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FAST TRACK COMMUNICATION

Enhanced photovoltaic device performance upon modification of indium tin oxide coated glass by liquid nitrogen treatment

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Abstract
We demonstrate the improvement in the surface properties of an indium tin oxide (ITO) anode contact to an organic bulk-heterojunction device via cooling down the ITO glass substrate by liquid nitrogen treatment. This treatment effectively improves the smoothness of ITO glass, the transmittance and the contact angle measurement, which thereby results in fairly good contact with organic material. The enhancement of short circuit current, efficiency and fill factor of the photovoltaic devices was also achieved. The surface properties of both the untreated and the treated ITO substrates were studied by atomic force microscopy and the electrical properties of the substrates were studied by the Hall effect measurement.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Improvement in the efficiency of organic optoelectronic devices is a challenge for scientists all over the world. This challenge is a great motivation for scientists to further improve organic devices in various ways such as surface treatment on ITO coated glass (hereafter called ITO) [1, 2], annealing effect [3], thickness of the organic material [3–5] and plasma treatment [6, 7]. In the field of organic devices, ITO is commonly used to inject positive charge carriers into the organic polymer layer. Device performance depends in a crucial way on the energy difference between the electrode work function and the highest occupied molecular orbital (HOMO) of the organic material. Efficient generation of exciton, dissociation and transport of free charge carriers to good contacts between the electrodes determine the efficiency of organic photovoltaic devices. In general, ITO is considered as a heavily doped and degenerate n-type indium oxide with both Sn dopants and oxygen vacancies contributing to its conduction [8]. Growing interest in the development of ITO focuses on optimizing charge injection and transport at a low cost. ITO is used as a transparent anode and holes are injected into the HOMO of organic semiconductor materials. Therefore, ITO is especially suited to hole injection due to its high work function (4.3–4.7 eV) [9, 10]. A change in the ITO work function will alter the charge carrier injection barrier at the ITO/organic interface.

Generally, poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) are commonly used in bulk-heterojunction (BHJ) organic devices due to their suitable absorbing property, crystallinity, easy solution processibility, etc. Under current technology, polymers still have limited absorption that cannot cover the whole solar spectrum so we should concentrate on the other factors

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to achieve higher efficiencies of the optoelectronic devices. In this work, we have tried a simple surface modification treatment on ITO glass, which results in an increase in the efficiency and other parameters of bulk-heterojunction organic solar cells. Here for the first time we have studied the effect of liquid nitrogen on the ITO glass substrate to replace the previously reported N_2 plasma treatment [6].

2. Experimental

Regioregular P3HT and PCBM were purchased from Sigma-Aldrich and Frontier Carbon Corp. respectively, and used without further purification. P3HT acts as the p-type donor polymer and PCBM as the n-type acceptor in the active layer. Composite solutions with a 1 : 1 weight ratio of P3HT to PCBM were prepared using 1,2-dichlorobenzene (DCB) and stirred well for a day [11]. Optical transmission spectra of the untreated ITO glass (FINE brand, Furuuchi kabushiki kaisha,15 $\Omega\,\mathrm{cm}^{-2}$) and liquid N_2 treated ITO glass were measured by a UV/VIS/NIR spectrophotometer (V-570, JASCO). Polymer solar cells were fabricated with a typical sandwich structure of ITO/PEDOT : PSS/P3HT : PCBM/Al (Cell-R1) and liquid N_2 treated ITO/PEDOT : PSS/ P3HT : PCBM/Al (Cell-R2). ITO glass substrates were cleaned in acetone and methanol followed by washing with a copious amount of water and dried using an N_2 blower. The dried ITO glass substrate was treated with liquid N_2 for 10 min and kept outside to reach room temperature in order to modify the surface. The conducting polymer, poly (3, 4-ethylenedioxythiophene) : poly (styrenesulfonate) (PEDOT : PSS, Sigma-Aldrich), which is a buffer layer for hole transport as well as to reduce the roughness of the ITO surface, was spin coated on both ITO glass substrates with a thickness of ~100 nm from an aqueous solution. Next, these layers were annealed at 100 °C for 10 min to remove the residual water. After spin coating the photo-active layer prepared from the P3HT : PCBM composite solution, the Al cathode layer with a thickness of ~100 nm was deposited by thermal evaporation in a vacuum chamber (3×10^{-4} Pa) on both the devices. After thermal evaporation of the Al cathode layer, both the devices were annealed at 140 °C for 10 min in a glove box. The active area of the device was defined by a shadow mask, resulting in 3 mm^2 of the cell area. The morphology difference of both untreated and liquid N_2 treated ITO glass (LNITO glass) substrates was observed using AFM (SPI-3800N, SII, Japan, contact mode). The current–voltage (I–V) characteristics of the devices were measured by a JASCO instrument with a white light xenon lamp under one-sun illumination (AM 1.5G, 100 $\mathrm{mW\,cm}^{-2}$). All characterizations were carried out in an ambient environment except for the I–V characteristics, which were carried out with flowing N_2 gas. The contact angle (sessile drop method) was measured with Dataphysics OCA 15plus instruments, Germany.

