Optimal Sputtering Parameters of Transparent Conducting ITO Films Deposited on PET Substrates

Hyun-Hoo Kim
Electronic Department, Doowon Technncal College, Kyeonggi-do 456-890, Korea

Sung-Ho Shin
Inorganic Chemistry Div., Agency for Technology and Standards, Kyeonggi-do 427-010, Korea

E-mail : hhkim@doowon.ac.kr

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Indium tin oxide (ITO) films have been deposited on PET and glass substrates by DC reactive magnetron sputtering without post-deposition thermal treatment. The high quality for microstructure, electrical and optical properties of the as-deposited ITO films on unheated substrates is dominated by the sputtering parameters. The influence of the working gas pressure, DC power, and oxygen partial pressure has been systematically investigated. The lowest resistivity of ITO films deposited on PET substrates was 6×10^{-4} Ωcm. It has been obtained at a working pressure of 3 mTorr and DC power of 30 W. The sheet resistance and optical transmittance of these films were 22 Ω/square and 84 %, respectively. The best values of figures of merit for the electrical and optical characteristics such as T/R_{sh} and T^{10}/R_{sh} are approximately 38.1 and 7.95 ($\times10^{-3}$ Ω^{-1}), respectively.

Keywords : Indium tin oxide (ITO), PET substrate, DC reactive magnetron sputter, Sputtering parameters, Room temperature.

1. INTRODUCTION

For optoelectronic applications, transparent conducting indium tin oxide films have been generally deposited on glass substrates. These applications include solar cells, flat panel displays, antireflection coatings and gas sensors, etc [1,2]. However, these devices are sometimes heavy and brittle due to the glass substrate. To overcome these problems, it has been recently suggested that ITO films are deposited on polymer substrates, which are usually lighter and more flexible than glass. For examples, they are applied to plastic LCD, flexible optoelectronic devices, and unbreakable heat reflecting mirrors, etc. However, the electrical and optical characteristics in both substrates have to be the same. The sheet resistance required in these applications should be as low as 10~50 Ω/square [3]. Furthermore, post deposition annealing of ITO films deposited on polymeric substrates is very restricted because polymers can not withstand high temperature.

In this research, we report the preparation of ITO films on PET substrate using DC reactive magnetron sputtering without post-annealing. The influence of working gas pressure, DC power and oxygen partial pressure on the electrical and optical properties of the deposited films have been investigated. The microstructure of the films was determined by atomic force microscopy (AFM). The chemical bonding state and composition of ITO films were determined using X-ray photoemission spectroscopy (XPS). Finally, the figures of merit for films deposited at different oxygen partial pressures were calculated.

2. EXPERIMENTAL

Indium tin oxide films were deposited on polyethylene terephthalate (PET) and soda-lime glass substrate at room temperature by DC reactive magnetron sputtering. The coated area of substrates was 7.6×2.6 cm (i.e., 3×1 inch). Prior to ITO deposition, all substrates were ultrasonically cleaned for 5 min using methanol as a solvent. In addition, the vacuum chamber was evacuated to a base pressure of 2×10^{-6} Torr and then backfilled with high purity argon (99.999 %) to ensure the desired working pressure. The target was presputtered in argon for about 10 min in order to remove the surface impurity layer which may have formed during exposure to air.

Table I. Ranges of sputtering parameters

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

The target-to-substrate distance was 4.5 cm and held constant throughout. Other parameters such as the DC power, working pressure, and oxygen partial pressure were investigated. The substrate holder was able to rotate in order to ensure better uniformity of the films. The investigated ranges of sputtering parameters are shown in Table I. A circular In 90 wt%-Sn 10 wt% target, supplied by Cerac, with a 2 inch diameter and 1/4 inch thick was used.

Film thickness measurements were carried out using an α-step 500 surface profilometer manufactured by Tensor. Optical transmittance measurements were performed using a UNICAM 8700 UV-visible spectrophotometer made by Phillips, in the spectral range of 200~900 nm. Electrical resistivity and sheet resistance measurements were carried out using a standard 4-point probe (CMT-SR 1000, Chang-Min Co.) and Hall measurement system (Lake-shore EMA-CS electro-magnet system and Keithly measurement system with 7065 Hall Card). The microstructure of the deposited films was studied using a DAFM 6300 Atomic Force Microscope (AFM), made by Dong-Il. Finally the composition of the films was determined using an ESCALAB-220i X-ray Photoelectron Spectroscope (XPS), manufactured by VG Scientific.

