Improvement of organic solar cells by flexible substrate and ITO surface treatments


A R T I C L E   I N F O

Article history:
Received 18 January 2010
Received in revised form 6 June 2010
Accepted 7 June 2010
Available online 12 June 2010

Keywords:
Polyethylene terephthalate (PET)
Flexible solar cells
Indium tin oxide (ITO)
Work function
Conversion efficiencies

A B S T R A C T

In this paper, surface treatments on polyethylene terephthalate with polymeric hard coating (PET-HC) substrates are described. The effect of the contact angle on the treatment is first investigated. It has been observed that detergent is quite effective in removing organic contamination on the flexible PET-HC substrates. Next, using a DC-reactive magnetron sputter, indium tin oxide (ITO) thin films of 90 nm are grown on a substrate treated by detergent. Then, various ITO surface treatments are made for improving the performance of the finally developed organic solar cells with structure Al/P3HT:PCBM/PEDOT:PSS/ITO/PET. It is found that the parameters of the ITO including resistivity, carrier concentration, transmittance, surface morphology, and work function depended on the surface treatments and significantly influence the solar cell performance. With the optimal conditions for detergent treatment on flexible PET substrates, the ITO film with a resistivity of $5.6 \times 10^{-4}\ \Omega \text{cm}$ and average optical transmittance of 84.1% in the visible region are obtained. The optimal ITO surface treated by detergent for 5 min and then by UV ozone for 20 min exhibits the best WF value of 5.22 eV. This improves about 8.30% in the WF compared with that of the untreated ITO film. In the case of optimal treatment with the organic photovoltaic device, meanwhile, 36.6% enhancement in short circuit current density ($J_{sc}$) and 92.7% enhancement in conversion efficiency ($\eta$) over the untreated solar cell are obtained.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Recently, flexible optoelectronic devices such as organic light emitting diodes (OLEDs), smart phones, personal digital assistants (PDAs), touch-panel displays and flexible polymer solar cells have become popular [1–5]. As these flexible solar cells grow, it is essential that indium tin oxide (ITO) as electrode material possess such special properties as excellent electrical conductivity, high transparency [6–8], and good chemical stability in the spectrum [9,10]. Therefore, ITO which has a wide band gap (3.3–4.3 eV) [11,12] and relatively high work function (WF) [13,14] are widely used. In order to evaluate the effects of lightness, thinness and high impact resistance, an ITO is usually sputtered onto a flexible transparent plastic substrate in various sizes and curvilinearly flexible shapes.

In general, polymers, which are transparent when visible, have the advantages of having high mechanical strength such as softness and low density [15]. Thus, the polymer material of polyethylene-terephthalate with polymeric hard coating (PET-HC) is considered as the flexible substrate in this research. This material has been widely used in the electrical and electronics industries due to the excellent dielectric, thermal, chemical and mechanical properties [16]. Moreover, effective surface treatments of a flexible PET-HC substrate enable us to make mechanically stable ITO electrode with good robustness, due to an improved adhesion between the ITO and the flexible PET-HC substrate. In addition, the treated ITO on a flexible PET-HC substrate will enhance the effective extraction of hole carriers from active organic layers [11].

If an ITO is deposited on an untreated substrate, the associated organic solar cell usually exhibits poor performance [17,18]. The surface properties of polymers with organic materials often do not satisfy the demands for wettability and adhesion etc. [19,20]. Additionally, the surface of ITOs on flexible PET-HC substrates cannot create new bonds with other atoms and thus can cause a decrease in the WF [4]. Since the WF of ITOs affects the efficiency of carrier injection into organic layers, it is important to investigate the relationships between cleaning methods and surface properties. Numerous researchers [21–23] have investigated into methods on how to improve the WF of ITO surface. The well known...
methods of surface treatment used to develop polymer substrate include plasma treatment [24,25], flame treatment [26] and chemical treatment [17,27–29]. Most of the previous works indicate that an increasing WF of an ITO surface reduces the energy barrier at ITO/polymer interface decreased with increasing WF of ITO. This fact creates certain good properties such as better adhesion. The interfacial adhesion between a polymeric layer and an ITO plays an important role in improving the photovoltaic (PV) performance. Because organic solar cells are thin–film devices, contamination on the surface must be avoided. A small amount of contamination on the surface can greatly alter the WF, or the interfacial barrier height between the polymer and the ITO. In this work, substrates and ITOs are cleaned respectively by detergent, ultraviolet (UV) ozone, and its combination (i.e., D&U stands for detergent and then UV ozone treatment) to eliminate surface pollutants and alter the chemical composition for improving their applications.

