# A one-step process for localized surface texturing and conductivity enhancement in organic solar cells

A. M. Zaniewski, M. Loster, and A. Zettl[a)]
*Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

(Received 3 June 2009; accepted 18 August 2009; published online 9 September 2009)

A process that improves organic solar cell local morphology and geometry is presented. Strong electric field gradients and current densities, generated by voltages locally applied between a conducting atomic force microscope tip and the device surface, induce enhanced conductivity and raise geometrical texturing features in solar cells formed from poly (3-hexylthiophene): [6,6]-phenyl-C61 butyric acid methyl ester blends. These results may open paths to organic solar cell efficiency enhancements through a single step process that simultaneously textures the surface for increased light trapping and enhances charge extraction. 
[doi:10.1063/1.3223624]

Organic solar cells, which can be made with relatively inexpensive materials and methods, offer an attractive route to solar energy generation. Polymer-based solar cells rely on a blend of semiconducting materials, such as Poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM). This combination, though promising, is handicapped by poor charge transport, which limits the thickness of the active layer, in turn reducing light absorption.[1] Of great interest, therefore, are methods by which the charge transport within organic solar cells can be improved, or, equally important, alternate methods by which light absorption can be independently enhanced. To this end, many different organic polymer-based blends have been explored[2] for enhanced charge transport. In addition, surface texturing, which effectively increases the path length of light through the active layer and thus enhances light absorption, has been applied to systems such as P3HT:PCBM via a soft-lithographic, master, and stamp approach.[3]

We here describe a method to enhance both charge transport, and light absorption via texturing, in an organic solar cell using a single post-production step. The step involves the local injection of electrical current into the surface of the device. Using small applied voltages and injection current density, the surface profile of the solar cell is unmodified but the local charge transport is significantly enhanced. Using higher applied voltages and injection current density, the local charge transport is again enhanced and the surface of the cell is advantageously textured.

To avoid statistical fluctuations in the inhomogeneous photoactive layers we have selected conductive atomic force microscopy (C-AFM) as the best tool for modifying and characterizing the same microscopic area of an organic photovoltaic device. In related C-AFM studies of organic solar cell devices, contact mode has been used to spatially resolve currents, and noncontact mode electrostatic force microscopy (EFM) has been used to map electrostatic interactions with the surface.[4–9] Polymer films such as polystyrene,[10] polymethylmethacrylate (PMMA),[11] and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)[12] have been shown to react to the proximity of a voltage-biased AFM tip by forming raised features. Unfortunately, in the case of PEDOT:PSS films, these features exhibit decreased conductivity.[12]

For the present studies solar cell devices were made by spin coating indium tin oxide substrates with successive layers of PEDOT:PSS and P3HT:PCBM. The substrates were first cleaned by sonication in acetone and isopropyl alcohol, and dried on a hot plate. An aqueous solution of PEDOT:PSS was spun on at 3000 rpm and dried on a hotplate at 120 °C in air. The active layer solution was prepared in an argon atmosphere by dissolving regioregular P3HT (Rieke) in chlorobenzene and letting it stir overnight. PCBM was added to make the active layer ratio 1:1 P3HT:PCBM at 1 wt %. The layer was then spin coated onto the PEDOT:PSS layer at a speed of 700 rpm, and annealed under argon at 140 °C.

An Asylum Research MFP-3D AFM was used in all measurements, with a platinum coated silicon probe (MikroMasch NSC 35 for noncontact and CSC 35 for contact mode images) in an Orca cantilever holder with a built-in current amplifier. All measurements were carried out in a dry argon atmosphere at room temperature and ambient pressure. The experimental setup is shown in Fig. 1(a). Figure 1(b) shows