3. Results and discussion

Liquid N_2 is a cryogenic liquid with a boiling point of −195.8 °C and used mainly as a refrigerant (cryogen). By considering these properties we boiled ITO glass at liquid N_2 temperature (77 K) to modify the surface, which acts as the anode for BHJ devices, and its results are described below.

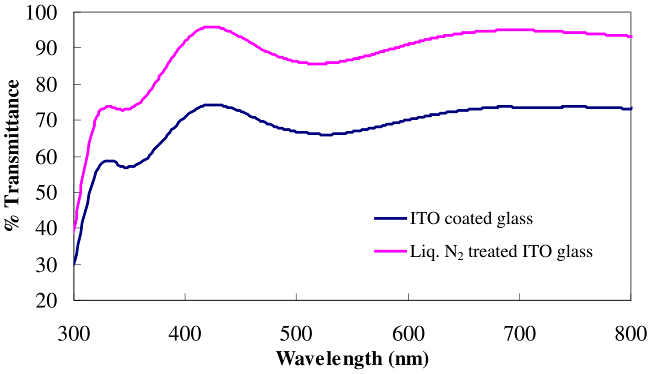

Figure 1. Optical transmission spectra of ITO and LNITO glass.

The ITO coated on the glass is etched out by sonication in concentrated HCl for 10 min. This glass is used as a reference for transmittance measurement and henceforth called a plane glass. Figure 1 describes the optical transmission spectra of ITO and LNITO glass that shows a substantial change in transmittance after liquid N_2 treatment, which reveals that ITO and LNITO glass can transmit 74% and 95% of light, respectively. This treatment enables transmission of almost 95% of light through ITO glass for conversion of light into electricity. Moreover, this increase in transmittance is due to the incorporation or adsorption of N_2 into the ITO film that increases the film diffuse transmittance or due to the cooling effect. Choi *et al* [12] have observed the same trend after B-doping in the ITO film. However, an optical transmittance is closely related to oxygen vacancies, which are associated with free electrons in the ITO films as mentioned earlier. We assume that many electrons or disordered lattice structures in ITO films are less scattered by incident light, thus increasing the transparency of the ITO films after liquid N_2 treatment. To check the reproducibility of the results, we used five ITO glass samples with and without treatment of liquid N_2 and characterized in a similar way. We found that out of five samples, three samples showed nearly similar results. Earlier, many different treatments were carried out to improve the surface of ITO such as various gas plasmas [6], surface assembled monolayers (SAMs) and acid treatments [13]. These techniques are time consuming as well as expensive compared with our method proposed here. The surface characteristics are responsible for improved cell performance. We believe that upon treatment with liquid N_2 the ITO surface morphology is modified, i.e. changes in the hole injection barrier and its work function. It was observed that the electrical resistivity for untreated ITO and LNITO substrates was $7.32\times10^{-5}\ \Omega$ cm and $6.47\times10^{-5}\ \Omega$ cm, respectively. However, the electrical resistivity is slightly less than that quoted before; this is attributed to the increase in conductivity as well as incorporation of N_2 in the ITO film.

Figures 2(*a*) and (*b*) show the AFM topography images of untreated ITO and LNITO glass. In figure 2(*b*), the arrow indicates that ITO grains merge with each other. Also it depicts