The correlation between the WF and the chemical composition on an ITO surface cleaned by various methods using UV/visible/near-infrared spectrometer and photoelectric detector is examined. Among all surface treatments, D&U treatment is the most effective technique to increase the WF of ITO. It is proposed that D&U is most effective in removing organic contamination from the substrate and surface of ITO thin film. In this study, the electrical and optical properties of an ITO thin film deposited on a flexible PET-HC substrate at room temperature by DC magnetron sputter deposition process. The X-ray diffraction (XRD, Siemens D5000 with Cu Kα radiation) is adjusted to the 2θ mode and scanning electron microscopy (SEM, Hitachi Field-Emission S-4800) is used to characterize the crystal structure. Transmittance and reflectance of the ITO layer are measured by a Shimadzu MPC-3100 UV/VIS/NIR spectrometer within a wavelength range from 400 to 700 nm. The WF and the visible light transmittance of the deposited ITO film are measured by a photoelectron spectrometer (Riken-Keiki, AC-2) and spectrophotometer (Hitachi, U4001) respectively. The sheet resistance of the sample is measured by a 4-point probe (Veeco, FPP-50000), and the resistivity of the film was calculated. Carrier concentration and mobility are obtained from Hall-effect measurement (Keithley 2420) at room temperature.

The schematic device structure of the proposed solar cell is illustrated in Fig. 1. The proposed structure consists of P3HT:PCBM/PEDOT:PSS layers which are inserted between the cathode Al and the anode ITO substrate. The procedure for fabricating a solar cell is described as follows: the substrate is cleaned by detergent, and ITO surface is treated by different manners. After cleaning and mounting the DC-reactive magnetron sputter is applied to deposit an ITO on a flexible PET-HC substrate at room temperature. The target consists of In2O3 and SnO2 at a weight proportion of 9:1, which is placed at a distance of 60 mm from a flexible PET-HC substrate. The sputtering power input to a target is adjusted to 50 W. The total working pressure of 4 × 10⁻⁶ Torr consists of a gas mixture of argon (Ar) and oxygen (O2). While the flow rate of O2 gas is maintained at a fixed value of 1 sccm, the Ar flow rate is adjusted in the range of 20–60 sccm during different film growth stages due to different substrate treatments. The thickness of ITO thin film is approximately 90 nm and the temperature is grown at room temperature during the whole processes.

In order to compare among different ITO surface treatments, the substrates treated with different manners are placed on a sample holder and all the solar cells are fabricated during the same deposition process. The X-ray diffraction (XRD, Siemens D5000 with Cu Kα radiation) is adjusted to the 2θ mode and scanning electron microscopy (SEM, Hitachi Field-Emission S-4800) is used to characterize the crystal structure. Transmittance and reflectance of the ITO layer are measured by a Shimadzu MPC-3100 UV/VIS/NIR spectrometer within a wavelength range from 400 to 700 nm. The WF and the visible light transmittance of the deposited ITO film are measured by a photoelectron spectrometer (Riken-Keiki, AC-2) and spectrophotometer (Hitachi, U4001) respectively. The sheet resistance of the sample is measured by a 4-point probe (Veeco, FPP-50000), and the resistivity of the film was calculated. Carrier concentration and mobility are obtained from Hall-effect measurement (Keithley 2420) at room temperature.

