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RF-enhanced DC-magnetron Sputtering of Indium Tin Oxide

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Indium tin oxide (ITO) films were deposited on glass substrates at 300°C in oxygen/argon mixtures by RF-enhanced DC-magnetron sputtering and were compared to those by conventional DC magnetron sputtering. The RF enhancement was performed using a coil above an ITO target. X-ray diffraction measurements revealed that RF-enhanced plasma affected the preferred orientation and the crystallinity of the films. The resistivity of the films prepared by RF-enhanced DC-magnetron sputtering was almost constant at oxygen content lower than 0.3% and then increased sharply with increasing oxygen content. However the resistivity of the films by conventional sputtering had little dependence on the oxygen content. Those results can be explained on the basis of the incorporation of oxygen into the ITO films due to the RF enhancement.

Key words: ITO, Thin film, DC magnetron sputtering, RF enhancement, Modified sputtering

I. Introduction

Indium tin oxide (ITO) films, as transparent conducting layers, have been widely used in optoelectronic fields such as flat panel displays[1] and solar cells.[2] Because of these interesting applications, many techniques have been used for depositing ITO films, such as evaporation,[3] chemical vapor deposition,[4] spray pyrolysis,[5] laser ablation,[6] and sputtering.[7] Although many techniques can be used to deposit ITO films, more attention has been paid to sputtering technique because of the easy control of the deposition parameters and the uniformity in film properties over a large area of the substrate. DC magnetron sputtering is one of the most important sputtering techniques and has been widely used for depositing ITO films. Several attempts have been made to modify this deposition process.[8,9]

RF-enhanced DC-sputtering[10] is a modification of conventional DC magnetron sputtering. With the addition of inductively coupled RF plasma in the region between the sputtering source and the substrate, the ionization fraction of the sputtered atoms has been reported to reach 80%.[11] In the previous work,[12] we have characterized the RF-enhanced DC-sputtering to deposit ITO films. This paper focuses on the effect of RF plasma on the properties of ITO films prepared by RF-enhanced DC-magnetron sputtering.

II. Experimantal

The schematic drawing of the RF-enhanced DC-magnetron sputter deposition system (Model BC3284, Ulvac, Japan) is shown in Fig. 1. One cathode was used in this study, although the system was equipped with three cathodes. A sintered disk made from a mixture of 90 wt% In_2O_3 and 10 wt% SnO_2, 5 cm in diameter, was used as a target. The distance between the target and the substrates was 15 cm. The inductively coupled RF plasma was set up by a one turn, water-cooled metal coil with a diameter slightly larger than that of the target. The coil was located 1 cm above the target. The substrate (soda-lime glass, 30×30×1 mm^3) was rotated with a speed of 10 rpm and the substrate temperature was kept at 300°C during deposition. Deposition was carried out in an argon gas and in a mixture of oxygen/argon gases. The

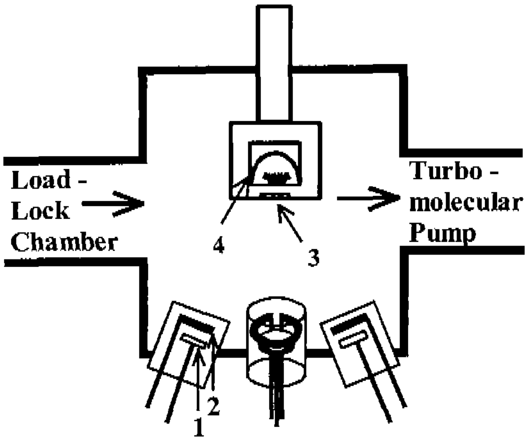

Fig. 1. Schematic diagram of RF-enhanced DC-magnetron sputtering system. 1. Target 2. RF coil, 3. Substrate 4. Heating lamp.

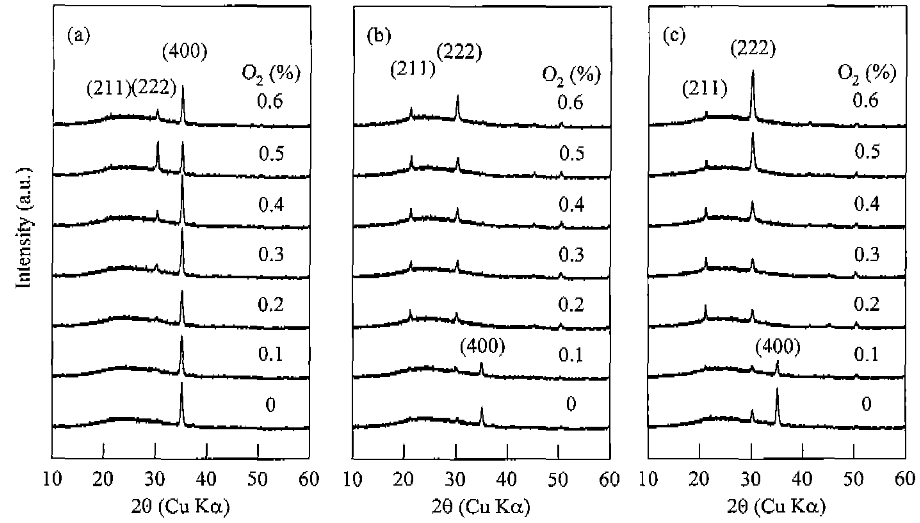

Fig. 2. X-ray diffraction patterns of ITO films deposited at various oxygen contents. RF coil power P_c=0 W (a), 30 W (b) and 50 W (c).

oxygen content was varied from 0 (pure argon) to 0.6%. The total gas pressure was kept at 0.5 Pa. The RF power (13.56 MHz) ranging from 0 to 50 W was introduced through the coil, while the target power was kept at 24 W.

