Enhanced Open Circuit Voltage in Aluminum Confined Post-Annealing of poly(3-hexylthiophene)/fullerene Bulk Heterojunction Solar Cells under Electric Field

Mukesh Kumar, Pavel Dutta and Venkat Bommisetty
Department of Electrical Engineering, South Dakota State University
Brookings SD 57007 (USA)

ABSTRACT

The effect of an external electric field during post-annealing on the device characteristics of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) bulk heterojunction solar cells was studied. The application of external electric field in forward bias resulted in significant enhancement in Voc and fill factor whereas devices annealed under reverse bias had an enhanced J_sc. Both forward and reverse bias annealing increased the shunt resistance. The Al - blend interface topography and carrier dynamics were studied using conducting atomic force microscopy and frequency dependent intensity modulated photocurrent spectroscopy (IMPS). The results indicate that post-annealing under external electric field can be used to engineer the interface composition to enhance the charge transport in bulk heterojunction solar cells to improve the device performance.

INTRODUCTION

Organic photovoltaics is emerging as a potential renewable source of electrical energy with low materials and processing costs [1, 2], flexible device designs and manufacturing scalability [3]. Bulk heterojunction (BHJ) solar cells using poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) blend as the photovoltaic active layer can produce power conversion efficiencies (PCE) in the range of 4% - 6% [4]. Newer low bandgap photon absorbers have shown PCSs up to 10% [5]. However, commercialization requires further improvements in the absorption characteristics of the active layer and engineering of charge transport processes within the active layer and at interfaces. Light absorption in organic solar cells leads to generation of bound electron-hole pairs (excitons) [6] which disassociate into free carriers at the donor-acceptor interfaces [7]. BHJ morphology enhances the donor-acceptor (D-A) interface area and provides independent pathways for holes and electrons to their respective electrodes [4]. Open circuit voltage (V OC) and short circuit current (J SC) are two important device merit factors. For P3HT:PCBM bulk heterojunction solar cells, J_sc has reached its practical limit (10-12 mA cm^-2) [8]. Therefore, enhancement in V OC can help increasing the efficiency of P3HT:PCBM solar cells. Various approaches have been developed to enhance the Voc, including application of electric field during post-annealing [9]. Lin et al., applied 500-1000 V across the cell and observed 60 mV increase in the open circuit voltage [9].

This study reports a systematic investigation of various post-annealing treatments under small (4 V) forward and reverse biases. A combination of scanning probe microscopy and intensity modulation photocurrent spectroscopy (IMPS) techniques were used to study the carrier dynamics and the interface structure, and helped explain the correlation between annealing process and V OC. Results showed a significant effect of bias polarity on device merit factors.
EXPERIMENTAL DETAILS

The BHJ cells were fabricated using following procedures: a 40 nm PEDOT:PSS layer was spun cast onto clean ITO (15 Ω/sq) substrates and annealed at 140°C for 10 min in atmosphere. The blend solution having 20 mg/ml each of P3HT and PCBM (wt. ratio 1:1) in 1,2 dichlorobenzene was spin coated to obtain a 140 nm thick active layer inside N₂ filled glove box. An Al electrode was thermally evaporated through a shadow mask with an active device area of about 0.1 cm². Four sets of devices were fabricated with different thermal treatments as illustrated in Fig.1: as-deposited (Al deposition without annealing), post-annealed (Al deposition followed by annealing at 140°C for 10 min.), Forward electric (FE) field post-annealed (Al deposition followed by annealing at 140°C with -4 V bias applied to Al electrode with respect to ITO and reverse electric (ER) field post-annealed (Al deposition followed by annealing at 140°C with +4 V bias applied to Al electrode with respect to ITO. The applied bias corresponded to 22 MV/m. The current density-voltage (J-V) characteristics were measured using Agilent 4155C semiconductor parameter analyzer under dark and simulated AM1.5 illumination (100 mW/cm²). Intensity modulated photocurrent spectroscopy (IMPS) was performed in the range 0.1 Hz - 20 kHz using a Solartron 1255 frequency response analyzer (FRA) inside a glove box. During IMPS measurements, the ac component of the light was maintained at 10% of the dc component. An Agilent 5500 Scanning probe microscope installed in a glove box was used to measure the nanoscale phase distribution of P3HT/PCBM. The Al bonding pads were removed using sticky tape. Current sensing AFM (CS-AFM) was performed in contact mode using a Pt/Ir coated Si tip (Budget Sensors ContE-G; radius ~ 20 nm; force constant of 0.2 N/m; resonance frequency ≈ 14 kHz). No interfacial layers (such as LiF or Ca) were deposited in this study to minimize the complexity of the Al-blend interface structure. The series (Rs) and shunt (Rsh) resistance were calculated from the inverse slope of J-V curve at J ~ 0 mA cm⁻² and V ~ 0 V, respectively, under illumination [10].

