preferential orientation along [100] direction is pronounced in ITO films when the films are prepared in the state of oxygen deficiency [5,6]. Since pure Ar is used as a sputtering gas in this study, it is believed that the oxygen deficient state is satisfied as the deposition time increased which led to the [100] orientation preferentially.

Because the thickness of film affects X-ray intensity, thin crystallized film might not represent the diffraction peaks. From this point of view, one can imagine that the X-ray diffraction of the film deposited for 5 or 10 min was not appeared even the films have crystallized. For a confirmation, ITO films were deposited for 5 and 10 min on glass substrates kept at 200°C.

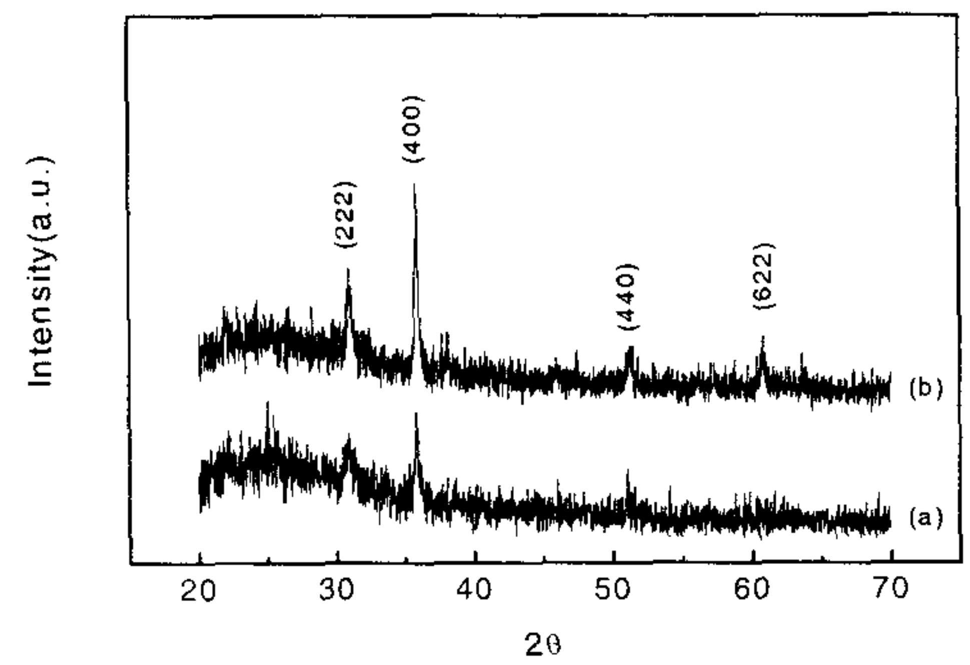

Fig. 2. X-ray diffraction profiles ITO films deposited for 5 and 10 min on glass during in-situ heating

Fig. 2 shows their X-ray diffraction profiles. Unlike the X-ray diffraction results in Fig. 1 (a) and (b), relatively sharp diffraction peaks of ITO were observed, which signifies that the films are well crystallized by the external heating. Therefore, the thickness effect on diffraction intensity can be ignored.

