RF Bias Effect of ITO Thin Films Reactively Sputtered on PET Substrates at RoomTemperature

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ITO films were deposited on polyethylene terephthalate substrate by a dc reactive magnetron sputtering using rf bias without substrate heater and post-deposition thermal treatment. The dependency of rf substrate bias on plasma sputter processing was investigated to control energetic particles and improve ITO film properties. The substrate was applied negative rf bias voltage from 0 to -80 V. The composition of indium, tin, and oxygen atoms is strongly depended on the rf substrate bias. Oxygen deficiency is the highest at rf bias of -20 V. The electrical and optical properties of ITO films also are dominated obviously by negative rf bias.

Keywords : Indium tin oxide (ITO), Polyethylene terephthalate (PET), RF bias, Reactive Sputtering, Room temperature

1. INTRODUCTION

Because indium tin oxide (ITO) films have high transparent properties in the visible wavelength region and a low electrical resistivity, they have been widely used in opto-electric applications such as flat panel display or solar cell[1]. However, it has been recently required that transparent conducting ITO(TC-ITO) thin films are prepared on several polymers as a substrate material using low or room temperature deposition processes[2,3]. Due to many merits of light weight, small size, easily carried and folded feature with polymer substrates, they can be applied to flexible opto-electric sensors, plastic LCD and unbreakable heat reflecting mirrors.

The various attempts for the improvement of fabrication and properties of ITO films with substrate temperature and post annealing treatment of low temperature have been extensively progressed. Ma et al. [4] reported that ITO films deposited on polyimide by reactive evaporation at low temperature of 200 °C had the resistivity of 7×10^{-4} Ω cm and optical transmittance of 80%. Bender et al.[5] showed that ITO films sputtered on glass using the rf-superimposed dc magnetron gas discharge of 50 % rf power and 50 % dc power had the electrical resistivity of 1.5×10^{-4} Ω cm at a substrate temperature of 200°C. Also it was reported by Futagami et al.[6] that the properties of ITO films were studied by the effect of rf-enhanced dc sputtering using a one-turn coil above target. On the other hand, Honda et al.[7] certified that the depth profile of oxygen content of ITO films on glass at 300 °C substrate temperature depended upon the strength of substrate bias voltage using hot-cathode Penning discharge sputtering (HC-PDS), and had been one of the important factors which influenced film properties. Their ITO films showed the resistivity of approximately 10^{-4} Ω cm and average transmittance of 40～80 % at the substrate voltage ranges of -100～0 V.

In general, the electrical and optical properties of ITO films exhibit a strong dependence of temperature in the sputtering process. However, the preparation of ITO thin films using polymer substrates should be performed possibly without heat treatment, so that the coating methods and deposition parameters of plasma processing are greatly important. Among the several deposition methods of ITO thin films, the dc magnetron sputter is used most often.

In this article, ITO films were deposited on flexible transparent substrate by a dc reactive magnetron sputtering. It was well known that the energetic particles such as negative ions and secondary electrons caused some damage on film surface during the sputtering deposition. In order to control the energetic particles, our attempt was to investigate an effect of rf substrate bias for the improvement of film properties. The plasma sputter processing was activated by an rf power supply connected to the substrate so that the negative rf bias was used due to the insulating nature of flexible substrate.

2. EXPERIMENTAL

ITO thin films were deposited on polyethylene terephthalate (PET) substrates by a dc reactive magnetron sputtering at room temperature (without heat treatment). The substrate was applied negative rf bias voltage from 0 to -80 V, and also the sputtering para- meters such as dc power and oxygen partial pressure (PO_2) were used to investigate the effects of ITO film composition and properties. The original target was made of 2 inch diameter and the target material was In-Sn (In:Sn=90:10 wt%) alloy supplied by Cerac. The reactive sputtering gases of high purity oxygen (99.999 %) and argon (99.999 %) were introduced into the chamber. Prior to ITO deposition, PET substrates were ultrasonically cleaned for 5 min. using methanol as a solvent, and subsequently dried by N_2 gas. A serious problem in reactive sputtering of alloy target is the oxidation of the target surface, so-called poisoning phenomena. Therefore, the target surface should be cleaned before every sputtering run, and the target was pre-sputtered in argon atmosphere for about 10 min to remove the surface oxide and impurity layer that may have caused due to exposure to air. The target-to-substrate distance was 4.5 cm and held constant throughout. Other sputtering parameters such as dc power, working pressure, and oxygen partial pressure are shown in Table I[8,9].

