EFFECT OF ITO SURFACE TREATMENT ON ORGANIC SOLAR CELLS

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ABSTRACT

The effect of N_2 plasma, O_2 plasma, and electron beam surface treatments on ITO-coated glass substrates for organic solar cells has been studied. The efficiency of ITO / PEDOT:PSS / CuPc / C_{60} / Al solar cells built on N_2 plasma-treated ITO substrates was nearly double that of cells built on untreated substrates. This improvement is attributed to an increased hydrophilic nature of the surface, decreased surface roughness, and a slight decrease in the In/Sn ratio in the ITO films.

INTRODUCTION

Organic solar cells incorporate transparent conducting substrates as an anode, with indium-tin-oxide (ITO) coated glass most often used. ITO films offer several positive characteristics as substrates for optical devices, including a high luminous transparency, good electrical conductivity, and good infrared reflectivity. For these reasons, ITO is widely adopted as transparent anodes in light-emitting diodes, liquid crystals, and solar cells [1-3]. ITO coated glass substrates are commercially produced by sputtering process followed by subsequent processes to improve surface roughness and microstructure. As-received substrate surface, however, has to be further processed prior to applying to the current flowing devices (e.g. OLEDs, solar cells, etc.), because sputter-deposited surface can be degraded in its microstructure and chemical composition during extended device operations. Surface treatment of ITO surface by several techniques can alter the chemical and physical property of surface such as workfunction, surface roughness and oxidation property, and thus it could affect the device performance.

In this study, nitrogen and oxygen plasma treatment along with electron bombardment of commercially available ITO-coated glass substrates were revisited as approaches to improving the efficiency and stability of organic solar cells. The effect of these surface treatments on the surface morphology and chemical composition was characterized, and organic solar cells with the structure ITO/PEDOT:PSS(50 nm)/CuPc(25 nm)/C_{60}(15 nm)/Al(100 nm) were fabricated and the device performance measured.

EXPERIMENTAL

The substrates used in this study were commercially available ITO-coated glasses with an ITO film thickness of ~ 1800 Å and sheet resistance of ~7 Ω/sq. As-received substrates were chemically cleaned by sequential ultrasonification in trichloroethylene (TCE), acetone, and methanol, followed by nitrogen blow-drying. The cleaned

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substrate was then exposed to either a nitrogen or oxygen plasma or an electron beam. Plasma treatment was carried out in a barrel-type plasma chamber for 10 min at a power input in the range 50 to 300 W and pressure in the range 50 mTorr to 1 Torr with N_2 gas flow. Electron beam irradiation was performed for 15 sec in a nitrogen environment with beam power varied from 0.5 to 2 kGy (kJ/kg). After treatment a PEDOT:PSS layer was spin-coated and dried in a vacuum oven. Organic films (CuPc and C_{60}) and aluminum were deposited at room temperature in a thermal evaporator with a base pressure of 2.0×10^{-6} Torr. The chemical composition and surface morphology of the ITO surface were measured using XPS, AFM, and a video contact angle system (VCAS). Power conversion efficiencies were measured under illumination from a solar simulator set to produce an AM 1.5 100 mW/cm^2 spectrum.

RESULTS AND DISCUSSION

The measured contact angle of a water droplet on an ITO substrate changed significantly after surface treatment. The contact angle for untreated ITO substrates was ~ 65º, while films subjected to electron beam treatment showed a reduced contact angle of ~ 50º. After exposure to the N_2 plasma, the contact angle decreased dramatically to a value < 10º. In both cases, the reduction is due to two effects. First, the exposure to reactive radicals removes contamination from the film surface that may have remained after the wet chemical cleaning. Secondly, these treatments increase the activity of the film surface by incorporating nitrogen radicals into the film. This effect is significantly stronger in the case of N_2 plasma than in the case of electron beam treatment because the plasma treatment supplied a greater flux of highly reactive nitrogen radicals to the film surface. The change in surface polarity In the case of electron beam treatment was not as significant as that in the case of plasma treatment, and as electron beam energy is further increased (larger than 2 kGy), the ITO film started to change its color to light gray, which degraded the luminous transparency of the substrate.

AFM measurements were performed to quantify the surface roughness of the ITO films. As-received ITO films showed a RMS surface roughness of 1.1 nm. This value was reduced to 0.8 nm by electron beam treatment and < 0.6 nm by N_2 plasma treatment at optimized conditions. Sputtered ITO film generally contains irregular surface features, even though the subsequent polishing and annealing of the film improves its roughness. The surface treatment procedures used in this study are expected to attack the higher surface features first, resulting in a decrease in surface roughness [4, 5]. The effect, however, was not very significant, because surface roughness of the as-received substrate was low enough.