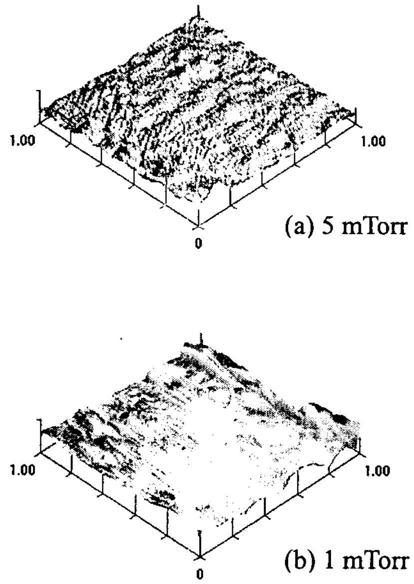

Fig. 1. AFM images of ITO films on PET substrates at different working pressures.

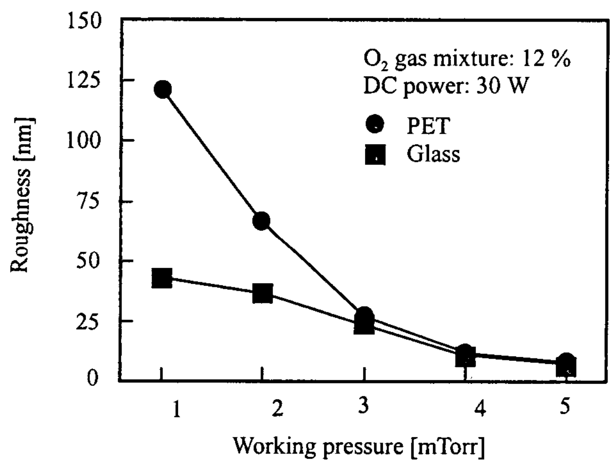

Fig. 2. Line roughness of ITO films on PET and glass substrate with different working pressure.

3. RESULTS AND DISCUSSION

X-ray diffraction peaks were not observed for ITO films deposited on PET substrates, an evidence of the non-crystalline nature of these films. In addition, thin ITO films may deform when they are examined using scanning electron microscopy (SEM). Furthermore, the electrical conduction of ITO films might be affected by carrier scattering from a rough surface [4]. Therefore, the surface morphology of ITO films was studied using an AFM. Figure 1 shows the AFM images of ITO thin films deposited on PET substrate at two working pressures. As the working pressure was increased from 1 mTorr to 5 mTorr, the surface structure of the deposited films became gradually uniform. This result is similar to that of films deposited on glass substrates. Figure 2 shows the line roughness of films deposited on PET substrate at the different working pressures. Danson [5] reported that the intrinsic stress of ITO films deposited on glass, at room temperature, decreased as the working pressure increased. Stress is an important parameter with these films, determining the thickness which can be deposited and the temperature range which can be endured cycling of the film-substrate combination. Therefore, it is believed that the reduction of line-roughness with the working pressure is an indication of a decrease in stress.

The dependence of sheet resistance on DC power is shown in Fig. 3. The experiments were carried out at a

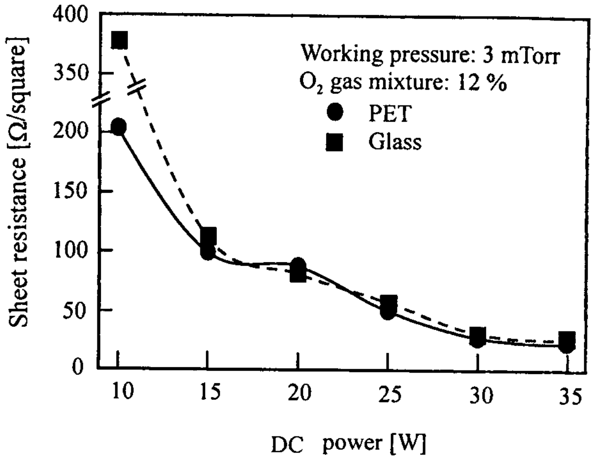

Fig. 3. Sheet resistance of ITO films on PET and glass.