DISCUSSION

Figure 1 (a) shows a schematic of process conditions for the four sets of samples used and figure 1 (b) shows their J-V characteristics. The conventional post-annealed and ER- post-annealed cell had an s-shaped J-V characteristics indicating charge injection barriers at metal electrode-blend interface [11]. This injection barrier may be due to lack of interfacial layers at this electrode. The short circuit current (J(SC)), open circuit voltage (V_OC), fill factor (FF) and photo conversion efficiency (η) are summarized in table 1. The as-deposited device shows an efficiency of 0.7% which increases to 2.3% after conventional post-annealing. Post-annealed devices had a substantial enhancement in the V_OC (600 mV) compared to as-deposited cells (340 mV). The post-annealing under forward bias resulted in further increases in V_oc to 660 mV (with η = 2.5%). While ER-post-annealing did not affect the V_OC but resulted-in an increase in the J_SC, as shown in Figure 1 (c). The R_SH for as-deposited device was 186 Ω cm² which increased nearly fourfold to 768 Ω after conventional post-annealing. However, the R_SH further increased to 873 Ω cm² and 1192 Ω cm² after EF-post-annealing and ER-post-annealing. Conversely, none of the annealing processes affected the series resistance significantly, except ER annealing which increased R_s to 46 Ω cm². To further probe the microscopic mechanisms responsible for these changes, nanoscale topography, CS-AFM measurements and the IMPS response was measured under different light intensities.
Table 1. Device parameters under different annealing conditions

<table>
<thead>
<tr>
<th></th>
<th>As-deposited</th>
<th>Post-annealed</th>
<th>EF-post annealed</th>
<th>ER-post annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{SC}$ (mA cm$^{-2}$)</td>
<td>9.37</td>
<td>11.79</td>
<td>8.98</td>
<td>12.12</td>
</tr>
<tr>
<td>$V_{OC}$ (mV)</td>
<td>340</td>
<td>600</td>
<td>660</td>
<td>600</td>
</tr>
<tr>
<td>FF (%)</td>
<td>24</td>
<td>33</td>
<td>42</td>
<td>34</td>
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<tr>
<td>$\eta$ (%)</td>
<td>0.7</td>
<td>2.3</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>$R_S$ (Ω cm$^2$)</td>
<td>35</td>
<td>34</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>$R_{SH}$ (Ω cm$^2$)</td>
<td>186</td>
<td>768</td>
<td>873</td>
<td>1192</td>
</tr>
</tbody>
</table>

Al-blend interface characterization

Figure 2 (a)-(d) shows confocal optical micrographs of the Al-blend interface of the four devices, after removing the Al-electrode (referred to as active layer surface). The active layer surface in as-deposited device was nearly featureless while annealed devices had patch like domains several microns in length. The size and density of such domains in post-annealed devices with both forward and reverse bias was much smaller. The surface topography images in figure 2 (e)-(h) show a detailed view of these domains while no such structures were observed on as-deposited or EF- and ER-post annealed blend surface. A Pt/Ir coated AFM tip was used for CS-AFM imaging, which is suitable for either injection or collection of holes from the blend. The brighter regions in the CS-AFM images are P3HT rich regions while the darker regions are PCBM rich regions [12]. The high resolution CS-AFM images are shown in figures 2 (i)-(l). The distribution of PCBM at the blend surface in all four cells was significantly different and the average cluster size distribution for as-deposited, post-annealed, EF-post-annealed and ER-post-annealed varies from 30 – 250 nm, 50 - 700 nm, 30 - 800 nm and 50 nm to 300 nm, respectively. Therefore, the high resolution CS-AFM images reveal that the Al-blend interface in post-
annealed cell under conventional method and under electric field was PCBM rich without any PCBM overgrowth as reported in the literature [13-14].

