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Deposition of amorphous ITO films by DC magnetron sputtering

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ABSTRACT

The key parameters that determines the crystallinity of ITO films were investigated for DC magnetron sputter deposition system, where the polycrystalline films could be deposited even at the RT substrate temperature. Entirely amorphous films were deposited under higher total gas pressure than 1.5 Pa in the case of using the oxide target, indicating that crystallinity of ITO films were heavily affected by the total gas pressure, hence the mean free path of the sputtered particles. Whereas, the crystallinity were found to be dominated not only by the total pressure but also by O_2 partial pressure in the case of reactive sputtering using In-Sn metal target. These results could be explained in terms of the kinetic energy of the sputtered particles which arrived at the substrate surface and stoichiometry of the films.

1. INTRODUCTION

ITO films are wide-gap semiconductors with a relatively low resistivity and a high transparency to visible region of light [1]. Because of these properties, ITO is widely used in opto-electronic applications, such as liquid crystal displays (LCD) [2-3]. In order to satisfy the recent demand for high-quality STN-LCD, ITO films are required to have even lower resistivity [4]. For the deposition on polymer color filter substrates, substrate temperature (Ts) is limited to values of typically 150℃ ~ 250℃ [5]. There are also such an additional requirements that the films should have good etchability to enable device patterning by photolithography. Recently, according to these requirements, low temperature deposition processes of ITO films with low resistivity has been investigated [6-7].

These properties are intimately associated with the microstructure of the ITO films. In turn, it is directly linked to the deposition method and process conditions. In the case of EB evaporation, amorphous ITO films (a-ITO) are obtained at bellow the crystallization temperature (Tc, about 150℃) [8]. Whereas, in case of sputtering method, it was reported that microstructure of ITO films deposited even at Ts of room temperature (RT) showed polycrystalline structure. Microstructure of ITO films deposited at nearly Ts of Tc were investigated to consist of two layers (polycrystalline top layer and amorphous bottom layer close to the substrate surface) by TEM cross-sectional analyses [9.10]. It was also reported that the ITO films deposited by DC magnetron sputtering at Ts = 150 - 200℃ consisted of two differently strained layers. The weakly strained layer was considered to be formed as a result of crystallization of the as-deposited amorphous layer close to the substrate surface upon thermal annealing during deposition (solid-phase crystallization), whereas the strongly strained layer was an as-deposited crystalline layer near the film surface (vapor-phase crystallization) [11]. In general the wet etching rate of amorphous layer adjacent to the substrate is very high, while the one of the polycrystalline top layer is much lower. In the result, the top layer of ITO films became

locally detached from the substrate and ruptured because of the different in the etchability and compressive stress of the two layers [12. 13]. It was reported that a-ITO films prepared on a Ts of 30℃ by Highly Dense Plasma-assisted EB evaporation showed the etching rate of 2.6 nm/sec and very sharp edges in patterning property [12]. So far as wet-etching is concerned, it seems reasonable to suppose that patterning properties of ITO films deposited with single layer (entirely amorphous phase or polycrystalline phase) better than that of ITO films composed of the two layers with the different phases. Despite that, there have been relatively few studies about mechanism of deposition process of amorphous ITO (a-ITO) films in which microstructure has been corelated with the deposition condition.

The present paper describes a detailed investigation on the growing mechanism of a-ITO films by DC magnetron sputtering method.

2. EXPERIMENTAL PROCEDURES

The a-ITO films were deposited on glass substrates using DC magnetron sputter system. The distance between substrates and target was 127 mm. Oxide ceramic ITO target (doped with 10 wt.% SnO_2) or metal alloy target (doped with 10 wt.% Sn) was used. The ITO films were deposited at different direct current power (30W, 50W, 100W and 200W) or total gas pressure (0.2 ~ 4.5 Pa). The back pressure was less than 10^{-4} Pa. Deposition time was adjusted to get the similar thickness of the films of about 150 nm. Prior to each deposition, the target surface was cleaned by pre-sputtering (20 min) without reactive gas. The ITO films were deposited without substrate heating, where the Ts was measured to be about below 35℃ by thermo-lavel. The film thicknesses were measured with a Talystep apparatus (Surfcom 470 A, Tokyo Seimitu Co.). The transmittance of the ITO films as a function of the wavelength (300 - 2600 nm) was measured using a U-3400 spectro-photometer (HITACHI Co.). X-ray diffraction (XRD) measurement was performed with 40 kV - 20 mA CuK α radiation using a Rint 2000 (Rigaku Co.).