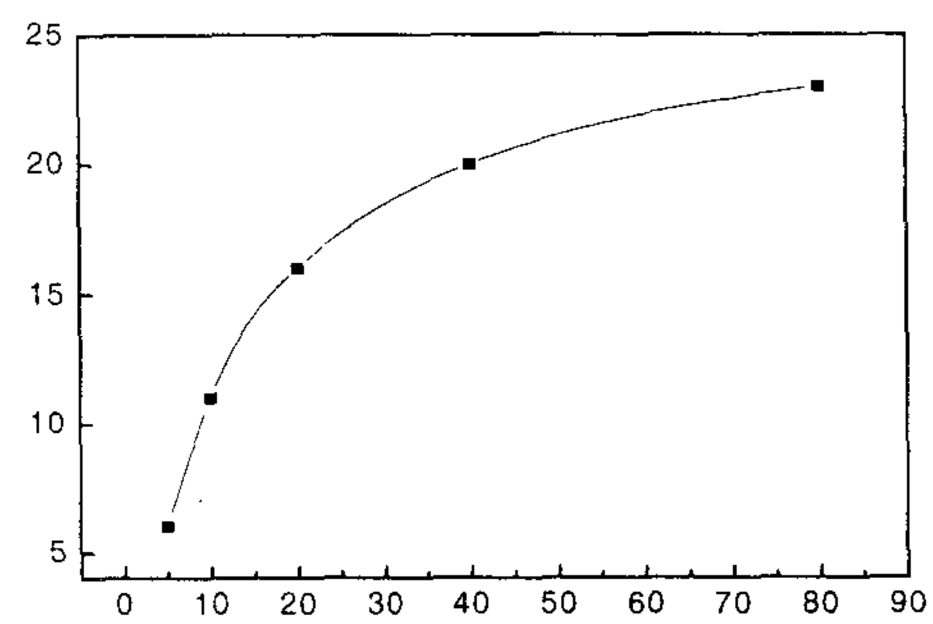

Fig.3. Change of substrate temperature measured at the back of the substrate using a thermocouple as a function of deposition time.

The crystallization without external heating is exceptional and disagrees with the fact that a thermal energy equivalent to 150 °C is necessary for the crystallization of ITO films [4,7,8].

In Fig. 3, the change of temperature of substrate as a function of deposition time is presented. The temperature was measured by a thermocouple attached to the back of the substrate. The temperature increased as the deposition time increased. One aspect of the plasma-surface interactions is the transfer of energy. Energy transfer from plasma to solid surfaces occurs through optical radiation and fluxes of neutral particles and ions. The optical radiation has components in the infrared, visible ultraviolet, and sometimes soft X-ray. When absorbed by a solid surface, the radiation usually transforms into heat. However, the energy of optical radiation is insignificant. In plasmas at pressures below 1 Pa (7.5 mTorr), the degree of ionization is very high, the density of neutrals is much lower than that of ions, and the ion collisions are predominant [9]. During the ion bombardment, the dissipation of the kinetic and vibrational energy fractions of ions causes heating of the substrate [9]. Therefore, a considerable rise in substrate temperature during sputtering is expected through the energetic ion bombardment. However, because the thermal conductivity of glass is very low compared to the value for silicon or other metals, it seems very likely that the ITO films on glass were deposited at a substantially higher temperature than the temperature measured [10]. Therefore, deposition up to 80 min resulted in a good crystallization by the prolonged energetic bombardment, while insufficient energy for the crystallization is transferred to the films when the deposition time is short.

On the other hand, one can bear in mind the crystallization by plasma heating. Taking into account the wide ranges of parameters, the plasmas are classified into two categories; one is thermal plasma and the other is cold plasma. The temperature of the gas in the center of the thermal plasma can reach to 20,000-30,000 K. However the temperature of the cold plasma can be as low as room temperature [9,11]. Moreover, the distance between the target and the substrate in this study is relatively long the plasma heating can be ignored. Because of the low temperature characteristic of the cold plasma, its application to polymers [12], and biological and chemical decontamination of media [13] has been increased.

If a sufficient thermal energy necessary for the crystallization were not accumulated during deposition, the films would not be crystallized. From this point of view, we can deposit films intermittently providing cooling intervals, i.e., ITO was sputtered for 2 min and the sputtering was stopped for 10 min for a cooling. Then sputtered again for 2 min. This process was repeated 20 times until the whole sputtering time is equivalent to 40 min. Another condition of deposition – 1 min sputtering repeated 40 times – was also conducted.