The IMPS response of the cells was measured to further probe the effect of PCBM redistribution at Al-blend interface. Figure 3 (a) shows experimental IMPS complex Nyquist plot for all four devices and figures (b) and (c) are corresponding Bode plots. The IMPS responses in quadrant I of the complex-plane plot indicated positive phase and produced a positive phase shift of ac photocurrent with respect to modulation frequency (see figure 3(b)). The dynamics of photogenerated carriers determined the amplitude and phase of ac photocurrent with modulation frequency and relate to the kinetics of recombination (see figure 3 (b) and (c). At the lowest modulation frequency (0.1 Hz), the ac photocurrent amplitude can be related to steady state current and hence substantial recombination of photogenerated carriers. The modulation frequency dependent ac photocurrent amplitude represents a change in the recombination dynamics. As the modulation frequency increases, the amplitude of ac photocurrent increases indicating reduced recombination. With further increase in the frequency, the ac photocurrent reaches Gartner limit which corresponds to the maximum extractable photocurrent [15, 16].

The positive phase of ac photocurrent and increase in its amplitude with modulation frequency has not been reported for DSSCs or inorganic solar cells. Both these characteristics
were attributed to the existence of interfacial recombination in BHJ cells. The modulation
frequency at the maxima of the complex-plane plot in quadrant I, \( f_{\text{max}} \), has been related to the rate
of recombination of photogenerated carriers at surface states as first approximation, and can be
considered equal to the pseudo-first-order rate constant (k) [15-17]. The value of \( f_{\text{max}} \) for as-
deposited, post-annealed, EF-post-annealed and ER-post-annealed cells are 1.98, 1.20, 1.54 and
1.54 Hz, respectively indicates a decrease its value for all post-annealed cells in comparison to
as-deposited cells. Therefore, the carrier recombination rate is smaller for post-annealed cells
compared to as-deposited cells.

The recombination losses of photogenerated charges in BHJ solar cells occur in time
scales \( > 10^{-6} \) sec in contrast to sub-nanosecond time scales of geminate exciton recombination.
The recombination that is being discussed here occur in later stages of carrier transport, possibly
through interfacial states at electrode-blend interfaces which typically correspond to microsecond
time scales [17,18].

The shape of IMPS complex-plane plot in quadrant IV for BHJ solar cells is similar to
that reported for dye sensitized solar cells (DSSC) where the modulation frequency has often
been related to the carrier transport time in the bulk of the active layer with high frequency
minima (\( f_{\text{min}} \)) as \( \tau_D=1/(2\pi f_{\text{min}}) \) [19]. The value of \( f_{\text{min}} \) for as-deposited, post-annealed, EF-post-
annealed and ER-post annealed cells were 544 Hz, 176 Hz, 371 Hz and 371 Hz, respectively.
The results indicate that the \( f_{\text{min}} \), which relates to the average transport time \( \tau_D=1/(2\pi f_{\text{min}}) \) of
photogenerated carriers through the bulk of the active layer, increases on EF and ER-post-
annealing treatment indicating shorter transit times in post-annealed samples under electric field.
Therefore, reduced non-geminate recombination due to the redistribution of PCBM at Al-blend
interface as well efficient transport through the bulk of the blend in post-annealed samples under
electric field, may have contributed to increase in \( V_{OC} \) of EF-post-annealed cells.

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**Figure 3.** (a) Experimental IMPS spectra for solar cell under different annealing
treatment under short circuit condition. The dc light (532 nm laser) intensity was
7.8×10^{15} cm^{-2} s^{-1} and ac modulation was 10% of dc intensity. (b) The phase and (c)
amplitude of ac photocurrent with respect to the modulation frequency.
CONCLUSIONS

The effect of external electric field during post-annealing on the device characteristics of P3HT:PCBM bulk heterojunction solar cells has been investigated in detail. Application of electric field in both forward and reverse bias resulted in similar PCE of about 2.5%, however, resulted in significant increase in \( V_{oc} \) for EF-post-annealing. The nanoscale topography and conducting images of the blend beneath Al- electrode showed re-distribution of P3HT and PCBM under different annealing treatments and PCBM rich Al-blend interface was observed in EF-post-annealed devices. The IMPS results gave insight into the dynamics of photogenerated carriers and showed evidence of reduced non-geminate recombination in post-annealed cells. This study reveals the importance of Al- confined post-annealing under electric field to reduce the non-geminate recombination, thereby, enhancing \( V_{oc} \) and hence device efficiency of BHJ solar cells.

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REFERENCES