The film thickness was measured with a stylus surface profiler (Model DEK-TAK III, Sloan technology corp., USA) and was nominally 130 nm. The sheet resistance of the samples was measured with a four-point probe and the resistivity of the film was calculated. The carrier concentration and the Hall mobility were obtained from the Hall effect measurement by the van der Pauw technique (Model HL5500-PC, Bio-rad laboratories Inc., UK). The transmittance of the films was measured with a double-beam spectrometer (Model UV-3100PC, Shimadzu Co., Japan) in the visible region, using glass as the reference. X-ray diffraction (XRD) measurements were performed with 40 kV-20 mA CuKα radiation (Model RINT2100, Rigaku Co., Japan).

III. Results and Discussion

1. XRD

The XRD measurements revealed that all the ITO films obtained in this study were polycrystalline and retained a cubic bixbyite structure of In_2O_3,[13] as shown in Fig. 2. According to the JCPDS powder diffraction file of In_2O_3,[14] the highest intensity peak is (222) and the third highest intensity peak is (400) with a relative intensity ratio I(400)/I(222) of 0.3. In this study, the two peaks of (222) and (400) appear prominently, indicating the existence of <111> and <100> oriented textures, although the minor peak of (211) is observed for some films. Both the orientation and the crystallinity were influenced by the RF coil power (P_c) and oxygen content. For P_c=0 W, the (222) peak emerged at the oxygen content of 0.2% and the intensity increased with increasing oxygen content from 0.2% to 0.5%, while the intensity of the (400) peak kept constant between 0-0.6 %. Similar dependence of I(400)/I(222) on oxygen content has been reported by Vink *et al.*[15] and by Meng *et al.*[16] For P_c =30 or 50 W, the (222) peak increased with increasing oxygen content from 0% to 0.6%, while the (400) peak disappeared when the oxygen content exceed 0.2%. These results imply that RF power enhances the oxidation of the ITO films. In the previous work,[12] we measured electron temperature in RF enhanced DC plasma by a Langmuir probe and noted that the RF power enhances electron temperature. It should be noted that the high-energy electrons can excite or ionize sputtered atoms and oxygen molecules. Therefore, the oxidation of the ITO films can be attributed to the high-energy electrons created by the RF enhancement.

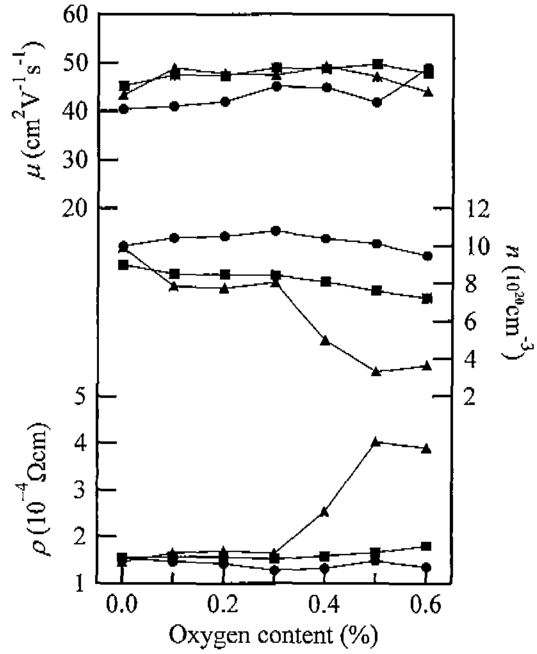

Fig. 3. The dependence of the film resistivity (ρ), carrier density (*n*) and Hall mobility (μ) on the oxygen content for ITO deposited at the RF coil power 0 W (●), 30 W (■), 50W (▲).

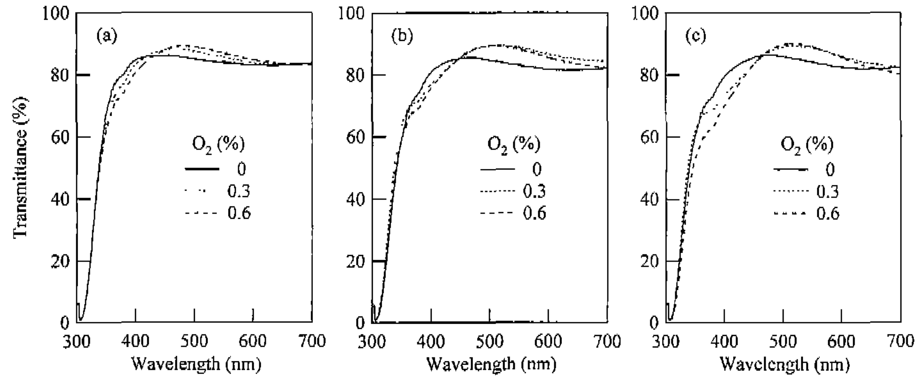

Fig. 4. The effect of oxygen content on the transmittance in the visible region of ITO films deposited at P_c=0 W (a), 30 W (b) and 50 W (c).

