

4.8% efficient poly(3-hexylthiophene)-fullerene derivative (1:0.8) bulk heterojunction photovoltaic devices with plasma treated AgO_x /indium tin oxide anode modification

Woo-Jun Yoon and Paul R. Berger^{a)}

Department of Electrical and Computer Engineering, The Ohio State University, Columbus, Ohio 43210, USA

(Received 8 November 2007; accepted 10 December 2007; published online 7 January 2008)

We report here an improved efficiency, up to 4.8% with a high fill factor of $\sim 63\%$ under AM 1.5G spectral illumination and 100 mW/cm^2 intensity, for poly(3-hexylthiophene) and [6,6]-phenyl C_{61} butyric acid methyl ester bulk heterojunction photovoltaic (PV) devices with a 1:0.8 weight ratio using surface modifications to the indium tin oxide (ITO) anodes through plasma oxidized silver. Here, an enhanced short-circuit current density was achieved without significant loss in the open-circuit voltage ($>0.6 \text{ V}$) nor the fill factor ($>63\%$), leading to an efficiency jump from 4.4% in the control devices to 4.8% with the surface modified ITO anode. The enhanced short-circuit current density is attributed to an interface energy step between the ITO and the polymer hole transporting layer. It has been theorized that the introduction of an interface energy step could alter the charge collection efficiency, resulting in an improved overall efficiency in PV devices. In our study, the current density–voltage characteristics under darkness clearly show an increased current density, especially under forward bias, for the anode treated cell, suggesting the presence of an interface energy step between the ITO and the hole transporting layer with surface modified ITO anodes. © 2008 American Institute of Physics. [DOI: 10.1063/1.2830619]

Organic photovoltaic (PV) devices are of tremendous interest now for their potential societal benefits and the opportunity for relatively low cost production on flexible substrates. Since high performance organic PV devices have been introduced,^{1–3} significant effort has been made toward improving the performance of organic PV devices. A key component among this organic PV work is interface engineering at the electrodes to improve the power conversion efficiency (η_{eff}) by an optimization of the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), and the fill factor (FF).^{4–12}

Comparatively, surface modifications to the ITO anode has been widely implemented for organic light emitting diodes (OLEDs) to improve their device performance by creating an interface energy step between the ITO and the HTL, thereby enhancing hole injection by effectively lowering the hole injection barrier and, therefore, leading to higher electroluminescent external quantum efficiencies.^{13,14}

However, similar surface modifications of ITO anodes have demonstrated improved η_{eff} for organic PV devices.¹⁵ The overall physical mechanisms behind this improvement are not clearly understood. Nevertheless, it has been proposed that the creation of an interface energy step could improve the charge collection efficiency in organic PV devices, leading to the increase of the η_{eff} by improving the J_{sc} .^{16,17} Here, we report on an improved η_{eff} for polymer-fullerene bulk heterojunction PV devices using surface modification of ITO through plasma oxidation of thin noncontinuous silver deposited atop an ITO substrate.

A nominally 1 nm thick film of AgO_x was then added atop the ITO-coated glass substrate by the following two

steps. First, a 1 nm thick Ag metal was electron beam evaporated at a low pressure range ($\sim 10^{-7}$ Torr) atop the ITO. Next, the Ag metal was oxidized using an inductively coupled plasma reactive ion etching system with an oxygen plasma at a rf power of 100 W for 1 min at room temperature. After the 1 nm thick AgO_x film was formed on the ITO-coated glass substrate, the sheet resistance monitored using four-point probe measurement was slightly increased from 11.9 ± 0.4 to $12.4 \pm 0.6 \Omega/\square$. The substrates were next spin cast using poly(3, 4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (H.C. Stark), then annealed at 140°C for 10 min in air.