working pressure of 3 mTorr, O_2 partial pressure of 12 % and a target-to-substrate distance of 4.5 cm. It can be seen that the sheet resistance decreased as the DC power increased from 10 to 35 W. That is, the resistivity and sheet resistance on PET and glass substrates were improved distinctly with the increasing power. The sheet resistance and electrical resistivity verse the working pressure are shown in Fig. 4. Both quantities increased with an increase of the working pressure at a DC power of 30 W and an O_2 partial pressure of 12 %. The best resistivities of ITO films prepared on PET and glass were 6×10^{-4} and 5×10^{-4} Ωcm, respectively and obtained

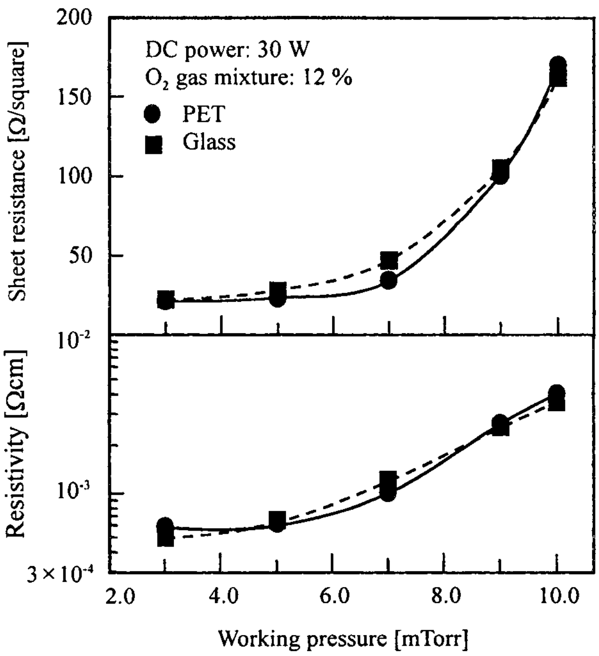

Fig. 4. Sheet resistance and resistivity of ITO films.

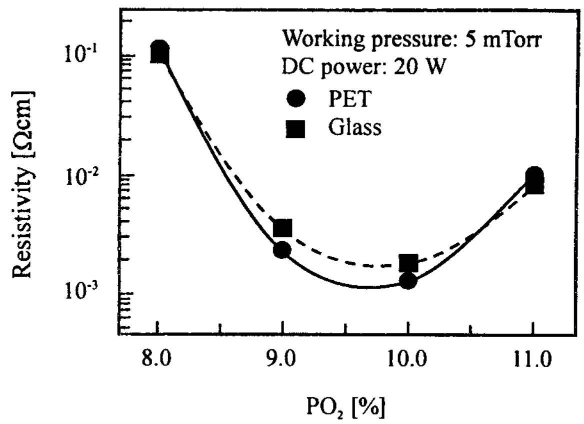

Fig. 5. Resistivity of ITO film on PET and glass as a function of PO_2.

at a working pressure of 3 mTorr.

Figure 5 shows the dependence of the resistivity of ITO films on oxygen partial pressure at a DC power of 20 W, target-to-substrate distance of 4.5 cm, and a working pressure of 5 mTorr. The resistivity decreased drastically with an increase of O_2 partial pressure from 8 to 10 % and then increased slightly. That is, the minimum resistivity was obtained at an O_2 partial pressure of about 10 %. It is considered that the higher values in the resistivity for oxygen partial pressure less than 10 % are due to the requirement of a critical oxygen content during plasma deposition to obtain completely oxidized ITO films. But, it is observed that the best film quality (i.e. minimum resistivity) is inclined with decreasing working pressure; the values are 11 and 13 % for the working pressure of 3 and 1 mTorr, respectively. It is clearly believed that the increasing trend of resistivity above the minimum value is due to the excess content of oxygen atoms in ITO films.

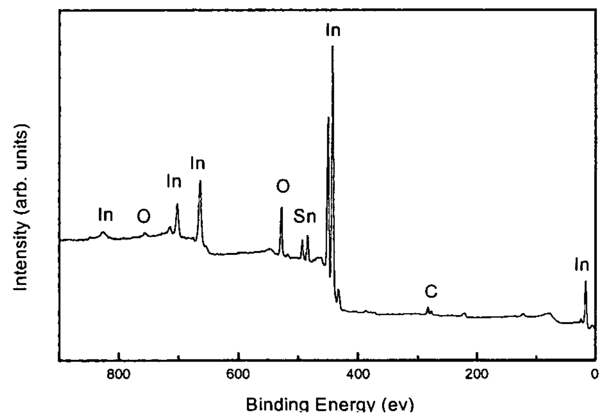

Fig. 6. Typical XPS spectrum of as-deposited ITO film prepared under 30 W of applied power and 5 mTorr.