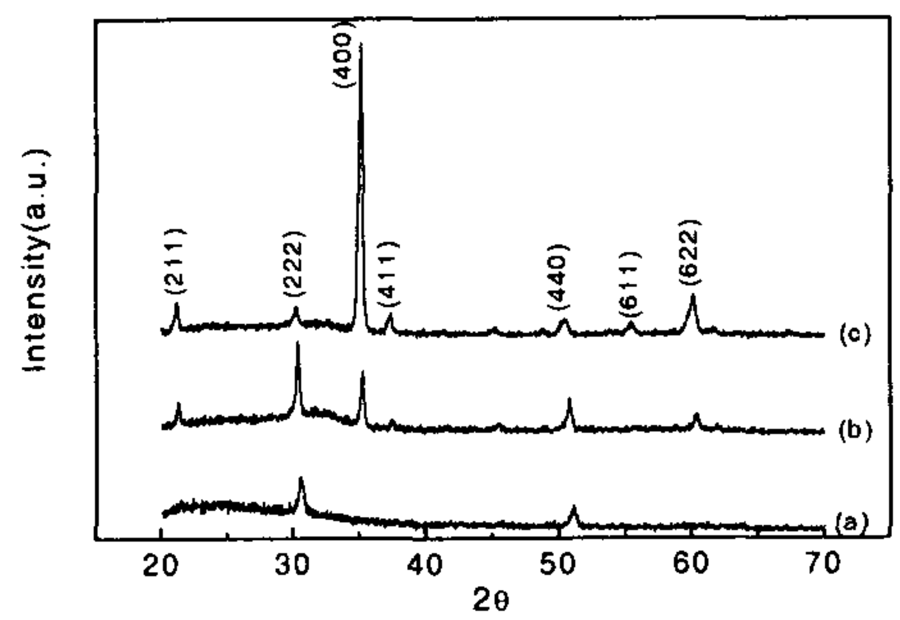

Fig. 4. X-ray diffraction profiles of ITO thin films deposited by (a) 1 min sputtering repeated 40 times, (b) 2 min sputtering repeated 20 times with a cooling interval of 10 min., and (c) 40 min continuous sputtering.

A comparison of X-ray diffraction between the samples sputtered for 40 min with and without the cooling interval is represented in Fig. 4. As we expected the intensity of the X-ray peaks, which could be regarded as the degree of crystallization, greatly decreased when the sputtering period between the cooling periods reduced. When the cooling process is provided during the sputtering, the temperature of the sample was almost invariant. From these results, it is obvious that continuous energetic ion bombardment is the source of the energy for the crystallization when external heating is absent.

The crystallization behavior of thin films can be influenced from the structure of substrates. In case of crystalline or single crystal substrate it could affect epitaxial or preferred orientation of films, while amorphous substrate might retard crystallization at the place adjacent to the amorphous substrate but allow crystallization at the place away from the substrate. So, crystallization might be easier in thick films. Since the surface of the substrate used in this study is coated with an amorphous SiO_2 layer on glass, one can imagine that crystallization is easier in thick films, that is, in the films deposited for a long time. But, as represented in Fig. 3, the degree of crystallization was clearly distinguishable even though the thickness of the film was the same. Therefore, the effect of film thickness on crystallization can be excluded.

4. Conclusions

When the ITO films are deposited by RF-magnetron sputtering without external heating, the film was in amorphous state initially. Prolonged deposition promoted crystallization of the films. Since RF-sputtering transfers the high-energy to the growing film by energetic bombardment, it is believed that considerable activation energy for the crystallization of the film has transferred during deposition. Assuming that the total kinetic energy transferred from the bombarding ions to the surface of thin films is the same when the total deposition time is the same, kinetic energy itself could not contribute to the crystallization and transferring to thermal energy and its accumulation is necessary until the temperature reach to the crystallization temperature. Such a material like ITO with low crystallization temperature could be crystallized by RF sputtering process without external heating.

5. Acknowledgement

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