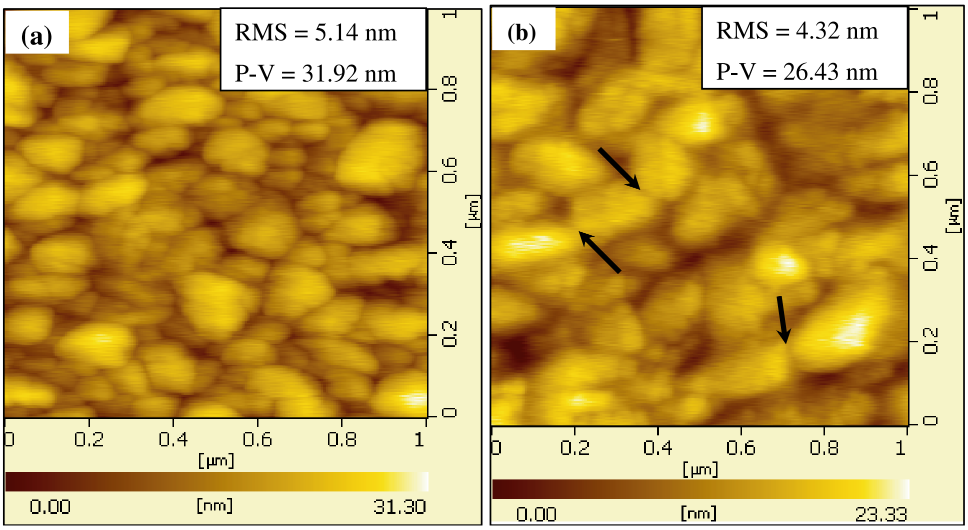

Figure 2. AFM images of ITO (*a*) and LNITO glass (*b*). Arrows indicate that the grains are merging into each other.

Table 1. Surface characteristics of untreated and liquid N_2 treated ITO glass.

	Water contact angle (°)	RMS roughness (nm)	Average roughness (nm)	*P–V* distance (nm)
Plane glass	31.08	—	—	—
ITO glass	81.82	5.14	4.21	31.92
LNITO	97.20	4.32	3.52	26.43

that the RMS roughness of ITO glass was reduced from 5.14 to 4.32 nm and the peak-to-valley distance was also reduced from 31.92 to 26.43 nm. The grain size had increased slightly because of the sudden temperature change in the ITO film from liquid N_2 temperature (77 K) to room temperature. Seol *et al* [6] have modified the surface of ITO glass by plasma treatment using different gases such as N_2 and O_2 and observed better performance of the device with N_2 plasma. In this study, we have tried to use a simple liquid N_2 treatment as a replacement for N_2 plasma. Nevertheless, O_2 plasma also helps in improving the surface of the ITO as observed in the previous work [7]. These cells were fabricated inside the glove box at R.T and 27% of relative humidity.

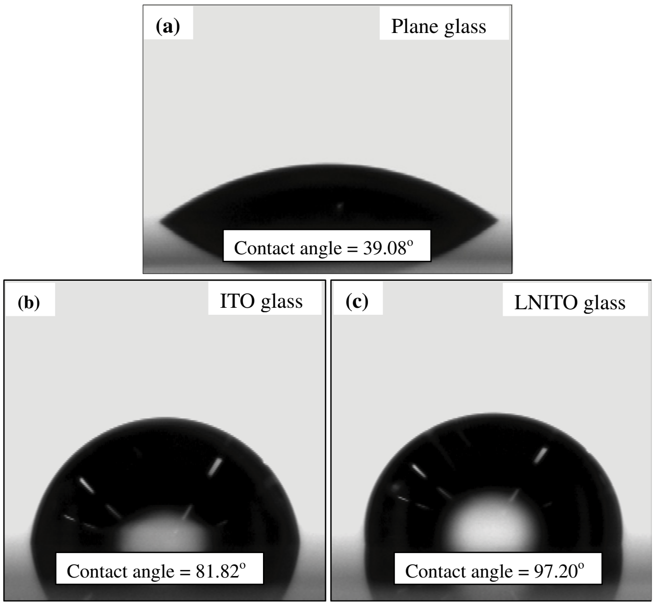

Figure 3. Optical images of the contact angle of water with plane glass (*a*), ITO coated glass (*b*) and LNITO glass (*c*), respectively.

Table 1 shows the water contact angle of plane, ITO and LNITO glass and their corresponding roughness values observed from AFM measurements. The optical images of the water contact angle with plane glass, untreated ITO and LNITO glass are shown in figure 3. The contact angle was measured at five different places for each sample and the average contact angle was calculated. It was observed here that the equilibrium contact angle of water is 39.08° for plane glass, 81.82° for ITO and 97.20° for LNITO glass, respectively. This indicates that after the liquid N_2 treatment, the surface of ITO glass is highly non-polar. The contact angle for ITO and LNITO obtained here is higher than the plane glass surface, which is probably due to the surface discrepancy between the ITO film and the glass after liquid N_2 treatment, which indicates that the surface energy of the substrate can be obviously reduced. The higher contact angle for LNITO indicates a higher hydrophobic nature of the surface. But Seol *et al* [6] have observed that a decrease in the contact angle ($<10°$) results in hydrophilic nature. Our results are in contrast to the results of Seol *et al* [6] because in the plasma treatment, the heat generated on the ITO surface is due to plasma, which makes it relatively smoother and hydrophilic. However, in the liquid N_2 treatment, the ITO surface is cooled down, which results in deformation of the ITO grains and makes it hydrophobic in nature. Using SAMs, an increase in the contact angle was observed as reported by Kobayashi *et al* [2]. However this increase in the contact angle does not largely affect the efficiency of the cell. As observed from the XPS analysis, no organic content was found on the surface of ITO except indium, tin, oxygen and nitrogen. It reflects that this simple technique can be used similarly to the plasma treatment for removing the organic residues and oxygen on the surface of the ITO film as well as incorporating N_2 in the

