Influence of Post Deposition Electro-Annealing on the Properties of ITO Thin Film Deposited on a Polymer Substrate

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Abstract   Transparent ITO films were deposited on a polycarbonate substrate with RF magnetron sputtering in a pure argon (Ar) and oxygen (O_2) gas atmosphere, and then post deposition electro annealed for 20 minutes in a 4×10^{-1} Pa vacuum. Electron bombardment with an accelerating voltage of 100 V increased the substrate temperature to 120°C. XRD analysis of the deposited ITO films did not show any diffraction peaks, while electro annealed films indicated the growth of crystallites on the (211), (222), and (400) planes. The sheet resistance of ITO films decreased from 103 to 82 $\Omega/\square$. The optical transmittance of ITO films in the visible wavelength region increased from 85 to 87%. Observation of the work function demonstrated that the electro-annealing increased the work function of ITO films from 4.4 to 4.6 eV. The electro annealed films demonstrated a larger figure of merit of $3.0 \times 10^{-3}\ \Omega^{-1}$ than that of as deposited films. Therefore, the electro annealed films had better optoelectrical performances than as deposited ITO films.

Key words   indium tin oxide, sputtering, electro-annealing, XRD.

1. Introduction

Transparent conducting indium tin oxide (ITO) films deposited on glass substrates have been used in various optoelectronic devices such as photovoltaic devices and displays.[1-2] However, a glass substrate is unsuitable for certain flexible displays and solar cell applications as stiff glass is brittle and heavy. In order to overcome these disadvantages, flexible polymer substrates have been recently used instead of glass.[3] Additionally, interest in ITO films deposited on transparent polymer substrates has been increased due to the potential application of flexible organic light emitting diodes (OLEDs).[4]

However, ITO films deposited on polymer substrates demonstrate a relatively high resistivity because substrate heating, which is used to assure low resistivity by grain growth, is limited due to the low thermal stability of the substrate. As a result, synthesis of polymer substrates with high glass transition temperatures has been investigated and various low temperature deposition methods have been implemented.[5-6]

In this study, the effect of post deposition electro annealing on the structural and optoelectrical properties of ITO films deposited on polycarbonate (PC) substrates with RF magnetron sputtering was investigated with X-ray diffraction (XRD), atomic force microscopy (AFM), four point probes and UV-Vis. spectrophotometer.

2. Experimental Procedures

A commercial, transparent PC substrate with a thickness of 100 μm and average surface roughness of 2 nm was used as a substrate for all depositions. ITO films were prepared by RF magnetron sputtering a Sn doped In_2O_3 target ($In_2O_3/SnO_2 = 90/10$ Wt. %, 3 Inch Dia.).

Fig. 1 shows the experimental sputter system and electron beam source used to deposit ITO films (INFO-RFE-60G, Infovion). The electron source was comprised of an inner RF (13.56 MHz) coil antenna to discharge Ar plasma and a two grid electrode to collimate and accelerate the electron beam to the substrate. Post deposition electro annealing was subsequently conducted in a 4×10^{-1} Pa vacuum. The distance from the target to the substrate was 100 mm.

Prior to deposition, the chamber was evacuated below 1×10^{-4} Pa and high purity argon (Ar) and oxygen (O_2) gases were injected with separate gas nozzles to sputter the target and substrate, respectively. During deposition, the working pressure was maintained at 2×10^{-1} Pa. Although the PC substrate was not heated intentionally, the substrate temperature increased to 70 ^{o}C by plasma

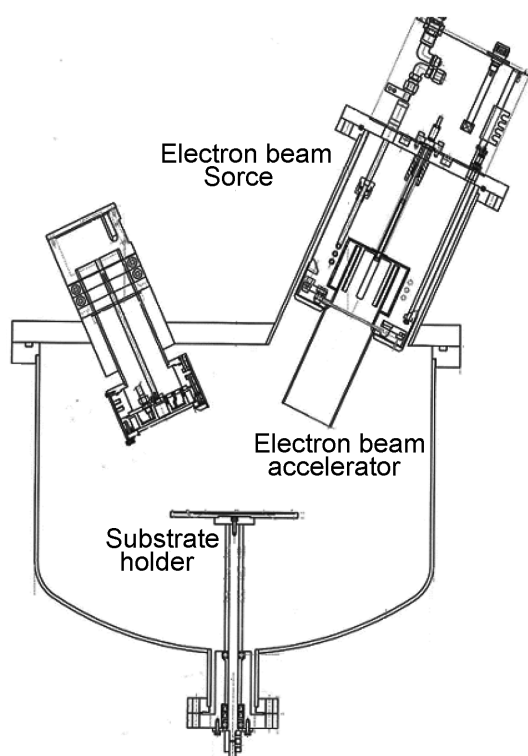[†]Corresponding author
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Fig. 1. A schematic diagram of reactive magnetron sputtering and electro-annealing system

Table 1. Deposition conditions of transparent ITO films.

