Investigating the role of efficiency enhancing interlayers for bulk heterojunction solar cells by scanning probe microscopy

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Abstract
Detailed optimization of the device architecture of bulk heterojunction organic solar cells is of crucial importance when eventually targeting commercial applications. It has been shown before that the efficiency of such devices can be increased significantly upon incorporation of an imidazolium-substituted polythiophene interlayer. The cause of this increase in efficiency was, however, still unclear and is investigated here by a combination of PeakForce Quantitative Nanomechanical Mapping, PeakForce TUNA and Kelvin Probe Force Microscopy. A link between the local morphological and electrical properties is established. We show that the conjugated polyelectrolyte interlayer acts as a hole blocking layer. Additionally, illuminated Kelvin Probe Force Microscopy indicates that the interlayer creates an extra built-in electric field promoting charge transfer from the bulk heterojunction active layer into the interlayer.

1. Introduction

The beneficial effect on photovoltaic properties of a broad variety of interlayers positioned between the electrodes and the photoactive layer has been reported in numerous manuscripts. Deschler and coworkers described the use of a polymer interlayer between the PEDOT:PSS and the bulk heterojunction active layer in organic solar cells. Not only did this additional layer absorb a significant portion of the light, it also resulted in an increase in short circuit current [1]. Kang et al. showed a similar reduction in current loss by adding a photo-crosslinkable interlayer between PEDOT:PSS and the donor–acceptor layer [2]. While Seo et al. were able to increase the efficiency by adding a conjugated polyelectrolyte interlayer at the cathode side [3]. Many different interpretations have been proposed to explain the origin of these beneficial effects. Guerrero reported that a possible interfacial effect exists in the form of a charge neutrality level and this level in turn controls the energy level alignment at the cathode contact [4].

As these interlayers are often no more than 10–20 nm thick, the need for appropriate characterization techniques arises. XPS and UPS are excellent methods to study interface effects but their spatial resolution is only in the millimeter range [5]. One of the only methods with a sufficient spatial resolution combined with the ability to analyze the local electrical and morphological properties and the possibility to study an organic solar cell under working conditions are scanning probe microscopy techniques [6,7]. While atomic force microscopy can be used to study the morphology of organic solar cells, other SPM techniques can address the local electrical properties: e.g. C-AFM
to assess the local conductivity and KPFM to study the surface potential [6–12].

In previous work we have shown that an alcohol-soluble imidazolium-substituted polythiophene (Fig. 1(a)) can be used as an effective electron-transporting interlayer material, significantly increasing the efficiency of PCDTBT:PC71BM (Fig. 1(b) and (c)) polymer solar cells [13]. In this manuscript, we describe the use of advanced scanning probe microscopy techniques to link the nanoscale morphological and electrical properties of the interlayer towards a better understanding of the efficiency-enhancing effect of the ionic polythiophene interlayer. More specifically, we correlate the local electrical conductivity with local morphology. In a second step we determined the local surface potential and the change in surface potential under the influence of illumination.

2. Experimental

Details on the synthesis of the imidazolium-substituted polythiophene used in this work can be found in the recent manuscript by Kesters et al. [13].

Sample fabrication: all samples were fabricated using a standard glass–ITO–PEDOT:PSS-active layer layout, without the traditional aluminum top contact. The indium tin oxide (ITO, Kintec, 100 nm, 20 Ω/sq) containing substrates were cleaned using soap, demineralized water, acetone, isopropanol and a UV/O3 treatment. Subsequently, the ITO substrates were covered by a 30 nm thick layer of PEDOT–PSS (poly (3,4-ethylenedioxythiophene)–poly(styrene-sulfonic acid)) (Heraeus Clevios) by spin coating. Processing was performed in a glovebox with a controlled nitrogen atmosphere, starting with an annealing step at 130 °C for 15 min to remove any residual water. The PCDTBT (poly[9-(1-octyl)carbazole-2,7-diyl]-2,5-thiophenediy1-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediy1]) donor polymer was obtained from SolarisChem (Mn = 79 kDa, D = 2.4) and used without further purification. The active layer consisting of PCDTBT:PC71BM [(6,6)-phenyl C71 butyric acid methyl ester) (Solenne) with an in blend ratio of 1:4 was spin coated with a thickness of 65 nm, as confirmed by DEKTAK. The active layer deposition step was followed by spin coating of the conjugated polyelectrolyte (CPE) interlayer. The CPE solution was prepared in a concentration of 0.02% in methanol.

This procedure led to a set of three different samples: a reference sample with only the active layer deposited on ITO covered glass, a methanol treated active layer on ITO covered glass and a CPE coated active layer on ITO covered glass. All of the samples were kept in an inert nitrogen atmosphere at all times.