The mixed solution consisting of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) in chlorobenzene was then spin cast on the top of the PEDOT:PSS layer. The mixed solution had a P3HT:PCBM weight ratio of 1:0.8 with a concentration of 10 mg/ml (P3HT). The P3HT (Merck) with 94.5% regio-regularity and PCBM (Nano-C) were used without further purification. After spin casting the photoactive layer, the devices were pumped down in vacuum ($\sim 10^{-7}$ Torr) and then the multilayer stack was completed by the shadow mask evaporation of a LiF/Al cathode. The final composite device structure is ITO/ AgO_x /PEDOT:PSS/P3HT:PCBM/LiF/Al. Postproduction thermal annealing was then performed by directly placing the completed device on a digitally controlled hot plate at 160°C for 30 min in an inert glove box. After annealing, the devices were cooled down to room temperature prior to subsequent measurements.

In our experiments, control devices (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) were also fabricated and tested without any surface modification of ITO anodes. In order to minimize variation in the results that might arise due to different processing conditions, both sets of PV devices (control

^{a)} Author to whom correspondence should be addressed. Also at: Department of Physics, The Ohio State University, Columbus, OH 43210-1106. Electronic mail: pberger@ieee.org.

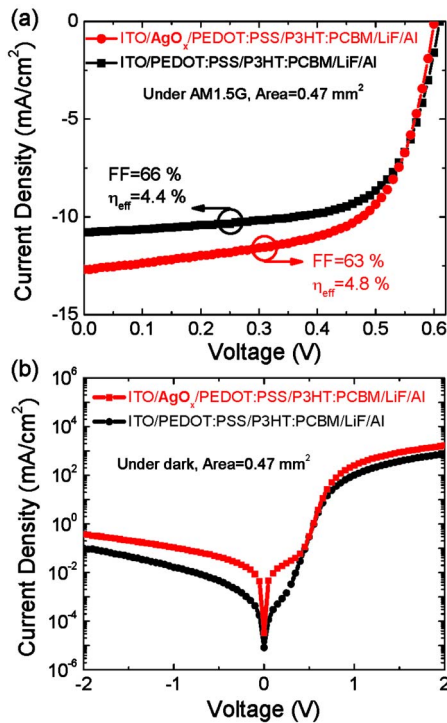


FIG. 1. (Color online) (a) J - V characteristics of polymer-fullerene bulk heterojunction photovoltaic devices (ITO/AgO_x/PEDOT:PSS/P3HT:PCBM/LiF/AI) under AM 1.5G filtered spectral illumination at an incident intensity of 100 mW/cm². (b) The corresponding J - V characteristics in darkness.

and experiment) with different anode structures were fabricated during the same batch processing.

The actual device area was determined with an XL30 environmental scanning electron microscope (Philips) in order to overcome shadow effects that could result in an error in calculated current-density values.¹⁸ The active area of the devices was 0.47 mm², which is slightly larger than the area (0.42 mm²) defined by the shadow mask. Electrical measurements were performed with a semiconductor characterization system (Keithley 4200) at room temperature in air without any device encapsulation under the spectral output from a 150 W solar simulator (Newport) using an AM 1.5G filter. The light intensity was precisely calibrated to a silicon-germanium solar cell that was calibrated by the National Renewable Energy Laboratory.

Figure 1(a) shows the current density–voltage (J - V) characteristics under AM 1.5G filtered illuminations for a calibrated solar simulator with an overall intensity of 100 mW/cm². The control device (ITO/PEDOT:PSS/P3HT:PCBM/LiF/AI) exhibited an η_{eff} of 4.4% with a very high FF of 66%. The V_{oc} and the J_{sc} of the control devices were 0.61 V and 10.8 mA/cm², respectively. For the experimental devices incorporating a 1 nm thick AgO_x layer between the ITO and the PEDOT:PSS, an η_{eff} of 4.8% with $V_{\text{oc}}=0.60$ V, $J_{\text{sc}}=12.7$ mA/cm², and FF=63% was measured. For both sets of devices, the series resistance (R_s), defined by the slope of the J - V curve at $J=0$ mA/cm² was estimated to be about ~ 6.9 Ω cm². Despite similar series resistances, the FF in the devices with modified anodes slightly decreased to 63% compared with 66% for the control devices because of an elevated shunt resistance, indicated by the higher slope for the J - V curves near 0 V while under illumination.