The growth rate of films was measured by a stylus profilometer. The composition of ITO films was investigated by X-ray photoemission spectroscopy (XPS). The electrical resistivity and sheet resistance were estimated by standard four-point probe method. The carrier concentration and Hall mobility were calculated by van der Pauw method of Hall effect measurement. The optical transmittance was analyzed by UV-visible spectrophotometer with the ranges of 200 ~ 900 nm.

Table 1. Sputtering parameters of ITO films on PET.

Sputtering parameters	Ranges
DC power density [W/cm^2]	0.49 - 2.47
Base pressure [Torr]	2×10^{-6}
Working pressure [mTorr]	1 ~ 5
T-S distance [cm]	4.5
Target material [In:Sn]	90:10
Oxygen partial pressure [%]	8 ~ 13
Rotation speed [rpm]	10

3. RESULTS AND DISCUSSION

Figure 1 shows typical XPS spectrum of as-deposited ITO film prepared under the dc power of 30 W, working pressure of 5 mTorr, oxygen partial pressure of 11 % and rf bias of 0 V. As shown in figure, XPS peaks of In 3d are located at 444 and 452 eV, and it shows the In-O (In^{3+}) bonding state. It also can be found that the XPS peak of Sn 3d shows Sn-O (Sn^{3+}) bonding from the position of Sn peak (486 and 495 eV), and the as-deposited film has small amount of oxygen deficiency from the asymmetry of O 1s peak. It is identified that the as-deposited films are composed of In_2O_3 and SnO_2.

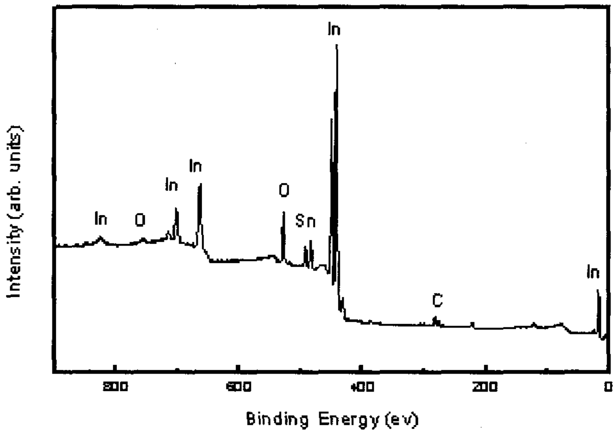

Fig. 1. Typical XPS spectrum of as-deposited ITO thin film.

Figure 2 shows the atomic concentration plots of ITO films deposited on PET substrate, obtained from the XPS spectrum, as a function of rf substrate bias. All film thickness in this work is around 150± 10 nm and the deposition conditions are: dc power of 30 W, working pressure of 3 mTorr and PO_2 of 11 %. In the case of no rf bias, the composition of indium, tin and oxygen atoms is 40.0, 4.7 and 55.3 %, respectively. The theoretical oxygen concentration (1.5In+2Sn), caused by the ideal stoichiometry ($In_2Sn_yO_{3+x}$) of ITO film based on In_2O_3 trivalent and SnO_2 bivalent, is 69.4 % and the compositional ratio of practical oxygen concentration to theoretical oxygen concentration, O/(1.5In+2Sn), is approximately 0.797. That is, the oxygen composition in no rf bias is lower than the stoichiometric oxygen content and it means oxygen deficiency in ITO film. The oxygen concentration in the case of -20 V is lower than that of no rf bias, while the indium content goes up to 46.3 %. As a result, the theoretical oxygen concentration increased and O/(1.5In+2Sn) ratio is reduced abruptly. In the case of above -40 V, the atomic concentration of oxygen and O/(1.5In+2Sn) ratio become slightly higher than those of -20 V case. The tin concentration of ITO films does not fluctuate so much with negatively increasing rf bias voltage. As the above results, the lowest oxygen concentration is given in the case of -20 V bias. The reason is that the oxygen atoms under the condition of relatively low rf bias may be resputtered selectively from ITO film grown on PET substrate by energetic Ar ions, because oxygen is due to light mass in ITO[7]. However, as the substrate bias is higher than -20 V, the oxygen and also indium atoms are damaged simultaneously by more energetic ions. After all, the oxygen deficiency is diminished as shown in Fig. 2 and the oxygen concentration in ITO film is dominated by rf bias voltage.