Measurements were done on a Bruker Multimode 8 atomic force microscope in combination with a V series controller. The AFM is enclosed in a glovebox allowing for a controlled atmosphere with a maximum relative humidity of 6%. KPFM imaging was done using the surface potential setting on the AFM with long platinum/iridium coated cantilevers with a force constant of 4 N/m and a lift...
scan height of 7–15 nm. PeakForce TUNA/QNM measure-
ments were done using a soft conducting platinum/iridium
cantilever with a force constant of 0.4 N/m.
A standard solar simulator with a xenon arc lamp was
used during KPFM imaging. The light was fed into the
glovebox via a high grade optical fiber, which reduced
the intensity by 50% over the visible spectrum. The light
from the optical fiber was calibrated using a standard
reference silicon solar cell.
All images were analyzed using the NanoScope Analysis
software.

3. Results and discussion

3.1. Morphology and mechanical properties

PeakForce Quantitative Nanomechanical Property
Mapping (QNM) probes the morphology and the mechanical
properties at the same time, by making a force distance
curve at each point and fitting this force distance curve
with the Derjaguin–Muller–Toporov (DMT) model of elastic
contact [14]. Depending on the types of materials under
investigation, a suited AFM probe needs to be selected.
With a fully calibrated tip it is possible to gain insight on
the absolute values of the local mechanical properties
(e.g. Young’s modulus, adhesion, deformation depth). If
absolute values are not of importance, a single
uncalibrated cantilever is sufficient. This still allows a
study of the coverage or the intermixing of certain materi-
als [15]. In this case, PeakForce QNM was used to study
surface coverage and therefore relative differences are
sufficient to draw conclusions.

When looking at the film morphologies (Fig. 2(a)–(c)) it
is clear that the calculated RMS roughness (0.6 nm, Table 1)
is similar for both the reference and methanol treated
samples. The biggest change in morphology was visible

Fig. 2. Overview of the morphology, adhesion and local current for the different samples, as analyzed by PeakForce QNM and TUNA. Images (a)–(c) show the
morphology of the reference, methanol treated and CPE covered sample, respectively; (d), (e) and (f) show the adhesion for the reference, methanol treated and
CPE covered sample, respectively; (g)–(i) show the cycle averaged local currents for the reference, methanol treated and CPE covered sample, respectively.
when the CPE was added. However, from the morphology images it is not clear if the additional CPE layer completely covers the surface or if the lower lying regions actually reveal the underlying active layer.

In this article the adhesion is presented, the adhesion represents how much your tip interacts with the surface. As interaction forces are different for different materials this will also result in different adhesion properties. Fig. 2(d)–(f) shows that there are clearly two distinct regions for the CPE treated sample compared to the reference and methanol treated samples. Moreover, a nice correlation between topography and adhesion exists for the CPE coated sample, thus it is possible to conclude that the CPE forms a web on top of the bulk heterojunction. The coverage is about 43%, as calculated by bearing analysis from 1 by 1 µm² and 4 by 4 µm² images.

The average thickness of the CPE layer was calculated by analysis of the thickness histogram (Fig. 3). This histogram shows the height distribution of the entire image. By fitting the two peaks with a normal distribution, the difference between the centers of the two peaks gives the average thickness of the CPE layer. This results in an average thickness of about 3.56 nm. At these thicknesses, the effect of tunneling can be excluded, as this phenomenon only has a major contribution to the current for layers thinner than 0.5 nm [16].

### 3.2. PeakForce TUNA and conductive AFM

While tunneling can be excluded as a possible mechanism, the local current is still of major importance. As the CPE layer is very thin, traditional conductive AFM might result in destruction of the interlayer. PeakForce TUNA is similar to PeakForce QNM with one major difference: PFT-UNA tips have a conductive coating which means that when the tip is in contact with the sample it is possible to measure the current while applying a certain bias. Due to the nature of this technique, the applied contact force is constant over the entire image regardless of the applied DC bias. Moreover, the applied force is perpendicular to the sample while conductive AFM has a resulting force parallel with the sample. Thus using PeakForce TUNA should ensure the least amount of sample damage. Nevertheless, conductive AFM images at both a negative and positive sample bias are included for completion. From PeakForce TUNA measurements three different currents are deduced, namely peak, contact and total current. The peak current is the current at the maximum amount of force during a force distance measurement, the contact current is the current during contact of the tip with the sample and the total current is the time averaged current over the duration of a force distance curve, which also includes the time when the tip is not in contact with the sample.

As the workfunction of the Pt/Ir coated tip is in the same range as the HOMO levels of the probed organic materials the contrast obtained by conductive AFM and PeakForce is due to a hole current [13,17]. Therefore, when applying a negative bias to the sample holes will be injected from tip into the organic layer. Fig. 2(g)–(i) shows the local contact current maps at a DC sample bias of −1.8 V.

In this work the contact current is shown as it lies closest to the classical current measured by conductive AFM. Small differences in hole current between the reference and the MeOH treated sample are visible (Table 1 and Fig. 2(g) and (h)) they are however negligible as on this scale the samples will always show some form of inhomogeneity. As evidenced from the KPFM results in Table 1 there is a small difference in contact potential and thus a small difference in barrier between tip and sample when comparing the reference and MeOH treated samples however, the applied bias of −1.8 V should be sufficient to overcome any barrier at the interface between surface and tip. The biggest difference is seen when looking at the CPE treated sample, wherever the CPE is present the hole current seems to be severely limited. The hole blocking nature of this interlayer could explain the increase in short circuit current as seen in [13] by reducing the interface recombination and thus resulting in more electrons reaching the aluminum top contact.