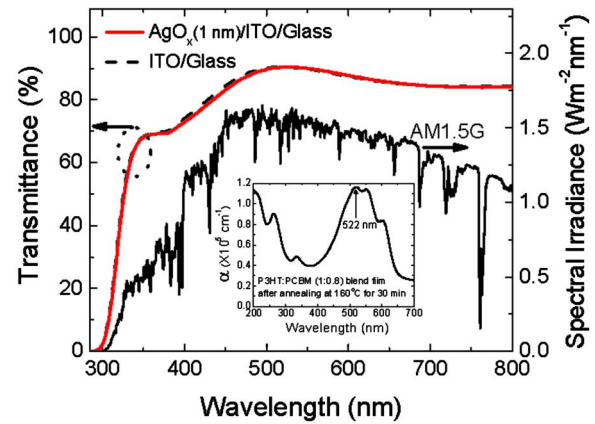


FIG. 2. (Color online) Optical transmittance of the AgO_x modified ITO anode with respect to the AM1.5G spectra. The inset shows the absorption of the P3HT:PCBM (1:0.8) blended film after annealing 160 °C for 30 min.

As expected, V_{oc} remains almost the same within ~ 100 mV or less, for both devices since the fabrication conditions for both the P3HT:PCBM blend film and cathode deposition were held constant.¹⁹ The sole differential was the AgO_x treatment, which significantly enhances J_{sc} , where J_{sc} increased from 10.8 mA/cm² for the bare ITO to 12.8 mA/cm² for the AgO_x/ITO anodes. As a result, the η_{eff} of the devices with surface modified anodes was increased from 4.4% for the control devices up to 4.8%.

Figure 1(b) shows the J - V characteristics for both devices under darkness. Under darkness, both devices exhibit high current rectification ratios of $\sim 4.6 \times 10^3$ for the devices with modified anode and $\sim 7.5 \times 10^3$ for the control devices at ± 2 V, indicating that the surface modifications on the ITO anodes did not significantly short the electrical junction between the anode and the cathode. The combination of elevated reverse saturation current and forward biased current for the experimental samples [Fig. 1(b)], while simultaneously exhibiting a similar ideality factor (~ 1.6) in the +0.5 V exponential region as determined from the J - V slope, suggests that the energy barrier between the ITO and the polymer has been lowered, while not introducing recombination centers. Indeed, a pronounced higher level of injected current is measured for the AgO_x treated sample for modest forward biases, below +0.4 V, where a reduced potential energy barrier between the anode and the polymer should more dramatically enhance injected hole diffusion current. The higher leakage current density in the devices with the AgO_x/ITO anode ($V < 0.5$ V) results in the slightly decreased FF measured.

From the AFM tapping mode images (5×5 μm^2) for ITO and AgO_x/ITO substrates (not shown here), the root mean square (rms) roughness of a bare ITO surface was ~ 2.6 nm with ~ 16 nm for the maximum peak-to-peak height. After depositing 1 nm of AgO_x on ITO, the rms roughness of the ITO surface was increased to 4.9 nm with a 40 nm maximum peak-to-peak height recorded.

Figure 2 shows the optical transmittance of both anodes over the visible range (400–700 nm). For this range, the averaged transmittance of the AgO_x/ITO-coated glass substrate over this range remains identical to a bare ITO-glass substrate, about 86%. The inset of Fig. 2 shows the UV-visible spectra of annealed P3HT:PCBM (1:0.8) blend films used in this study. For the blend films (1:0.8) studied here, the absorption coefficient peak was observed at