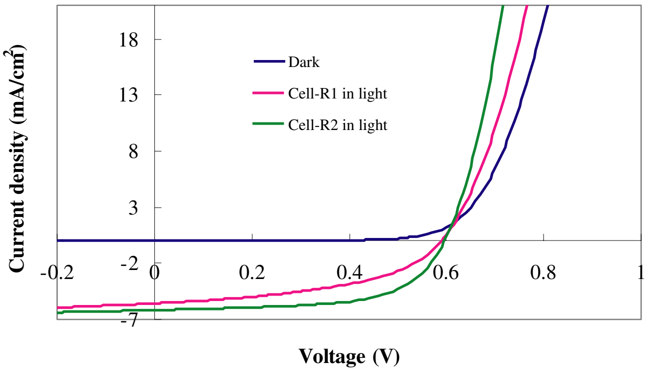

Figure 4. The current density/voltage (J–V) characteristics of cell-R1 and cell-R2 under dark and illumination of white light (RT, AM1.5 condition, 100 mW cm^{-2}).

Table 2. Calculated values of V_{OC}, I_{SC}, FF and PCE.

	V_{OC} (V)	I_{SC} (mA cm^{-2})	Fill factor	η (%)
Cell-R1	0.59	5.57	0.47	1.55
Cell-R2	0.59	6.16	0.62	2.27

ITO film. By calculating the In/Sn and O/In ratio, it was found that there was decrease in the In/Sn ratio and an increase in the O/In ratio for LNITO compared with ITO [14]. This means that there is a decrease in the electron affinity of the ITO film and therefore the lowering of the work function that improves the charge collection efficiency.

The most important point in the organic solar cell is its current–voltage (I–V) characteristics. In order to investigate the photovoltaic performance of a cell, the I–V characteristics in dark and illumination are considered. Figure 4 shows the I–V characteristics of the devices structured on untreated ITO and LNITO glass measured while flowing the N_2 gas at room temperature. A dramatic improvement in the short circuit current (I_{SC}), the fill factor (FF) and the power conversion efficiency (PCE) η was observed and summarized in table 2. For the untreated ITO glass I_{SC}, FF and PCE are 5.57 mA cm^{-2}, 0.47 and 1.55% while for LNITO it was 6.16 mA cm^{-2}, 0.62 and 2.26%, respectively. The open circuit voltage (V_{OC}) remains unaltered in both cases. The series resistance was also reduced by this treatment as can be seen from the I–V characteristics of the cells. This was maybe due to the N_2 atoms being adsorbed in the ITO anode to inject holes for exciton dissociation and the subsequent conversion of photons into electricity. On the other hand, we have tried liquid N_2 treatment on ITO for 30 and 60 min; it was observed that the 10 min treatment was comparatively better. Longer treatment of liquid N_2 on the ITO film may damage the surface of ITO. Kim *et al* [1] have mentioned that when the active layer is coated on a hydrophilic surface, extreme phase separation results in a lower power conversion efficiency in spite of the improvement in the hole injection barrier. In contrast, a hydrophobic surface results in a higher power conversion efficiency. All the results produced here give a different insight into the improvement in optoelectronic devices.

The mechanism behind this liquid N_2 treatment on ITO glass is critical to our understanding at this moment and seems interesting for further research in the future. Further efforts in our research are needed to understand the exact mechanism behind this change.

4. Conclusions

In conclusion, we described the effect of liquid N_2 on an ITO glass surface. It was observed that this simple and cost-effective treatment considerably modifies the ITO surface resulting in enhancement of I_{SC}, FF and the conversion efficiency. The RMS roughness of the ITO surface was reduced and the contact angle as well as the transmittance of ITO was improved. The increase in the contact angle and the decrease in roughness of the ITO surface may result in the presence of fewer grain boundary sites that can increase exciton dissociation at the interface, thereby increasing the charge generation. N_2 is easily incorporated into the film to enhance the charge transport in the active layer. This treatment is an alternative to N_2 plasma treatment for reducing surface carbon contamination and increasing the surface stoichiometry of ITO glass.

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