These results are confirmed by classical conductive AFM measurements clearly showing that at both negative (hole injection) and positive (hole extraction) bias the hole current is severely limited by the conjugated polyelectrolyte interlayer (Fig. 4).

#### 3.3. KPFM

In the case of metals, Kelvin Probe Force Microscopy probes the local workfunction, while for blended organic

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS roughness (nm)</th>
<th>Contact current (pA)</th>
<th>Contact potential difference (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.67</td>
<td>−1.31</td>
<td>−0.30</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.62</td>
<td>−2.22</td>
<td>−0.26</td>
</tr>
<tr>
<td>CPE</td>
<td>2.64</td>
<td>−9.47</td>
<td>−0.10</td>
</tr>
</tbody>
</table>

**Fig. 3.** Histogram corresponding to a 1 by 1 µm scan made by PeakForce measurements.
materials one most likely measures a combination of the HOMO levels of the materials present in the bulk hetero-junction [18].

Fig. 5(d)–(f) shows the contact potential difference for the reference, the methanol treated and the CPE coated sample, respectively. A shift of 30 mV is seen (Table 1) when going from the reference to the methanol treated sample, an effect also described recently by Zhou et al. [19]. When the CPE is added, a contact potential difference shift of around 0.2 V compared to the reference sample is observed. This difference in surface potential coincides with the estimated difference in HOMO level of PCDTBT (5.4 eV) and the CPE (5.2 eV) [13]. This change in contact potential difference indicates a lower barrier between the Pt/Ir tip and the sample.

From the analysis of the KPFM image of the CPE coated layer it becomes clear that there are areas with a lower surface potential, which are correlated with the holes that are present in the CPE layer. Topographic artefacts can be excluded as the lateral resolution of KPFM is about

**Fig. 4.** Topography (a) and corresponding C-AFM results (b) top part made at a negative sample bias of −1.3 V while the bottom was made at a sample bias of 2.4 V

**Fig. 5.** Morphology and surface potential images of the reference (a) and (d), the methanol treated (b) and (e) and the CPE covered samples (c) and (f), respectively.
25 nm [20] and the holes present in the CPE are in the order of 100 nm in diameter. This means that there are areas with a higher and a lower surface potential, indicating the existence of a built-in electric field. From simple electrostatics and a measurement of the CPE layer thickness, this field can be estimated at about $10^6$ V/m. Moreover, Hoven et al. have shown that tetrakis (imidazolyl)-borate ions will redistribute when used as a counterion in a PFN based CPE. As the Br- ions used in this work are much smaller they are most likely mobile and will react to a change in local electrostatic potential and the resulting redistribution of the internal electric field can act as a mechanism to enable efficient electron extraction [21].

Further insights into the mechanism at work can be obtained by measuring the change in surface potential upon illumination. Without illumination, the potential difference inside a lower lying region and on top of the CPE layer is around 50 mV, while with illumination, estimated at 0.7 suns, this potential difference is lower, around 20 mV (Fig. 6). Two possible explanations can be proposed. At first, one could think that this is merely a screening effect. However, the surface potential difference between the donor–acceptor blend and the CPE layer decreases upon illumination, and this contradicts the idea of a screening effect. A second possibility is charge transfer. A difference in surface potential indicates the existence of regions with a certain amount of positive and negative charges. When the potential difference between the donor–acceptor blend and the CPE is high (in dark), the difference in charges is high. With illumination, both positive and negative charge carriers will be generated inside the active layer. These charges will feel the effect of the built-in potential coming from the CPE layer. Electrons generated in the donor–acceptor blend will move to the CPE, resulting in a decrease of positive charge in the CPE and thus reducing the potential difference, as seen in Fig. 7. Moreover, the aluminum top contact acts as an electron extracting contact and the energy barrier between these two materials is most likely beneficial for electron transfer from one layer to the next as shown by Siddiki et al. [22].

Fig. 8 shows the response of the surface potential to a square wave pulse. This square wave was achieved by simply turning the illumination on and off. Every drop in surface potential corresponds with the illumination being turned on. The drop in surface potential seen here is in the same order of magnitude and direction as shown by Maturová et al. [8]. Moreover, the response seems to be a process on a millisecond time scale (Fig. 8(c)), indicating that the electrons transferred from the donor–acceptor blend are weakly bonded. This is of crucial importance as strong bonding would act as a trap center for electrons and thus not result in an increase in short circuit current.

4. Conclusions

In conclusion, we propose the following mechanisms to contribute to an increase in short circuit current and power conversion efficiency upon application of an imidazole-functionalized ionic polythiophene interlayer. First of all, the CPE layer acts as a hole blocking layer resulting in less recombination at the interface. Moreover, the addition of the CPE also increases the surface potential and thus has an influence on band alignment. Finally, it creates an extra
built-in electric field promoting electron transfer from the active layer to the CPE under illumination.

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References