The schematic device structure of the proposed solar cell is illustrated in Fig. 1. The proposed structure consists of P3HT:PCBM/PEDOT:PSS layers which are inserted between the cathode Al and the anode ITO substrate. The procedure for fabricating a solar cell is described as follows: the substrate is cleaned by detergent, and ITO surface is treated by different manners. After

![Fig. 1. Schematic configuration of plastic solar cell in Al/P3HT:PCBM/ PEDOT:PSS/ITO/PET-HC structure.](image-url)
having been treated by different manners, carbon contamination is to residual carbon molecules that can enlarge contact angle. After results are attributed to the surfaces of substrates reacting rapidly contact angles are achieved at 5 min treating time. These optimal P3HT and PCBM solution in the ratio 1:1 and then heated to 80 separately. The solution for photoactive layer is achieved by mixing 1,2-dichlorobenzene (DCB) in the concentration of 16 mg/ml separately. The solution for photoactive layer is achieved by mixing P3HT and PCBM solution in the ratio 1:1 and then heated to 80 °C for 1 h. The photoactive layer is then spin-coated on the buffer layer at 600 rpm for 60 s and naturally dried in the glove box. The thickness of the photoactive layer is about 150 nm. Al cathode is then deposited by evaporation through a shadow mask to the thickness of 100 nm. Organic solar cells have been prepared using the approved layer setup Al/P3HT:PCBM/PEDOT:PSS/ITO/PET-HC. For simplification of terrestrial solar-cell characterization, the induced current density–voltage (J–V) curves of the developed devices are measured under the air mass (AM1.5G) of the solar simulator (Wacom, Model: WXS-220S-L2) at 1000 W/m² irradiation power.

3. Results and discussion

Measuring the contact angle is a useful technique to determine the free energy of a surface [33]. The substrate treated by various manners to inspect each sample's surface cleanliness is measured. Fig. 2 (bottom-left axes) shows the treating time variation of a contact angle for flexible PET-HC substrates treated by detergent and UV ozone. The contact angle of the untreated substrate is about 67°. For these two treatment methods, the lowest contact angles are achieved at 5 min treating time. These optimal results are attributed to the surfaces of substrates reacting rapidly to residual carbon molecules that can enlarge contact angle. After having been treated by different manners, carbon contamination is significantly reduced [14].

The aging deterioration of different treatments is also investigated (top-right of Fig. 2), while each sample is exposed to atmosphere for 0, 3, 6, 9, and 24 h, respectively. In the case of the flexible PET-HC substrate, the contact angle slightly varies within the first 6 h. After 9 h aging time, the detergent treatment holds constant with stable contact angles, and the curve of UV-ozone treatment varies greatly with oxygen damage on the substrate surface. This phenomenon is agreed with previous researches [34], resulting from continuous chemical reactions from the remaining active radicals on the PET-HC surface with O₂ or moisture in ambient air, or from free rotation of the O₂-containing hydrophilic polar groups into the inside of PET-HC. Obviously, the detergent treatment produces the lowest contact angle (14.1°) at 5 min treating time, and slightly varies within 24 h aging duration.

The ITO films are deposited on flexible PET-HC substrates differed by untreated, detergent, and UV-ozone treatment, separately. Fig. 3 shows that both resistivity and carrier concentration is a function of Ar flow rate when ITO thin films are deposited on the flexible PET-HC substrate at room temperature. It is clear that the resistivity and carrier concentration of the ITO films dramatically changes with the rate of Ar. The resistivity of the ITO grown at flow ratio 20:1 (Ar:O₂) is lower than that at higher flow ratio 30:1 (Ar:O₂). However, flow ratio 20:1 (Ar:O₂) results in an abrupt increase of the carrier concentration. We conclude that increasing Ar flow rate enhances carrier concentration and decreases Hall mobility due to the dissipation of oxygen vacancies. The optimal condition of flow ratio (Ar:O₂) at 20:1 for growing an ITO film can get the lowest resistivity. The reason is the enhanced carrier mobility resulting from the dissipation of oxygen vacancy. The optimized growth conditions of flow ratio (Ar:O₂), DC sputter power, working pressure, and deposition time are 20:1, 50 W, 4 × 10⁻⁶ Torr, and 20 min, respectively. Meanwhile, the high quality thin film with resistivity as low as 5.6 × 10⁻⁴ Ω cm and carrier concentration as 0.535 × 10¹⁸ cm⁻³ can be obtained by controlling the Ar:O₂ flow ratio on the substrate with detergent treatment.