3. RESULTS AND DISCUSSION

XRD profiles of the ITO films deposited under different total pressure on soda-lime glass using oxide ITO target (doped with 10 wt.% SnO_2) at discharge power of 50 W and Ts below 35℃ are shown in Fig. 1. The ITO films that were deposited at the total

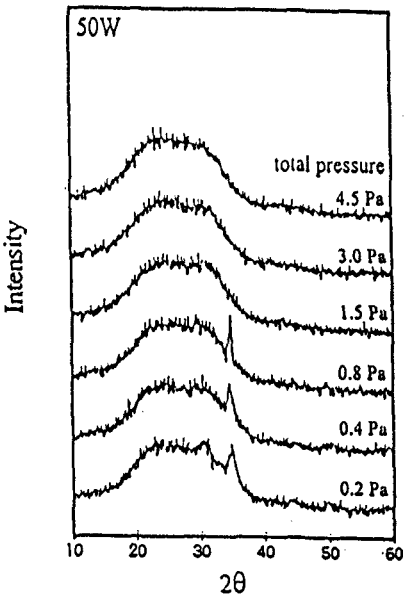

Fig. 1. XRD patterns of the ITO films deposited under different total gas pressure at discharge power of 50 W, Ts of 35 ℃ and O2/Ar flow rate of 0%

pressure below 0.8 Pa showed polycrystalline structure. While, The ITO films that were deposited at higher total pressure than 1.5 Pa showed amorphous structure. In order to explain the deposition condition of a-ITO films, a comparison with deposition processes of EB evaporation and sputtering may be helpful. In case of EB evaporation method, the structure of ITO films deposited at Ts below Tc (about 150 ℃) was invariably amorphous. While, it was reported that both of amorphous and polycrystalline phases coexisted in ITO films which were deposited by sputtering method even at Ts of RT [9].

It is desirable to describe the energy of the evaporated particles (about 0.2-0.3 eV) and the sputtered particles (about 1-3 eV) before moving on to the main task. It is not too far from the truth to say that ITO films are easy to crystallize even at the low Ts because of the sputtered In or Sn particles with the higher kinetic energy than evaporated particles are able to find the most stable site when they arrived at the substrate surface. It was also reported that activation energy for O_2 diffusion in In_2O_3 films was about 1.7 eV [14]. As the activation energy of In particles to migrate at the film surface during the deposition should be lower than the one in In_2O_3 films, ITO films could be crystallized in sputtering processing of low total gas pressure if sputtered In particles have enough kinetic energy of about 1-3 eV. The mean free path of the sputtered In particles was estimated to be about 8 mm at total gas pressure of 1.5 Pa. The number of collisions of the sputtered particles with sputter gas was about 16 times at 1.5 Pa. If the sputtered In particles come into 16 times collision with sputter gas, their kinetic energy could be considerably decreased to be thermalized [15], therefore, it seems reasonable to suppose that a-ITO films of metastable state could be deposited because of the sputtered In particles could be stopped at someplace before arrive at the most stable site to form crystal. There is considerable validity to this concept, though it should not be pushed too far.

XRD profiles of the ITO films deposited under different O_2 partial pressure (P_{O_2}) on soda-lime glass using metal alloy target (doped with 10 wt.% Sn) at discharge power of 50 W and total pressure of 0.4 Pa are shown in Fig. 2. XRD patterns of the films deposited at P_{O_2} of 0 Pa were metal of In and Sn. With increase in P_{O_2}, the structure changed from amorphous phase to poly-crystalline phase. This means that the structure of ITO films was strongly dominated by P_{O_2} in the reactive sputtering process.

Transmittance of the films were measured in order to certify the amorphous phase deposited at P_{O_2} of 0.10 Pa and 0.22 Pa. It was certified as sub-oxide because of transmittance of that samples was nearly 0% in the region of visible light.