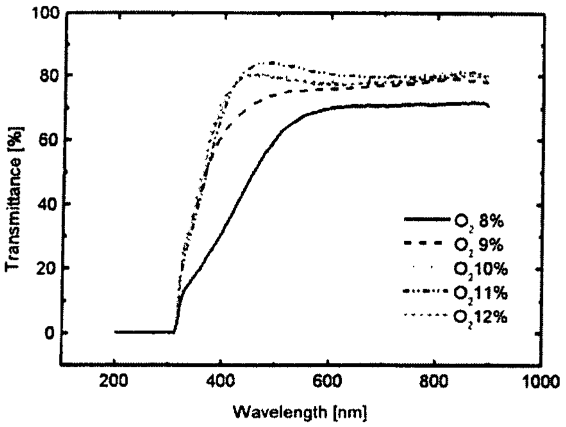

Fig. 7. Optical transmittance of as-deposited ITO films as a function of oxygen gas pressure at thickness of 125±5 nm.

Figure 6 shows typical XPS spectrum of as-deposited ITO film prepared under the DC power of 30 W, working pressure of 5 mTorr and oxygen partial pressure of 11 %. 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. Table II shows the composition of ITO films obtained from the XPS spectra at different oxygen partial pressure. The ratio of O/(In+Sn) in these films increased with an increase of O_2 partial pressure. Generally, the oxygen addition in magnetron plasma formation introduces a weak influence on the plasma density, and the sputtering yield of In and Sn decreases due to the change of plasma ions with the increasing oxygen. Subsequently, the In atoms ejected from the ITO target are reduced. Matsuda [6] reported that the optical emission intensity profile of the excited In atoms decreased because of the decrease in the sputtered In atoms from ITO target with increasing oxygen partial pressure which is in a good agreement with our results. Table III. shows the composition, obtained from the XPS spectra, as a function of DC power, of ITO films deposited on PET substrate at a working pressure of 5 mTorr, DC power of 30 W, and an O_2 partial pressure of 11 %. The In and Sn atoms ejected from the ITO target increased with an increase of DC power. Therefore, oxygen to indium and tin ratio (O/(In+Sn)) of ITO films decreased and In/O ratio increased with an increase of DC power.

Table II. Composition of ITO films with O_2 partial pressure.

PO_2[%]	In	Sn	O	O/(In+Sn)
8	45.40	1.67	52.90	1.12
9	44.71	1.77	53.70	1.15
10	43.85	1.89	54.06	1.18
11	39.19	1.40	59.41	1.46

Table III. Composition of ITO films as a function of dc power.

Power[W]	In	Sn	O	O/(In+Sn)
10	36.98	1.34	61.6	1.61
20	37.19	1.40	60.21	1.56
30	38.02	1.53	60.45	1.53
40	40.71	1.69	57.59	1.35
50	42.76	1.73	55.51	1.25

Plots of the optical transmittances of the deposited films versus oxygen partial pressure are shown in Fig. 7. No major difference, between the films deposited on glass and those deposited on PET substrates, was observed. The transmittance on PET films for the change of O_2 gas pressure from 8 to 11 % increased and reduced slightly at O_2 gas pressure above 11 %, as well as this tendency may have intimate relation to the decreasing effect of electrical resistivity as shown in Fig. 5. The enhancement of the transmittance above the O_2 gas pressure of 9 % becomes slowly saturated. A similar behavior has been reported by Ma [7] in ITO films

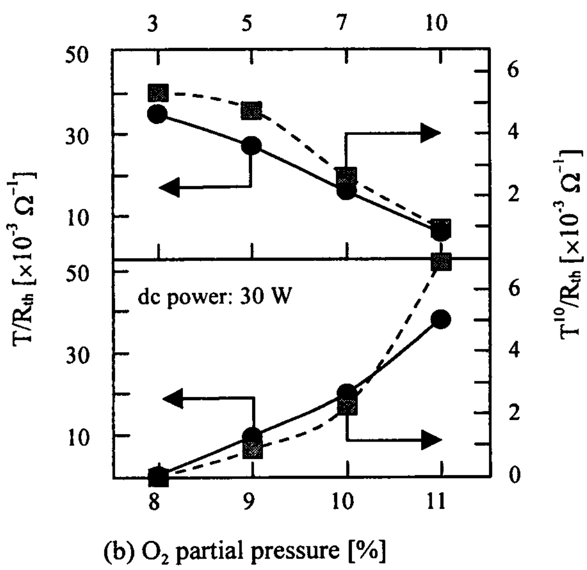

Fig. 8. Figure of merit for ITO films on PET as functions of working pressure (a) and O_2 partial pressure (b).

deposited on PET and glass at a higher substrate temperature. This result is due to a change in micro-structure and crystallinity of the deposited ITO films with the oxygen addition.