Fig. 4 depicts the total visible transmittance spectra (400–700 nm) of ITO thin films deposited by a DC-reactive magnetron sputter at room temperature on the flexible PET-HC substrates by detergent and UV-ozone treatments, respectively. The transmittance spectrum of an untreated substrate is presented for comparison. All ITO films' thicknesses are about 90 ± 5 nm. It is significant that transmittances of ITO films reach the saturation stage (>80%) in the 470–600 nm range which is much higher than that in the 400–460 nm region [35]. The sharp absorption edges in the transmittance spectra are caused by an extrinsic band gap of ITO film in the range of 3.3–4.3 eV [11,12]. The best value of average transmittance (in the insert of Fig. 4) is 84.10% treated by the detergent method. However, all of the average transmittance within visible range of a treated PET-HC substrate is higher than 83%, which is usable for optoelectronic applications [36].

Fig. 5 shows the typical 2θ mode XRD spectra of ITO films grown on substrates treated by different manners. For comparison, the XRD spectrum of ITO film deposited on an untreated flexible
PET-HC substrate is also shown where no significant diffraction peak may be observed indicating an amorphous structure within the untreated flexible PET-HC substrate. However, the ITO film deposited on substrate surface treated by detergent and UV ozone are polycrystalline. The diffraction peaks at 2θ correspond to diffractions of In$_2$O$_3$ cubic crystalline structure (30.51°, 35.38°, 50.9°, and 61.51° correspond respectively to (2 2 2), (4 0 0), (4 4 0), and (6 2 2)) [36]. This indicates that the degree of crystalline of the substrate surface treated by detergent is higher than that of the untreated substrate surface. The residual carbon and the contaminants can be removed by the detergent and UV ozone treatments [14].

Fig. 6 shows the SEM morphologies of an ITO deposited on substrates by different treatments. Compared with the untreated image in Fig. 6(a), the morphology of the ITO film (as shown in Fig. 6(b)) deposited on the 5 min detergent treatment substrate does not significantly vary, thus dispersing the surface spherical particles and showing the flat surface with low roughness. Further, there is no defect such as pinholes, cracks on the ITO films treated by detergent treatment. Moreover, Fig. 6(c) with 5 min UV ozone treatment shows a flat ITO without a pinhole. Fig. 6(d) shows high-resolution cross-sectional SEM images of an 89 nm ITO film. The substrate is treated by detergent manner. No defects are found on the coatings, and the surface is smooth on this length scale. From Figs. 2, 5 and 6 discussed above, the optimal surface condition is 5 min detergent treatment on a flexible PET-HC substrate. For those ITO films as-deposited on the treated substrate, it is confirmed that we need to make surface treatment, thus determining the optimum process parameters for solar-cell applications.
The WF properties of ITO surface treated by different manners are analyzed by a photoelectron spectrometer. Fig. 7 shows that WF is a function of two variables, i.e., treatments and treatment time. In which, the highest WF values 4.96 eV and 5.15 eV treated by 5 min detergent and 20 min UV ozone methods can be obtained respectively. However, the D&U-treatment as 5 min detergent plus 20 min UV-ozone treatment as shown in Fig. 7 is defined in this research. Obviously, the optimal WF value of 5.22 eV by D&U treatment can be achieved. This improves about 8.30% in the WF compared with that of the untreated (4.82 eV, as-deposited) ITO film. The inserted SEM images illustrate extreme conditions of 7 min detergent and 25 min UV ozone treatment that generates defects such as flakes peeled (left photo) and pinholes punched (right photo) on the ITO surface. This clearly shows that the increase of WF is closely related to the oxidative degree (created during the UV-irradiation) on the ITO surface. This phenomenon is consistent with most of defect states created below the edge of the conduction band pushing the Fermi level to lower values. However, comparing these data with ITO film deposited on substrate treated by detergent, we can conclude that the surface of the ITO films treated by D&U is the best judged from WF value. Finally, D&U is a simple, attractive, and promising technique for the production of ITO thin films on the substrates treated by detergent.