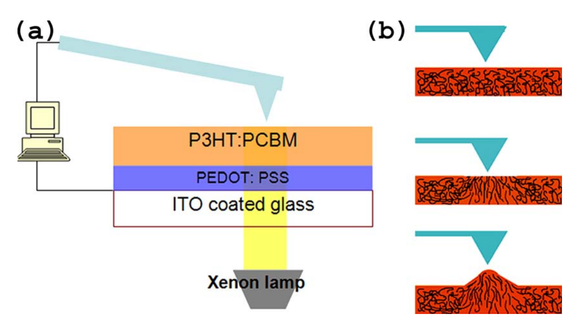


FIG. 1. (Color online) (a) Experimental setup. A conducting tip is used to image films and apply voltages to the sample. A xenon lamp is focused on the sample (~10 $W/cm^2$ light intensity) during photocurrent measurements. The cantilever and sample are in an argon environment. (b) Schematic of before (top) and after applying a moderate (middle) and high (bottom) voltage between the tip and the sample for local current injection. Mechanism of feature formation and conductivity enhancement is postulated to be the transport and realigning of polymer chains to lie parallel to the electric field, causing increased crystallinity and a preferred orientation with respect to the electrode.

a)Electronic mail: azettl@physics.berkeley.edu.

 

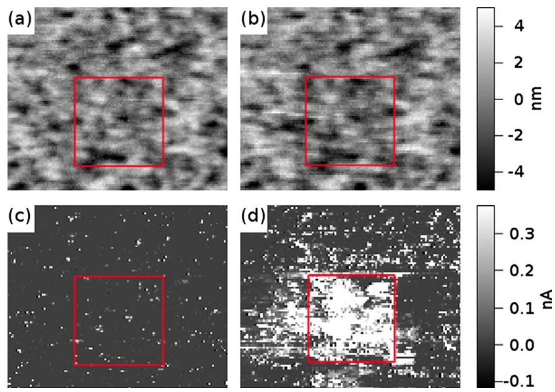


FIG. 2. (Color online) The $1 \times 1$ $\mu m^2$ region outlined in red was scanned with a tip bias of 500 mV. Topographic maps of before (a) and after (b) reveal little change in the height profile, while the current maps before (c) and after (d) reveal a dramatic increase in conductivity.

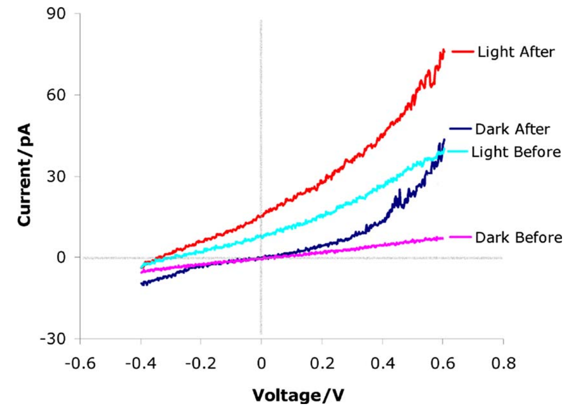


FIG. 4. (Color online) Current vs voltage response of the spot from Fig. 3 in dark and illuminated conditions before and after feature formation. Note that after the film has been locally current-injection treated, it exhibited much higher conductivity than before. The open circuit voltage increases from 0.29 to 0.33 V, and the short circuit current doubles from 7.6 pA before to 15 pA after.

schematically the desired post-production cell processing. The top image shows the as-produced device morphology, prior to post-processing. In the center image, a small injection current density, applied via the C-AFM tip, has locally restructured the polymer blend thereby enhancing local transport characteristics of the film. The bottom image shows the device after a large injection current density has been applied; the polymer blend is locally restructured to improve transport, and, simultaneously, the rear surface has been textured for additional light absorption capability. Rear surface texturing with a planar front surface has been shown to be effective at encouraging total internal reflection, and thus absorption, within the active layer.[13]

We first describe local transport enhancement without texturing in the PEDOT:PSS/P3HT:PCBM devices. Figure 2 shows contact mode topographic and current scans made with a 30 mV probe bias before and after scanning a $1 \times 1$ $\mu m^2$ area (indicated in red) at 500 mV at the rate of 1 line/s. The results reveal an enhanced region of conductivity in the area that was in contact with the tip biased at 500 mV, without significant change in the height profile. The response of the film to this voltage is not uniform, a result of the inhomogeneous nature of the film, composed of a blend of polymers with different thermal and electrical characteristics. As is evident in the figure, the conductivity modification has extended slightly beyond the region of the 500 mV scan. This is likely due to film modifications occurring as a result of the probe voltages applied to map the current response of the extended area, and by longer-reach current path and electric field influences of the tip biased at 500 mV.