Parameter	Condition
Base pressure (Pa)	1×10^{-4}
Deposition pressure (Pa)	2×10^{-1}
Power density (W/cm^2)	RF, 3
Deposition rate (nm/min)	14
Gas flow rate (Ar/O$_2$ sccm)	6 / 0.04

bombardment. All of the 100 nm ITO films were obtained with a RF sputtering power density of 3 W/cm^2. After post deposition, electro annealing with an electron accelerating voltage of 100 V increased the substrate temperature up to 120 °C.

Tables 1 and 2 show the deposition conditions and annealing parameters. The crystallinity of the post deposition electro-annealed films was investigated with XRD (X'Pert APD, Phillips) using Cu Kα (1.54Å) radiation at the Korea Basic Science Institute (KBSI). The optical transmittance and sheet resistance (Rs) were measured with a UV-Vis. spectrophotometer (Carry100 Cone, Varian) and a four point probe (MCP-T610, Hitachi), respectively. The surface morphology and root mean square (RMS) roughness of the films were measured at atmosphere with tapping mode AFM (Nanoscope II, Digital Instruments),

Table 2. Electro-annealing conditions of transparent ITO films

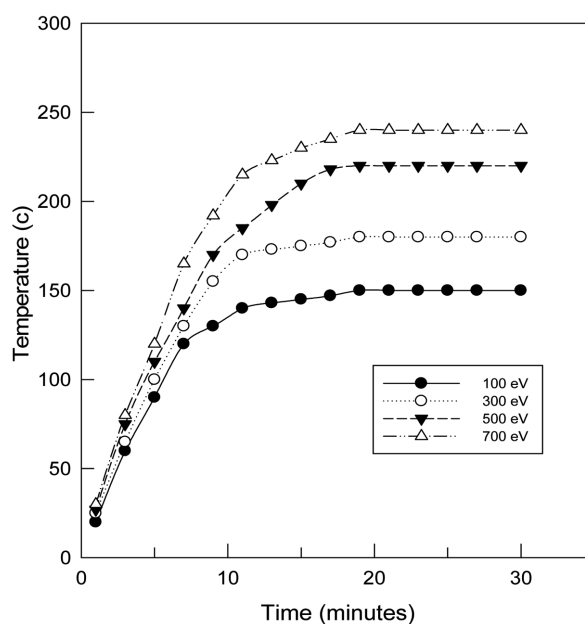| Parameter	Condition
Process pressure (Pa)	4.1×10^{-2}
RF Power (W)	4 K
Accelerating Voltage (V)	300, 600, 900
Ar gas flow (sccm)	5
Annealing Time (Min.)	20

Fig. 2. The variation of temperature of ITO film as a function of electron accelerating voltages.

respectively. In addition, for organic light emitting diode (OLED) applications of electro annealed ITO films, the variation of the work function was observed with a Kelvin probe system (KP 6500, McAllister Technical Services).

3. Results and discussion

Fig. 2 shows the relationship between the electron accelerating voltage and substrate temperature. Although electro annealing may increase the substrate temperature up to 300 °C, ITO films were electro annealed with an accelerating voltage of 100 V, which assures a substrate temperature of 120 °C due to the low melting temperature of the flexible polymer substrate. The structural characterization was very important for explaining the optical transmittance and electrical resistivity of transparent conducting oxide (TCO) films.