2. *Electrical properties*

Fig. 3 shows the variation of the resistivity (ρ), the carrier density (*n*), and the Hall mobility (μ) with oxygen content for various RF powers. For P_c=0 or 30 W, the resistivity, the mobility and the carrier density were independent of the oxygen content. For P_c=50 W, the resistivity stayed constant, then increased rapidly. This is attributed to the change in carrier concentration. Charge carriers are generated[17)] by doubly charged oxygen vacancies ($V_O^{\cdot\cdot}$):

$$O_O = V_O^{\cdot\cdot} + 2e' + \frac{1}{2}O_2(g)\,. \tag{1}$$

and Sn^{4+} ion on In^{3+} site ($Sn_{In}^{\cdot}$):

$$2SnO_2(g) = 2Sn_{In}^{\cdot} + 3O_o + 2e' + \frac{1}{2}O_2(g) \tag{2}$$

The incorporation of oxygen leads to a decrease in oxygen vacancies on regular anion sites of the bixbyite structure and to an increase in interstitial oxygen on quasi-anion sites. Interstitial oxygen atoms are attracted by $Sn_{In}^{\cdot}$ dopant, forming neutral complexes such as loosely bound complexes ($Sn_2^{\cdot}O''$) and strongly bound complexes $(Sn_2O_4)^x$.[17)] Therefore, the incorporation of oxygen into the ITO film can reduce the carrier density. It is likely that RF power enhanced the oxidation of the growing film, thereby increased its resistivity. It should be noted that the resistivity of the ITO films grown without oxygen was fairly low regardless of RF power in this study. RF enhancement could reduce the resistivity of the ITO films deposited under much lower oxygen pressures.

3. *Transmittance*

Fig. 4 shows the transmittance of the film deposited under various oxygen contents and RF powers. The maximum transmittance increased from 86% to 90% with increasing oxygen content from 0% to 0.6%. Similar results are reported by many researchers.[16, 18)] The increase in transmittance could be attributed to the decrease in absorption by oxygen deficient regions[18)] and/or to the decrease in reflectance by a rough surface.[19)] It should be noted that surface roughness also depends on the oxygen partial pressure during deposition.[19)] Therefore the transmittance is closely correlated with the oxygen deficiency. The peak position shifted to longer wavelength when oxygen gas was added, regardless of RF power. As shown in Fig. 5, RF power also improved the maximum transmittance and moved the peak position to longer wavelength, suggesting that the ITO deposited without RF power is oxygen deficient compared with the samples deposited with RF power when the oxygen content is 0.3%. The results are consistent with those of the XRD experiments and the electrical properties.

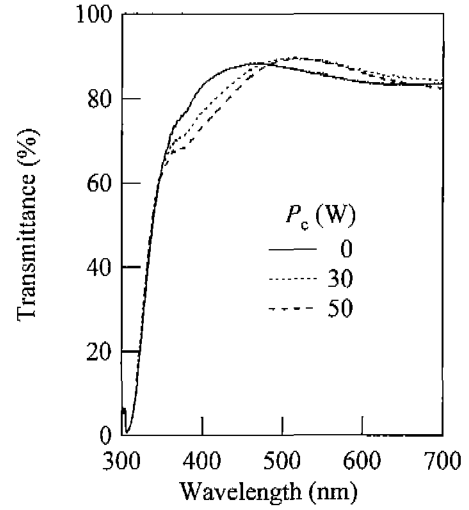

Fig. 5. The effect of P_c on the transmittance in the visible region of ITO films deposited at the oxygen content=0.3%.

IV. Conclusions

1. The addition of inductively coupled RF plasma in the magnetron sputtering affects the structural orientation of the ITO films obtained. For P_c=30 or 50 W, the (400) peak disappears in the oxygen content range from 0.2 to 0.6%, whereas for P_c=0 W, the (400) peak stays predominant in this oxygen content range. Regardless of RF power, the (400) peak is predominant in the oxygen content range from 0 to 0.1% and the (222) peak becomes predominant as oxy-

gen content increases from 0.2 to 0.6%.

2. The electrical resistivity of the ITO film deposited at P_c=50 W is kept constant in the oxygen content range from 0 to 0.3%, then increases at the oxygen content of 0.4%. This tendency is attributed to the change in the carrier concentration of the film. The carrier concentration decreases due to the incorporation of oxygen into the film by RF enhancement.

3. The optical transmission of ITO film in the visible range increased with increasing RF power or with increasing oxygen content.

4. The oxidation of the ITO films is enhanced by the addition of RF power through a coil in the magnetron sputtering system.

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