Effect of Ar Ion Beam Pre-Treatment of Poly(ethylene terephthalate) Substrate on the Mechanical and Electrical Stability of Flexible InSnO Films Grown by Roll-to-Roll Sputtering System

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We investigated the effects of Ar ion beam irradiation on a flexible poly(ethylene terephthalate) (PET) substrate as surface pre-treatment method in the roll-to-roll (R2R) sputtering system and its contribution to the electrical durability of flexible InSnO (ITO) electrode upon that the flexible PET substrate under repeated mechanical stresses. It was found that the Ar ion beam irradiation of the flexible PET surface could improve an adhesion between R2R sputter-grown ITO film and the PET substrate. X-ray photoelectron spectroscopy results showed that the Ar ion beam irradiation lead to an increase of hydrophilic functional groups when the working pressure, Ar ion beam power, and exposure time increases. Repetitive bending stresses for the flexible ITO/PET film which fabricated through the surface pre-treatment by Ar ion beam irradiation showed more stable electrical durability than those of ITO films on the wet-cleaned PET substrate due to enhanced interfacial adhesion between the ITO film and PET surface. This suggests that the Ar ion beam pre-treatment before sputtering of ITO film in R2R sputtering system is an effective technique to improve the adhesion between ITO film and PET substrate. © 2013 The Japan Society of Applied Physics

1. Introduction
Flexible transparent conducting oxide (TCO) has been considered one of the key components for flexible displays and solar cells. Especially roll-to-roll (R2R) sputtered TCO films have been extensively used as a flexible electrode in flexible optoelectronic devices and touch panels due to its merits such as mass and fast production and large-area coating. Until now, Sn-doped In$_2$O$_3$ (ITO) films prepared by R2R sputtering has mainly employed in flexible displays, solar cells and touch panels due to its high conductivity and transparency. To obtain high quality flexible ITO films, a good adhesion between ITO and flexible substrate should be considered because the flexibility or mechanical properties of the R2R sputtered ITO film was critically dependent on the adhesion of the ITO films. For this reason, several research groups have investigated the cleaning techniques of flexible substrates.\(^1\)–\(^6\) However, considering roll-type flexible substrates in a R2R sputtering system, the organic solvents-based batch-type cleaning process is unsuitable. Therefore, ion beam treatment technique has been the subject of considerable attention as a pre-treatment process for flexible substrate in the R2R sputtering process. Even though the basic studies for single cell ion irradiation effects of polymer substrates have been carried out, the characteristics of linear Ar ion beam irradiation effect on the properties of the ITO film grown and its contribution to the electrical durability of flexible ITO electrode upon that the flexible poly(ethylene terephthalate) (PET) substrate under repeated mechanical stresses in R2R sputtering system have not been investigated in detail.\(^7\)\(^,\)\(^8\)

In this work, we investigated the effect of energetic Ar ion beam pre-treatment on the surface of the PET substrate and electrical durability of the R2R sputtered ITO films on the surface modified PET substrate. The details of chemical states of the surface of the PET substrates before and after ion irradiation were analyzed by means of X-ray photoelectron spectroscopy (XPS). Furthermore electrical and mechanical stabilities of the R2R sputtered ITO films on PET substrates before and after ion irradiation were compared by using a lab-scale bending test system.

2. Experimental Methods
Flexible ITO films were prepared on a commercial PET substrate by using lab-scale R2R sputtering system (Sntek). Prior to ITO sputtering, the surface of PET substrate was pre-treated by means of a specially designed linear ion beam treatment system. The linear ion beam source was equipped below cooling drum in the R2R sputtering system. A schematic of the linear ion source in the R2R sputtering system is shown in Fig. 1. It was designed that neutral Ar gas could be easily ionized between the cathodes in the linear source by collision with energetic electrons, which was controlled by internal magnetic fields. High positive voltage applied in anode led to emission of ionized Ar ions as a shape of linear beam. The picture in Fig. 1 showed the Ar ion beam ejected from linear ion gun. For ion beam treatment, the 200 mm width roll-type PET substrate with a thickness of 188 \(\mu\)m was passed over the cooling drum by motion of unwind and rewind roller. The rolling speed of the PET substrate can be exactly controlled by the motor speed by unwind and rewind roller. The linear ion source was placed at a distance of 100 mm from a PET substrate and Ar ion beam incidence angle was 90\(^\circ\). Prior to the ITO sputtering, the surface of PET substrate was pre-treated by the irradiation of an Ar ion beam at constant Ar flow rate of 20 sccm as a function of working pressure, pulsed DC power, and rolling speed. Subsequently, the 150-nm-thick ITO film was sputtered on the PET substrate, which is mechanically attached on cooling drum. Chemical binding energy of the PET substrate before and after Ar ion beam treatment was analyzed by means of XPS analysis. To compare the Ar ion beam treatment with chemical cleaning, solvent cleaned PET substrate was also prepared. The XPS spectra were obtained using a ESCALAB 210 system with monochromatic Al K\(\alpha\) source. The surface of all Ar beam irradiated samples was immediately investigated by water contact angle measurements. The contact angles between the
distilled water and the ion beam modified PET substrate were measured at room temperature with a droplet method. The electrical durability of the ITO films grown on the PET substrates before/after Ar ion beam treatment was measured by lab-made bending test system. Repeated bending frequency and bending radius were maintained at 60 Hz and 8 mm, respectively.