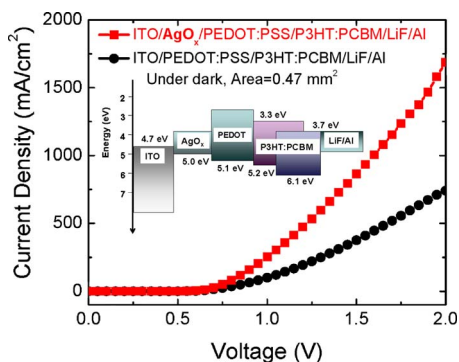


FIG. 3. (Color online) Forward biased J - V characteristics of both polymer-fullerene bulk heterojunction PV cells under darkness. The inset is the proposed energy level diagram indicating the interfacial energy barrier created by the AgO_x treatment.

~ 522 nm. AgO_x surface modifications did not measurably affect the overall transmittance, specifically at the absorption peak of blend film, which showed transmittances of both anode configurations at about $\sim 90.4\%$.

However, in spite of the identical absorption spectra of the blend layers from both sets of devices, an increased J_{sc} was measured for the devices with AgO_x /ITO anodes versus the control devices. Since the coverage of AgO_x on ITO is very low with small island formation, it is unlikely that the difference of optical-field distribution for both devices could explain the measured J_{sc} differences. Moreover, the optical transmittance for both anodes was the same at the visible range as well as at the absorption peak of the active blend film, indicating almost no loss of incident light delivered to the active region when under illumination.

Without significant variation to the series resistance, the physical mechanisms behind the enhanced J_{sc} under illumination are not clearly understood. However, it has been suggested in the literature that the insertion of an interface energy step could alter charge collection efficiency.^{15–17} Khodabakhsh *et al.*¹⁵ investigated the performance of an organic solar cell through surface modifications of ITO anode using self-assembled monolayers (SAMs), which similarly enhanced J_{sc} without any significant change to V_{oc} . By introducing the interfacial energy step, it was shown that the J_{sc} in the device with SAM-modified ITO anode was ~ 4.6 times greater than that of devices with bare ITO, while V_{oc} remained nearly the same.

For the devices with AgO_x /ITO anodes, the presence of an interfacial energy step between the ITO and the PEDOT:PSS is indicated from the forward bias J - V characteristics under darkness, as shown in Fig. 3, where current injection is dramatically enhanced. It is observed that the dark current density was increased at a given voltage upon insertion of AgO_x between ITO and PEDOT:PSS layers in agreement with previous studies, which reported that modified silver oxide, either Ag_2O or AgO_x between an anode and the HTL in OLEDs, resulted in enhanced hole injection by creating an interfacial energy step.^{20–22} Generally, it is known that silver oxides are p -type semiconductors with their work function ranging from 4.8 to 5.1 eV, depending on the processing condition.²³ The inset of Fig. 3 shows a proposed energy band diagram for the composite device with AgO_x /ITO anode, showing a proposed interface energy step by AgO_x

(~ 5.0 eV) between the ITO (~ 4.7 eV) and the PEDOT:PSS (~ 5.2 eV). In these devices, the LiF/Al cathode is considered to be an Ohmic contact.²⁴

In conclusion, we have shown an improved η_{eff} for polymer-fullerene bulk heterojunction PV devices, mainly due to the enhanced J_{sc} , through the usage of a thin islanded AgO_x film atop ITO anodes. Considering the enhanced hole injection from their J - V curves under darkness with formation of AgO_x on ITO surface, the measured increased J_{sc} without significant changes to V_{oc} , FF, and the R_s suggest the improved charge collection efficiency occurs by creating interfacial energy step between ITO anode and PEDOT:PSS.

The authors would like to thank Steven A. Ringel and Maria Gonzalez for supplying the calibration PV devices, Malcolm H. Chisholm, Yi-Hsuan Chou, and Yagnaseni Ghosh for optical measurements, and James Jones for help with equipment maintenance. This work was supported by the Center for Photovoltaics Innovation and Commercialization (PVIC) and the Institute for Materials Research (IMR).