Figure 3 shows the effects of film texturing by applying

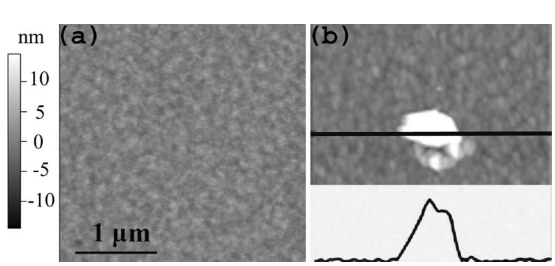


FIG. 3. Topographic map of the active layer of an organic solar cell device before (a) and after (b) forming a raised feature via C-AFM. The bottom part of (b) shows the height profile at the black line. The height of the feature is 60 nm.

a large tip bias to a small film region. The area was scanned in noncontact mode before and after the application of a 10 V bias pulse of 1 s duration with the AFM probe to the center of the scanning region. During the voltage application, and the subsequent current-voltage measurements, the tip was held at a constant height above the surface. The large applied bias results in the formation of an elevated feature with a height of ~60 nm at the contact point and a diameter of ~1 $\mu$m. The features were found to be fully formed upon scanning the region immediately after the voltage application, indicating they formed within the 1 s pulse.

In addition to modifying the surface geometry, the local application of a large conditioning voltage and injected current density improves the electrical characteristics of the layer. Figure 4 shows the current-voltage (*I*-*V*) characteristics of a raised spot in a PEDOT:PSS/P3HT:PCBM blend under dark and illuminated conditions before and after the application of the 10 V conditioning pulse. The probe voltage was increased linearly over 1 s from −1 to 1 V for the current response measurements. A dramatic increase in film conductivity is observed, evident by a doubling of the short circuit current, from 7.6 to 15 pA. The shape of the *IV* curve transforms from a linear curve, dominated by the series resistance, to one with a more diodelike characteristic. The open circuit voltage shifted from 0.29 to 0.33 V. The low magnitude of $V_{oc}$ may be related to surface charging[14] around the AFM tip and the large work function[14] of platinum, 5.6 eV. If this device were instead contacted by a conformal film of work function 4.2 eV, corresponding to the lowest unoccupied molecular orbital (LUMO) of PCBM, the $V_{oc}$ should be closer to the difference between the highest occupied molecular orbital (HOMO) of P3HT and the LUMO of PCBM,[2] around 1 eV. The rectifying behavior leading to the observed photovoltaic response arises from the holes preferentially traveling through the electron-blocking PEDOT:PSS layer.

The surface-modification experiment has been repeated at different locations on the film, as well as on multiple films to confirm reproducibility. For the same film, the voltage required for feature formation is generally uniform, although some regions required a higher or lower voltage, likely a result of the inhomogeneous nature of the bulk heterojunction. Both forward and reverse biases were found to produce the features.

We briefly examine the mechanism of voltage pulse induced transport enhancement and texturing in the devices. It is well established that the morphology of polymer-based solar cells is critical to charge extraction.[15] In our case, we postulate that the crystallinity and alignment of the polymer chains are improved during the voltage application. The small distance between the AFM tip and the conducting substrate ($\sim$100 nm), results in large fields ($5\times10^6$–$5\times10^8$ V/m) for an applied 0.5 to 10 V. Furthermore, the sharp AFM tip results in large gradients in the electric field, and an electrostatic force on the surrounding area. While applying the voltage pulse, currents of $>1$ nA are typical, indicating a large local current density and making heating above the glass transition temperature likely. It is known that mobile polymer chains polarize and align with external electric fields,[16] in this case perpendicular to the electrodes, providing better crystallinity[16] and more direct charge extraction routes. In addition, a reverse bias, if sufficiently large to overwhelm the diode nature of the device, also induces large current densities and electrostatic forces. The effect has also been observed in the post-treatment of macroscopic solar cells with thermal annealing in the presence of an external electric field.[17] In the present case, the electric field gradients are much higher, given the geometry of the AFM tip, and we observe more significant gains in conductivity enhancement.