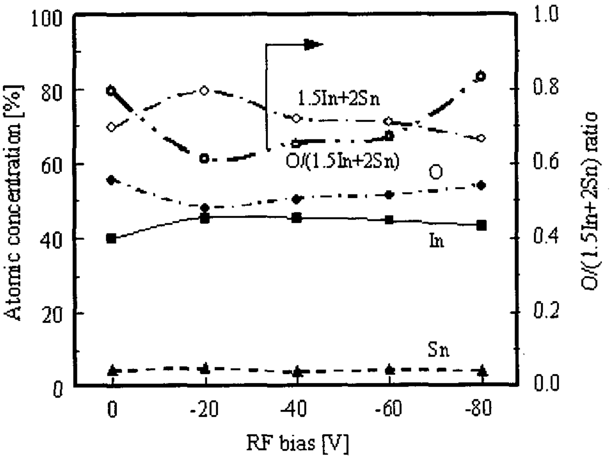

Fig. 2. Atomic composition of ITO films on PET substrate with different rf bias.

The carrier concentration, mobility and resistivity of ITO films as a function of rf bias voltage are represented in figure 3. The carrier concentration of ITO film increases abruptly in the case of -20 V, and may be related to oxygen deficiency. On the other hand, the electrical resistivity of ITO is reduced, and it seems that lower resistivity is not caused by the mobility but by an increased carrier concentration. The mechanism of carrier concentration can be explained by a reduction of oxygen vacancies as donors and an increase of bivalent In or Sn as acceptors [1]. The carrier concentration increases with increasing oxygen deficiency, and the resistivity, which strongly depends on the carrier concentration, is decreased. The mobility shows the increasing trend in the case of beyond -20 V and it is considered that an increase of mobility is closely related on Ar^+ radiation with increasing rf bias voltage. Kumar, et al. [10] reported the dependence of resistivity, carrier concentration, and mobility of ITO films on rf power. They found the mobility increased with increasing rf power and showed a saturation at high power of 150 W. The reason is that the film orientation changes with increasing rf power.

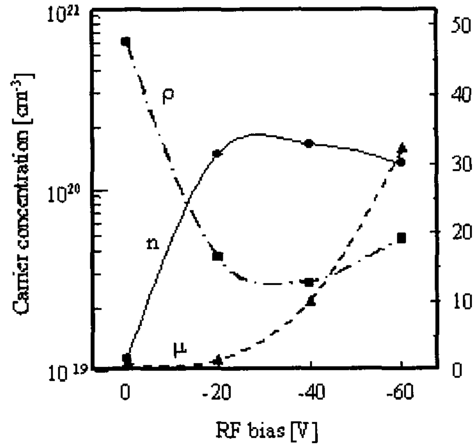

Fig. 3. The carrier concentration, mobility and resistivity of ITO films grown on PET as a function of rf substrate bias.