Fig. 8 shows the current density–voltage (J–V) characteristics of the Al/P3HT:PCBM/PEDOT:PSS/ITO/PET-HC device under AM1.5G illumination with intensity of 100 mW/cm² at room temperature. All organic solar cells on the substrate treated by detergent shows comparable results. This demonstration indicates the good quality of the photoactive layer on the treated surface. Detailed characteristics of solar cells such as $J_{sc}$, $V_{oc}$, fill factor (FF) and efficiency values are also shown in the inset table, respectively. It can be seen that the $J_{sc}$ (in mA/cm²) of ITO surfaces treated by detergent, UV-ozone, and D&U are 6.7, 8.48, 8.77, respectively. The $J_{sc}$ for ITO surface with D&U treatment increases from 6.42 to 8.77, which is 36.6% enhancement as compared to the untreated organic solar cell. This may result from the differences in the PEDOT:PSS layer or higher shunts caused by the influence of film preparation procedures [37]. Nevertheless, the discrepancy in $J_{sc}$ of the direct comparable (untreated) cells should be a consequence of differences in film morphology resulting from the ever individual preparation procedure. As can be seen in inset table, $V_{oc}$ slightly changes because of different treating methods. It is found that the $V_{oc}$ of the organic solar cell directly correlates with the acceptor strength, i.e., it is determined by the HOMO-LUMO energy gap of donor and acceptor, respectively [38–41]. As a consequence, the conversion efficiency for ITO surface treated by D&U (2.12%) is higher than ITO surfaces treated by detergent (1.42%) and UV-ozone (1.91%). Moreover, the efficiency increased from 1.1% to 2.12%, which is 92.7% enhancement as compared to the untreated organic solar cell. The larger enhancement for conversion efficiency as compared to $J_{sc}$ results from the increase of the FF. The short circuit current is the parameter showing the highest dependency on the ITO surface treatments. Compared with the untreated solar cell, high $J_{sc}$ is obtained under all three treatments. It could be seen that the carrier collection efficiency and $J_{sc}$ are influenced by the concentration of traps and defects on the ITO surface having connection with the surface treatments [42].
4. Conclusions

The effects on the flexible PET-HC substrates treated by different manners have been investigated as contact angle technique is a known method for assessing the cleanliness of the substrates. The ITO films are deposited at room temperature by DC magnetron sputtering from a ceramic target of a 90% In–10% Sn alloy. It is found that optical properties of the ITO (resistivity and carrier concentration) are critically dependent on the flow ratio of Ar to O₂ during sputtering. Even though the surface of the ITO film is treated by detergent, the ITO film with a resistivity of 5.6 × 10⁻⁴ Ω cm and average optical transmittance of 84.1% in the visible-region can be obtained. The cleanliness can also be monitored by complementary XPS. Detergent can significantly enhance the degree of crystalline of organic solar cells. In addition, the ITO film shows morphological structure and a very smooth surface area. In conclusion, the relationship between the methods used to clean ITO surface and the WF using photoelectron spectrometer are investigated. ITO surface cleaned by detergent for 5 min and by UV ozone for 20 min results in significant increase in the WF value (5.22 eV). The optimal surface treatment (detergent for 5 min and UV ozone for 20 min) increases conversion efficiency of Al/P3HT:PCBM/PEDOT:PS5/ITO/PET-HC organic solar cell with conversion efficiency of 2.12% being the best. These results show that polymer-based materials and manufacturing techniques are suitable for flexible solar cells. Using the best treatment, 36.6% enhancement in J_c and 92.7% enhancement in conversion efficiency over the untreated organic solar cell have been demonstrated.

Acknowledgments

The authors acknowledge financial support from The National Science Council of Taiwan, R.O.C. under contract Nos. NSC 98-2622-E-019-006-CC3 and NSC 98-2221-E-019-003.

References