Fig. 3 shows the XRD patterns of as deposited and electro annealed films. As deposited ITO films did not show any diffraction peaks. Similarly, Sun et al.
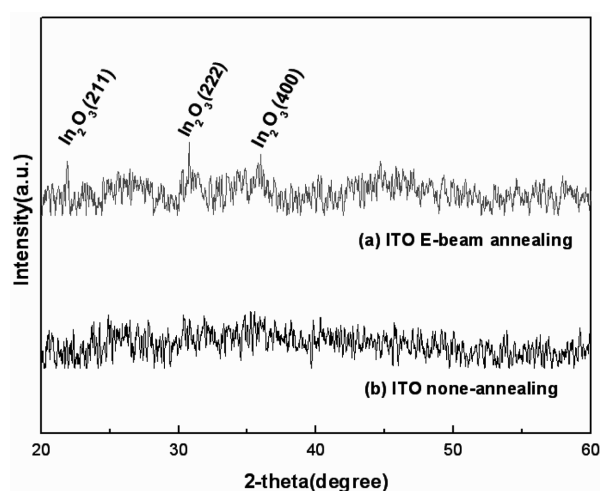
Fig. 3. XRD patterns of as deposited and post deposition electro-annealed ITO films.

Fig. 4. AFM images of as deposited (a) and post deposition electro-annealed ITO films (b). (X scale: 0.5 m/Div., Y scale: 10 nm/Div.)

Investigated the initial growth mode of ITO on a glass substrate over the substrate temperature range of 20-400 ^{o}C and suggested that ITO films formed at substrate temperatures below 150 ^{o}C had an amorphous structure.[7] The amorphous XRD pattern of as deposited ITO films in Fig. 3(a) was consistent with the results of Sun et al.[7] However, electro annealed films demonstrated the same diffraction peaks for In_2O_3 that correspond to the refractions of (211), (222), and (400). The intensity of the (222) diffraction peak was greater than that of other planes, demonstrating that electro annealed ITO films crystallized into a cubic bixbyite structure. To this end, electro annealing may promote crystallization of the ITO films, even at a low substrate temperature of 120 ^{o}C.

For OLED's, organic films are directly deposited on the ITO film and the surface morphology will affect the characteristics of the OLED as well as the optoelectrical properties of the films.[8] Fig. 4 shows the AFM image of ITO films with and without electro annealing. The average roughness of as deposited and electro annealed ITO films was 0.5 and 0.7 nm, respectively. As deposited ITO films manifested a smooth surface, while annealed films showed a few aggregations, resulting in a rougher surface than that of the as deposited films.

The transmittance of ITO films was also important for its application in displays. The optical transmittance spectra in the UV-Vis. regions of ITO films with or without electro-annealing are shown in Fig. 5. It is evident that both as deposited and electro annealed films have comparable transmittance, with a better performance for as deposited
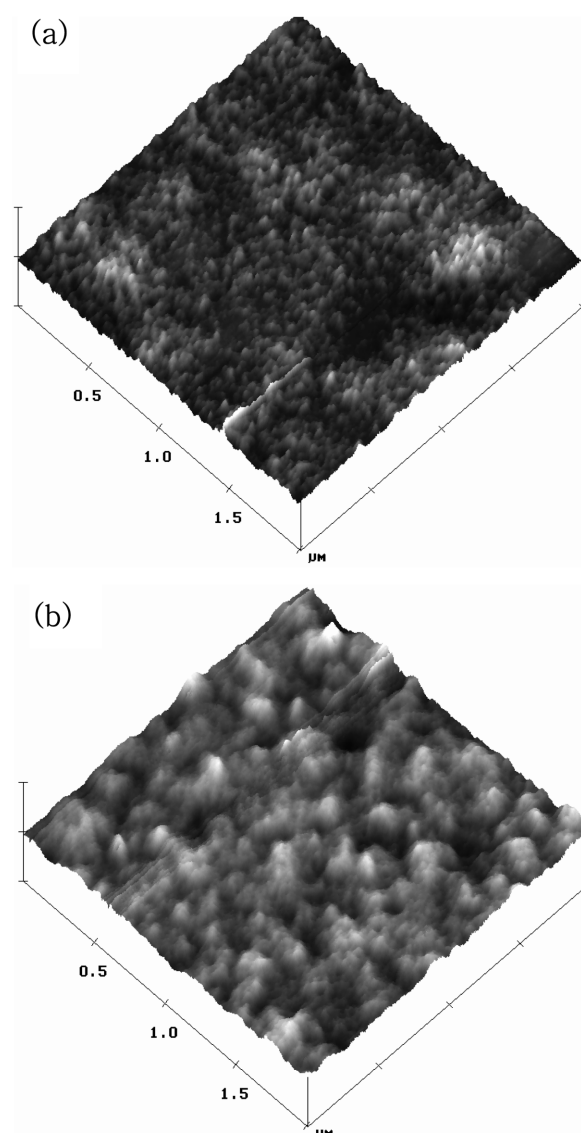
ITO at long wavelengths and for annealed ITO films at short wavelengths. The transmittance of as deposited films in the visible wavelength region was about 85% and increased to 87% after electro-annealing. It is well known that the transmittance of ITO films depends upon the crystallinity because large grains reduce grain boundary scattering and absorption of visible light.[9] As shown in the XRD pattern, the improved transmittance of annealed ITO films was attributed to the crystallization of the films. Recently D. Lee reported similar results that electro-annealed ITO films show the higher transmittance than that of as deposited ITO films for wavelength longer than
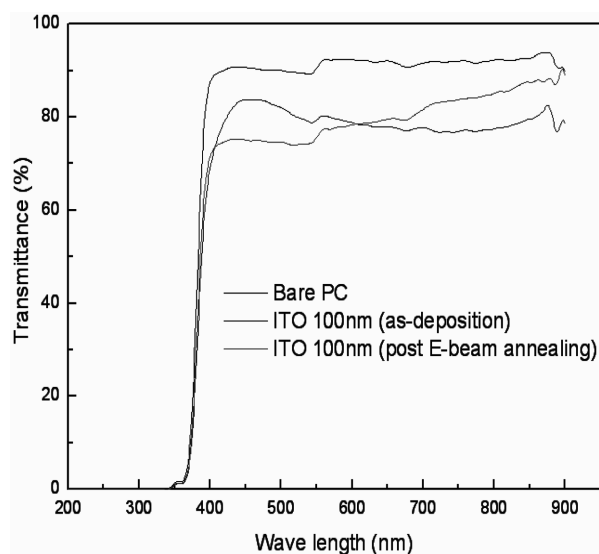
Fig. 5. Optical transmittance of as deposited and post deposition electro-annealed ITO films.