3. Results and Discussion

Figure 2(a) shows driving voltage of linear ion gun as a function of driving current for difference working pressure levels from 0.8 to 7 mTorr. It was found that there were threshold working pressure levels required to sustain the Ar ion beam in the system. At working pressure of 0.8 and 0.9 mTorr, we could not sustain the Ar plasma at driving current above 0.1 A. However, higher working pressure levels above 1 mTorr, we were able to obtain a stable Ar ion beam over the measured driving current region that exhibits relative small voltage changes to maintain the Ar ion beam. Therefore, we set the working pressure levels above 1 mTorr for stable Ar ion beam operation. Figure 2(b) shows water contact angle on Ar ion beam irradiated PET surface as a function of working pressure. With increasing working pressure levels above 1 mTorr, the contact angle of Ar ion beam treated PET substrate was dramatically decreased to 45, indicating a hydrophilic surface by Ar ion beam treatment. However, further increase of working pressure led to increase of a contact angle due to reduced electron temperature relating to ionization energy and Ar ion-neutral collisions. Kausik et al. reported that increasing the chamber pressure resulted in a decrease of electron temperature. Therefore, we fixed the optimized working pressure for surface treatment as 5 mTorr for stable Ar ion beam operation. Figure 2(c) shows water contact angle on Ar ion beam irradiated PET surface as a function of working pressure. With increasing working pressure up to 5 mTorr, the contact angle of Ar ion beam-treated PET substrate was dramatically decreased to 45, indicating a hydrophilic surface by Ar ion beam treatment. However, further increase of working pressure led to increase of a contact angle due to reduced electron temperature relating to ionization energy and Ar ion-neutral collisions. Kausik et al. reported that increasing the chamber pressure resulted in a decrease of electron temperature. Therefore, we fixed the optimized working pressure for surface treatment as 5 mTorr. Figure 2(c) shows the water contact angle of Ar ion beam-treated PET surface prepared at constant working pressure of 5 mTorr, rolling speed of 0.1 cm/s, and Ar flow rate of 20 sccm as a function of pulsed DC power. With increase of pulsed DC power from 0 to 200 W, a significant decrease in contact angle from 61.8 to 26.7 was observed from the PET surface indicating improved wettability after Ar ion beam treatment. Similar results were obtained from the Ar ion irradiated PET substrate as a function of the rolling speed at fixed DC power injection of 200 W, working pressure of 5 mTorr, and Ar flow rate of 20 sccm as shows in Fig. 2(d). In the R2R Ar ion beam system, an exposure time was mainly controlled by rolling speed of substrate. With decreasing rolling speed, the water contact angle significantly decreased from 60.4 to 20.6. These pulsed DC power and exposure time dependencies of hydrophilic behavior of PET surface can be explained by ionized Ar beam intensity (ion flux). Because an increase of pulsed DC power at the linear ion source region can yield an increase of the ionization of neutral Ar gas, the surface of PET substrate can be effectively treated by elevated Ar ions (Ar ion flux: Φ). On the other hand, longer exposure time of Ar ion beam enables the PET surface to meet a quantitatively more ionized Ar particles in surface treatment process.