The raised features are most likely due to mass transport toward the tip,[10] occurring in tandem with polymer chain alignment. These features represent a valuable method for texturing the solar cell rear surface. Though the concept of using a single AFM tip for the modification of a large solar cell is not practical, an array of sharp electrodes could be utilized for the treatment of large areas.

In summary, we have observed significant morphological and electrical changes in response to large electric fields applied using an AFM tip in organic solar cell devices. This technique improves light capturing via texturing while enhancing charge extraction capabilities of the photoactive polymer-fullerene blend. The scale-up of this technique could improve macroscopic organic solar cell devices in the future.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. A.M.Z. acknowledges the NSF Graduate Research Fellowship. We thank David Okawa for useful discussions and technical assistance.

[1]K. M. Coakley and M. D. McGehee, Chem. Mater. **16**, 4533 (2004).
[2]H. Hoppe and N. S. Sariciftci, J. Mater. Res. **19**, 1924 (2004).
[3]S.-I. Na, S.-S. Kim, S.-S. Kwon, J. Jo, J. Kim, T. Lee, and D.-Y. Kim, Appl. Phys. Lett. **91**, 173509 (2007).
[4]O. Douhéret, L. Lutsen, A. Swinnen, M. Breselge, K. Vandewal, L. Goris, and J. Manca, Appl. Phys. Lett. **89**, 032107 (2006).
[5]L. S. C. Pingree, O. G. Reid, and D. S. Ginger, Adv. Mater. **21**, 19 (2009).
[6]B. J. Leever, M. F. Durstock, M. D. Irwin, A. W. Hains, T. J. Marks, L. S. C. Pingree, and M. C. Hersam, Appl. Phys. Lett. **92**, 013302 (2008).
[7]O. Douhéret, A. Swinnen, S. Bertho, I. Haeldermans, J. D'Haen, M. D'Olieslaeger, D. Vanderzande, and J. V. Manca, Prog. Photovoltaics **15**, 713 (2007).
[8]S. C. Veenstra, J. Loos, and J. M. Kroon, Prog. Photovoltaics **15**, 727 (2007).
[9]D. C. Coffey, O. G. Reid, D. B. Rodovsky, G. P. Bartholomew, and D. S. Ginger, Nano Lett. **7**, 738 (2007).
[10]S. F. Lyuksyutov, R. A. Vaia, P. B. Paramonov, S. Juhl, L. Waterhouse, R. M. Ralich, G. Sigalov, and E. Sancaktar, Nature Mater. **2**, 468 (2003).
[11]S. F. Lyuksyutov, P. B. Paramonov, S. Juhl, and R. A. Vaia, Appl. Phys. Lett. **83**, 4405 (2003).
[12]X.-D. Dang, M. Dante, and T.-Q. Nguyen, Appl. Phys. Lett. **93**, 241911 (2008).
[13]E. Yablonovitch, J. Opt. Soc. Am. **72**, 899 (1982).
[14]D. Mihailetchi, P. W. M. Blom, J. C. Hummelen, and M. T. Rispens, J. Appl. Phys. **94**, 6849 (2003).
[15]W. L. Ma, C. Y. Yang, X. Gong, K. Lee, and A. J. Heeger, Adv. Funct. Mater. **15**, 1617 (2005).
[16]*Mathematical Modeling for Polymer Processing*, edited by V. Capasso (Springer, Berlin, 2003).
[17]F. Padinger, R. S. Rittberger, and N. S. Sariciftci, Adv. Funct. Mater. **13**, 85 (2003).