XPS spectra from treated films showed a change in the chemical composition of the film surface. Films treated with N_2 plasma and electron beam bombardment showed an increase in nitrogen content accompanied by a decrease in oxygen composition, confirming that oxygen is replaced by nitrogen in films subjected to these treatments (see Table 1). In the case of N_2 plasma exposure, there was a decrease in the In/Sn ratio of the films as well, which can cause a slight decrease in the work function of the films [6]. It is believed this change is a result of indium reacting with nitrogen radicals to form InN, which is subsequently removed from the film. Chemical shift of In-Sn-O bonding was also investigated by XPS, but noticeable change in chemical shift was not observed in the treatment conditions investigated in this study.

Table 1. Chemical Composition of ITO Films

Condition	Atomic Percent				Atomic Ratio	
	O	Sn	In	N	O/In	In/Sn
No Treatment	56.75	2.65	40.6	-	1.397	15.32
N_2 Plasma[a]	55.49	2.67	40.49	1.35	1.37	15.16
e-Beam[b]	56.67	2.38	38.76	2.19	1.462	16.28

[a] After N2 Plasma Treatment at 50 W, 1 Torr, 10 min

[b] After e-Beam Treatment at 2kGy

The incorporation of nitrogen into the near surface region of films treated in N_2 plasma was confirmed by glow discharge spectroscopy (GDS). Films exposed to the plasma at a constant power but increasing pressure showed an increase in nitrogen levels in the film up to 700 mTorr. At higher pressures the nitrogen level decreased slightly, due to a decrease in nitrogen radical activity in the plasma.

Organic solar cell devices were fabricated from the surface-treated ITO films to determine the impact on device performance (see Fig. 1 and Table 2). Electron beam treatment produced no change in device efficiency; however, there was a decrease in V_{OC} and an increase in J_{SC} in these devices. O_2 plasma treatment gave a slight increase in J_{SC}, but a significant drop in V_{OC} led to a reduction in overall device efficiency. N_2 plasma treatment resulted in cells with efficiency nearly double that of the untreated ITO cells. All treated ITO devices showed an improvement in the shape of the I-V curve compared to that of untreated ITO devices. The changes in performance can be attributed to several effects due to the treatment, including surface roughness, chemical stability, and reduced work function. Electron beam and N_2 plasma treatment replace oxygen with nitrogen, reducing the electron affinity of the ITO film and resulting in a lowering of the work function that improves the charge collection efficiency.

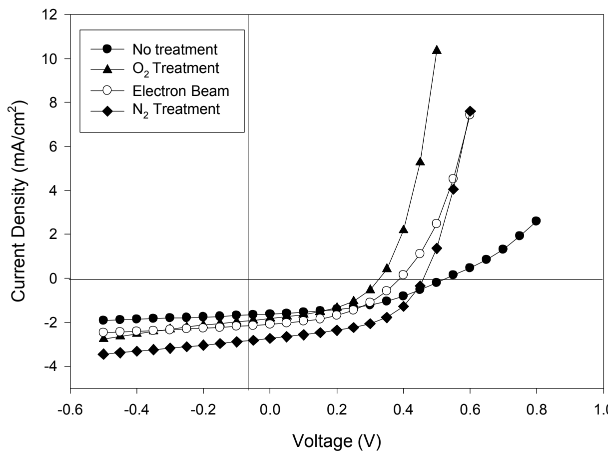

Figure 1. I-V Curves of Organic Solar Cells

Table 2. Performance of Solar Cells

Treatment	V_{OC} (V)	J_{SC} (mA/cm^2)	η (%)
None	0.52	1.61	0.36
N_2 Plasma	0.46	2.73	0.62
E-Beam	0.38	2.08	0.36
O_2 Plasma	0.32	1.82	0.27

SUMMARY

The effect of several ITO surface treatments on the performance of organic solar cells was determined. It was shown that exposure to a N_2 plasma was more beneficial than either the oxygen plasma or e-beam treatment. The N_2 plasma was most successful in improving the surface characteristics, as evidenced by the extent of lowering the contact angle and decreasing the surface roughness (AFM). This treatment incorporates nitrogen into the near surface region and produces a slight change in the In/Sn ratio, which reduces the ITO work function. These changes optimize the energy band diagram and improve charge collection at the ITO anode.

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