¹W. Ma, C. Yang, X. Gong, K. H. Lee, and A. J. Heeger, *Adv. Funct. Mater.* **15**, 1617 (2005).

²Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, and M. Ree, *Nat. Mater.* **5**, 197 (2006).

³J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, *Appl. Phys. Lett.* **84**, 3013 (2001).

⁴K. Schulze, B. Maennig, K. Leo, Y. Tomita, C. May, J. Hüpkes, E. Brier, E. Reinold, and P. Bäuerle, *Appl. Phys. Lett.* **91**, 073521 (2007).

⁵F. Yang and S. R. Forrest, *Adv. Mater. (Weinheim, Ger.)* **18**, 2018 (2006).

⁶N. R. Armstrong, C. Carter, C. Donley, A. Simmonds, P. Lee, M. Brumbach, B. Kippelen, B. Domercq, and S. Yoo, *Thin Solid Films* **445**, 342 (2003).

⁷Z. R. Hong, C. J. Liang, X. Y. Sun, and X. T. Zeng, *J. Appl. Phys.* **100**, 093711 (2006).

⁸F. L. Zhang, A. Gadisa, O. Inganäs, M. Svensson, and M. R. Andersson, *Appl. Phys. Lett.* **84**, 3906 (2004).

⁹C. Ko, Y. Lin, F. Chen, and C. Chu, *Appl. Phys. Lett.* **90**, 063509 (2007).

¹⁰V. Shrotriya, G. Li, Y. Yao, C.-W. Chu, and Y. Yang, *Appl. Phys. Lett.* **88**, 073508 (2006).

¹¹P. Peumans and S. R. Forrest, *Appl. Phys. Lett.* **79**, 126 (2001).

¹²F. Zhang, M. Ceder, and O. Inganäs, *Adv. Mater. (Weinheim, Ger.)* **19**, 1835 (2007).

¹³R. A. Hutton, M. R. Willis, M. A. Chesters, F. J. M. Rutten, and D. Briggs, *J. Mater. Chem.* **13**, 38 (2003).

¹⁴Y. Shen, D. B. Jacobs, G. G. Malliaras, G. Koley, M. G. Spencer, and A. Ioannidis, *Adv. Mater. (Weinheim, Ger.)* **13**, 1234 (2001).

¹⁵S. Khodabakhsh, B. M. Sanderson, J. Nelson, and T. S. Jones, *Adv. Funct. Mater.* **16**, 95 (2006).

¹⁶P. Ravirajan, S. A. Haque, J. R. Durrant, D. Poplavskyy, D. D. C. Bradley, and J. Nelson, *J. Appl. Phys.* **95**, 1473 (2004).

¹⁷J. Nelson, J. Kirkpatrick, and P. Ravirajan, *Phys. Rev. B* **69**, 035337 (2004).

¹⁸V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Adv. Funct. Mater.* **16**, 2016 (2006).

¹⁹C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, and J. C. Hummelen, *Adv. Funct. Mater.* **11**, 374 (2001).

²⁰C.-W. Chen, P.-Y. Hsieh, H.-H. Chiang, C.-L. Lin, H.-M. Wu, and C.-C. Wu, *Appl. Phys. Lett.* **83**, 5127 (2003).

²¹H. W. Choi, S. Y. Kim, K.-B. Kim, Y.-H. Tak, and J.-N. Lee, *Appl. Phys. Lett.* **86**, 012104 (2005).

²²J.-M. Moon, J.-H. Bae, J.-A. Jeong, S.-W. Jeong, J.-W. Kang, J.-J. Kim, and M.-S. Yi, *Appl. Phys. Lett.* **90**, 163516 (2007).

²³U. K. Barik, S. Srinivasan, C. L. Nagendra, and A. Subrahmanyam, *Thin Solid Films* **429**, 129 (2003).

²⁴V. D. Mihailetschi, L. J. A. Koster, and P. W. M. Blom, *Appl. Phys. Lett.* **85**, 970 (2004).