Transparent and conducting ITO films have two important factors such as optical transmittance and electrical resistivity, and those qualities are somewhat inversely related in estimating method of ITO films depending on the application. Fraser and Cook [8], and Haacke [9] reported that the figures of merit, which were based on the ratios of transmittance to sheet resistance, were frequently used to optimize the performance of TC-ITO applications. An equation defining a figure of merit is developed by Fraser and Cook F_{FC} as follows:

$$F_{FC} = T / R_{sh} \tag{1}$$

where T is the transmittance and R_{sh} is the sheet resistance. The higher values in figure of merit become, the better qualities in the TC applications are obtained. However, the figure of merit in TC-ITO applications which is more emphasis on the optical transmittance is given by Haacke and is:

$$F_{10} = T^{10} / R_{sh} \tag{2}$$

where, T^{10} is the tenth power of transmittance. The above two figures of merit are dependent on the film thickness, because both optical transmittance and sheet resistance are as a function of the film thickness. Figure 8 (a) and (b) show the figures of merit for ITO films on PET as function of working pressure and oxygen partial pressure. The figures of merit (T / R_{sh} and T^{10} / R_{sh}) reduce with an increase of working pressure. This reason is that the sheet resistance used as a denominator from the above equations increased with an increasing of working pressure as shown in Fig. 4. On the other hand, the figures of merit increase with an increase of oxygen partial pressure. In this study, the best values of T / R_{sh} and T^{10} / R_{sh} for ITO films on PET substrate are approximately 38.1 and 7.95 ($\times 10^{-3}$ Ω^{-1}), respectively, and these are sufficiently good results in comparison with other data.

4. CONCLUSIONS

ITO films are deposited on the flexible PET and glass substrates by DC reactive magnetron sputtering. In fact, the electrical and optical properties of ITO films prepared on both substrates, without post-annealing, are similar. The results are summarized as follows.

(1) From the AFM results, the surface structure of the films becomes gradually uniform with an increase of working pressure.

(2) The minimum resistivity at the fixed working pressure in Fig. 5 is obtained as a function of O_2 partial pressure. The lowest resistivities of the ITO films deposited on PET and glass substrates, at a working pressure of 3 mTorr, oxygen partial pressure of 12 % and a DC power of 30 W are 6×10^{-4} and 5×10^{-4} Ωcm, respectively.

(3) Optical transmittance on PET films increases with an increase of O_2 partial pressure from 8 to 11 % and reduced slightly at O_2 gas pressure above 11 %. This trend may have close relation to the decreasing effect of electrical resistivity.

(4) The figures of merit reduce with an increase of working pressure, and increase with an increase of oxygen partial pressure. It is due to the sheet resistance used as a denominator.

REFERENCES

[1] S. Knickerbocker and A. Kulkarni, *J. Vac. Sci. Technol.*, Vol. A14, No. 3, p. 757, 1996.

[2] S. Shin, and H. Kim, *Kor. J. Appl. Phys.*, Vol. 10, p. 453, 1997.

[3] P. Lippens, A. Segers, J. Haemers, R. de Gryse, *Thin Solid Films*, Vol. 317, p. 405, 1998.

[4] T. Minami, H. Sonohara, T. Kakumu, S. Takata, *Thin Solid Films*, Vol. 270, p. 37, 1995.

[5] N. Danson, I. Safi, G. Hall, R. Howson, *Surf. Coatings Technol.*, Vol. 99, p. 147, 1998.

[6] Y. Matsuda, Y. Yamori, M. Muta, H, Fusiyama, *Jpn. J. Appl. Phys.*, Vol. 36, p. 4922, 1997.

[7] J. Ma, S. Li, J. Zhao, H. Ma, *Thin Solid Films*, Vol. 307, p. 200, 1997.

[8] D. Fraser and H. Cook, *J. Electrochem. Soc.*, Vol. 119, p. 1368, 1972.

[9] G. Haacke, *J. Appl. Phys.*, Vol. 47, p. 4086, 1976.