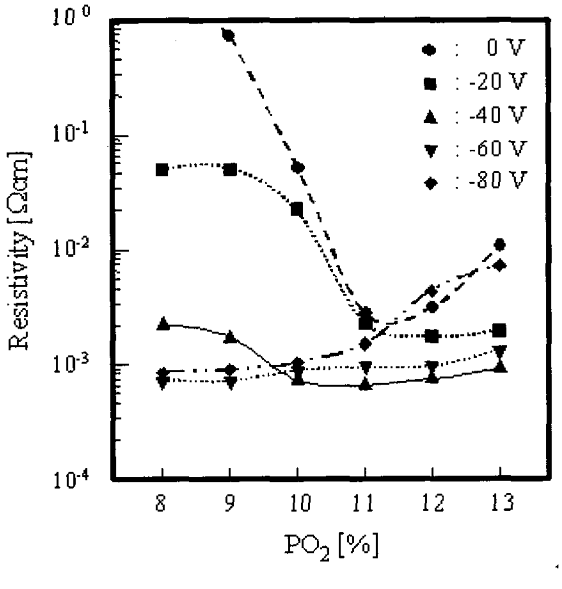

Fig. 4. The electrical resistivity of ITO films on PET at different rf bias as a function of PO_2.

Figure 4 shows the electrical resistivity as a function of PO_2 for as-deposited ITO films at different rf bias voltages. At no bias voltage, the resistivity of ITO films is greatly influenced by PO_2, and relatively low resistivity is only able to obtain within a limited region of PO_2. The minimum resistivity is observed at PO_2 of 11%. However, the concave shape of resistivity is lowered and expanded broadly as the negative rf bias is increased. In the case of -60 V, the resistivity is almost constant and remains low with a change of PO_2. The higher resistivity at low bias voltage is considered to be due to an ITO surface damage caused by resputtering oxygen atoms in ITO film selectively. The low resistivity may be deeply related to the changes of plasma formation with the sputtering conditions such as PO_2, negative rf bias and dc target power.

Figure 5 presents the optical transmittance of ITO films grown on PET at wavelength of 550 nm as a function of rf substrate bias. The optical transmittance at dc power of 10 W displays a little increasing tendency at low rf bias and does not change too much. However, the transmittance at dc target powers of 30 and 50 W exhibits obviously the increasing trend with an increase of rf bias. It is found that the low optical transmittance at lower rf bias than -40 V may be positively related to oxygen deficiency and carrier concentration as the above mentioned in Fig. 2 and 3. The transmittance is as much as 75 % at higher rf bias than -40 V.

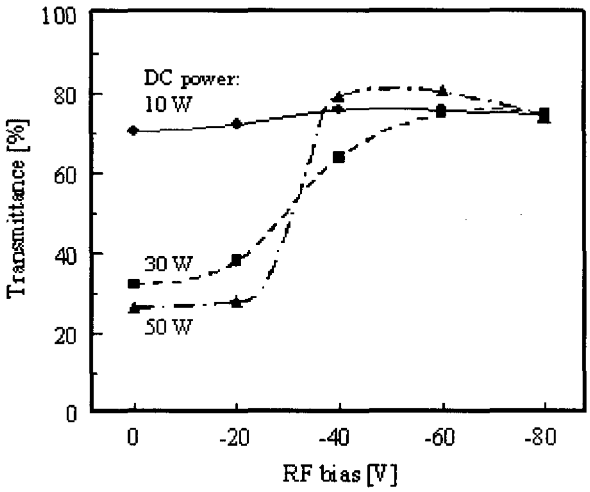

Fig. 5. The optical transmittance of ITO films on PET substrate at 550 nm wavelength with different rf bias.

4. CONCLUSIONS

The sputtering conditions such as rf substrate bias, PO_2 and dc target power in ITO films deposited on PET substrate without substrate temperature or post-heat treatment were dominant factors to determine better stoichiometric composition, resistivity and optical transmittance. The electrical and optical properties of the ITO film depend critically upon the oxidation state of the metal component (stoichiometry of the oxide) and on the nature and quantity of impurities incorporated in the films. In this measurement, the best resistivity of 5.5× 10^{-4} Ω cm is obtained under the following conditions: dc power of 50 W, rf bias of -60 V and PO_2 of 10 %. The highest transmittance of ITO film is approximately 85 % at dc power of 30 W, rf bias of -80 V and PO_2 of 6 %.

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