With the objective to analyze the surface chemical binding energy of Ar ion beam-irradiated PET substrate, XPS measurement was carried out as shown in Fig. 3. Figures 3(a) and 3(b) show the XPS results obtained from core C 1s and O 1s levels with untreated, solvent-cleaned, Ar ion beam irradiated PET surfaces at pulsed DC power of 200 W, respectively. The XPS spectra were curve fitted and each curve was assigned to the corresponding bond of the PET. The C 1s spectra were convoluted into the three distinct peaks located at 284.5, 286.18, and 288.5 eV, corresponding to the carbon bonds of the phenyl ring (C–C), methylene carbon atoms singly-bonded to oxygen (C–O), and ester carbons (O–C=O), respectively. After solvent cleaning of PET surface, PET surface showed slightly shift chemical state as shown in Fig. 3(a). However,
it can be observed that Ar ion beam-irradiated PET surface that C 1s components, methylene carbon atoms singly-bonded to oxygen (C–O), and ester carbons (O–C=O), had remarkable reduction of relative XPS signal intensity compared with phenyl carbon bonds. Figure 3(b) shows O 1s peaks resulting from the untreated, solvent treated and Ar ion beam treated PET samples. Two distinct binding energies can be assigned by the doubly-bounded oxygen species corresponding to the peak located at 531.52 eV and the singly-bounded oxygen at 533.09 eV. Before the Ar ion beam treatment, singly-bounded and doubly-bounded oxygen chemical states of PET surface would be regarded to have equal intensity indicating one carbonyl and one ester oxygen in the ester group. However, dramatic reduction in peak intensity of singly-bounded oxygen (533.09 eV) and doubly-bounded oxygen states (531.52 eV) were observed after Ar ion beam irradiation of PET surface. It is noteworthy that the C–O and C=O chemical states at the surface are significantly reduced after Ar ion beam irradiation. Especially, those values showed lower peak intensities than that of chemical states of PET surface prepared through the organic solvent treatment. In our experiment the oxygen inflow was completely excluded during the Ar ion beam irradiation, the chemical states changes at the film surface can be interpreted as a consequence from the energetic Ar ion particle bombardment. Therefore, it can be thought that the energetic Ar ion particles effectively modified the metal-stable chemical states at PET polymer surface related to C=O, C–O states, and thus offered the hydrophilic functional groups at the PET surface.

To investigate the mechanical stability and flexibility of the R2R sputtered ITO films on a PET substrate before and after Ar ion beam treatment, a laboratory-made bending test system was employed as shown in Fig. 4(a).
sputtering conditions and showed a sheet resistance of 22Ω/square and transmittance of 80% (not shown here). The change in resistance was expressed as \( \Delta R = R - R_0 \), where \( R_0 \) is the initial resistance and \( R \) is the measured resistance after bending and stretching. Figure 4(b) shows changes in the resistance of the R2R sputtered ITO film before and after Ar ion beam treatment of the PET substrate. Ar ion beam was irradiated to the PET substrate at a power of 200 W, working pressure of 5 mTorr and rolling speed of 0.1 cm/s. In case of the ITO film grown on the untreated or solvent treated PET substrate, they showed larger \( \Delta R/R_0 \) values with increasing bending cycles due to the generation and propagation of cracks. Whereas the R2R sputtered ITO film grown on the Ar ion beam irradiated PET substrate showed a fairly constant \( \Delta R/R_0 \) value throughout the bending and stretching test. Compared to the ITO films grown on the untreated and solvent-cleaned PET substrates, the ITO films grown on the Ar ion beam irradiated PET substrate showed better mechanical and electrical stability under repeated stresses. Ratchev et al. reported that the ion beam treatment of PC substrates caused substantial improvement in adhesion strength between Al film and PC substrates.\(^{22}\) Therefore, the Ar ion beam irradiated the PET substrate during R2R sputtering process could result in the improvement of the adhesion between the ITO electrode and PET substrate.

4. Conclusions

We investigated the effect of Ar ion beam pre-treatment of PET substrates on the electrical and mechanical properties of ITO films grown by R2R sputtering. It was found that the Ar ion beam irradiation on the flexible PET surface before ITO deposition could effectively improve an adhesion between ITO film and the PET substrate. XPS results showed that the Ar ion beam irradiation led to decrease in yield of hydrophilic functional groups while an increase of Ar ion beam power and working pressure led to increase hydrophilic functional groups. Repeated bending test of the ITO films grown on the Ar ion beam treated PET substrate showed more stable mechanical and electrical properties than ITO films grown on the wet cleaned PET substrate due to better adhesion between the ITO film and PET substrate. This suggests that the Ar ion beam pre-treatment before deposition of ITO film in R2R sputtering is an effective technique to improve the adhesion between ITO film and PET substrate.

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Fig. 4. (Color online) (a) A picture of lab-scale bending tester system and (b) electrical stability measurement results under the repeated mechanical stresses of the ITO/PET electrodes which experienced the various surface treatments of PET substrate.