500 nm, while under lower wavelength condition (≤ 500 nm) there is no big difference between as deposited ITO and electro-annealed ITO films. However it needs more study to explain the cross-over of the transmittance spectra at wavelength of 600 nm in Fig. 5.[10]

Table 3 shows the Rs and figure of merit (F_{TC}) of as deposited and electro annealed ITO films. The Rs of electro annealed films (82 Ω/□) was lower than that of thermal annealed films (103 Ω/□). The lower Rs values in electro annealed films were attributed to increased crystallization as indicated by the XRD analysis. Table 3 also shows the work function of as deposited and surface treated films with variant methods. It is well known that the work function of Ar plasma treated ITO films is 4.3 eV.[11] Recently, K. Sugiyama reported a work function of 4.5 eV on ITO film cleaned acetone and propanol vapor.[12] In Table 3, the measured work function of electro annealed ITO films was greater than that of K. Sugiyama's and as deposited ITO films. Thus, it may be concluded that electro annealing is a useful method to increase the work

Table 3. Comparison of sheet resistance (Ω/□), optical transmittance (%, without substrate), work function (eV) and figure of merit ($10^{-3}\Omega^{-1}$) of as deposited and electro-annealed ITO films.

	As deposited ITO	Electro-annealed ITO
Sheet resistance	103.2	82.3
Transmittance	85	87
Work function	4.4	4.6
Figure of merit	0.3	6.4

function of ITO films deposited on flexible polymer substrates at low temperature (≤ 120 °C). The figure of merit (F_{TC}) is an important index for evaluating the performance of TCO films.[13] The F_{TC} is defined by

$$F_{TC} = T^{10} / R_s$$

where T is the optical transmittance in the visible wavelength region and R_s is a sheet resistance. The F_{TC} for ITO films with and without electro annealing is compared in Table 2. The F_{TC} reaches a maximum at $3.0 \times 10^{-3} \Omega^{-1}$ for electro annealed films, which was greater than the F_{TC} ($1.9 \times 10^{-3} \Omega^{-1}$) of as deposited ITO films.

4. Conclusions

ITO films were deposited on PC substrates by RF magnetron sputtering without intentional substrate heating and the effect of post deposition electro annealing on the crystallinity and optoelectrical properties was investigated by electron beam irradiation. The electron beam irradiated ITO films show the diffraction peaks from the (222), (222) and (400) planes by thin film crystallization. The Rs also reduced from 103 to 82 Ω/□. The transmittance in the visible wavelength region improved by electro annealing, however, the average roughness of electro annealed ITO films increased due to thin film crystallization.

The electro annealing method was quite effective for increasing the optoelectrical performance of ITO films. Electro annealed ITO films that were deposited on PC can be applied for the transparent electrodes of variant flexible displays.

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