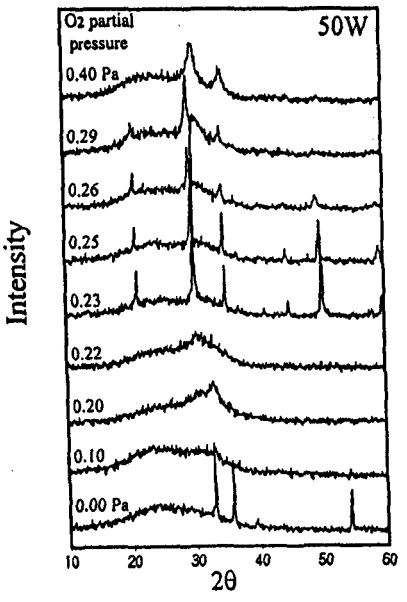

Fig. 2. XRD profiles of IT or ITO films deposited PO2 using metal alloy target (doped with 10 wt.% Sn) at discharge power of 50 W, Ts of 35℃and total gas pressure of 0.4 Pa

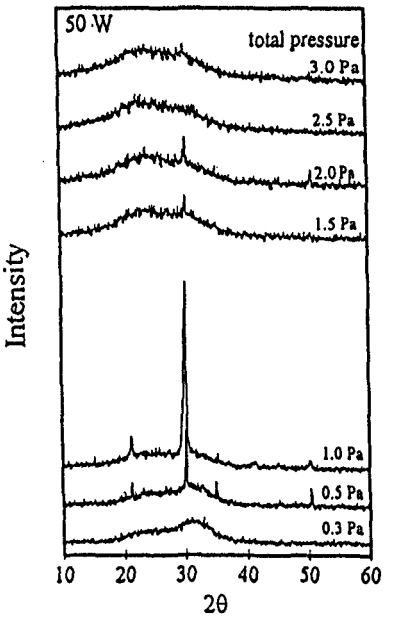

Fig. 3. XRD profiles of IT or ITO films deposited under different total gas pressure using metal alloy target (doped with 10 wt.% Sn) at O2/Ar flow rate of 24.7%, discharge power of 50 W and Ts of 35℃

The dependence of microstructure on total gas pressure for a-ITO films deposited at O_2/Ar flow rate of 24.7% by reactive sputtering system is shown in Fig. 3. The result showed that the structure of samples deposited at total gas pressure of 0.3 Pa and 2.5 Pa were amorphous phase.

Results of the transmittance that was investigated for samples deposited at P_{O_2} of 0.3 Pa and 2.5 Pa are shown in Fig. 4. The transmittance of the samples deposited at P_{O_2} of 2.5 Pa showed nearly 85% in visible region of light (300-800 nm), while the transmittance of the samples deposited at P_{O_2} of 0.3 Pa was nearly 0%. Therefore, it is obvious that the sample deposited at 2.5 Pa is a-ITO films. This result lead to the conclusion that the structure of ITO films depended on total gas pressure.

In the case of metal alloy target, it follows from what has been said that the deposition condition to deposit entirely amorphous films was strongly dominated not only by the total gas pressure but also P_{O_2}.

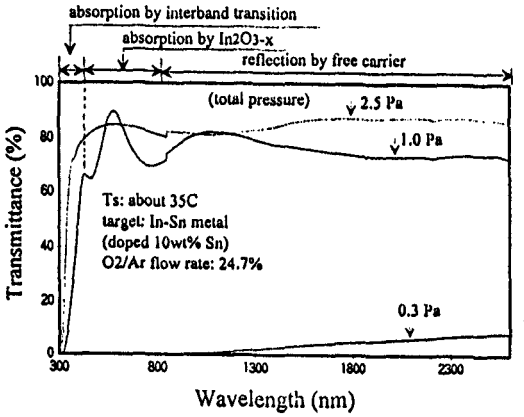

Fig. 4. Transmittance of IT or ITO films deposited under different total gas pressure at O2/Ar flow rate of 24.7% and Ts of 35℃

4. CONCLUSION

The microstructure of ITO films deposited by DC magnetron sputtering using oxide target at low substrate temperature (about 35℃) and high total pressure (above 1.5 Pa) appeared to be amorphous. It is concluded that a-ITO films are dominated by total pressure during the deposition. In case of reactive sputtering using metal alloy target, structure of the films was dominated not only by the total pressure but also O_2 partial pressure.

It was confirmed that the crystallinity of ITO films was strongly dominated by the kinetic energy of sputtered particles for the both processes. For these a-ITO films, very high wet-etching rate is expected.

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