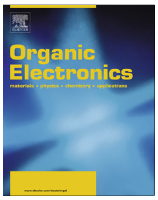
Organic Electronics 15 (2014) 1282–1289

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



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

Jeroen Drijkoningen [a,b,*], Jurgen Kesters [a], Tim Vangerven [a], Emilie Bourgeois [a], Laurence Lutsen [a], Dirk Vanderzande [a], Wouter Maes [a], Jan D'Haen [a], Jean Manca [a,b]

[a] *Hasselt University, Institute for Materials Research & IMEC-associated lab IMOMEC, Wetenschapspark 1, B-3590 Diepenbeek, Belgium*
[b] *SIM (Flemish Strategic Initiative on Materials), SoPPoM Program, Belgium*

ARTICLE INFO

Article history:
Received 13 September 2013
Received in revised form 24 February 2014
Accepted 26 February 2014
Available online 12 March 2014

Keywords:
Organic photovoltaics
Interlayer
Conjugated polyelectrolyte
Interface modification
PeakForce scanning probe microscopy

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

---

* Corresponding author at: Hasselt University, Institute for Materials Research & IMEC-associated lab IMOMEC, Wetenschapspark 1, B-3590 Diepenbeek, Belgium. Tel.: +32 11 268870.

E-mail address: jeroen.drijkoningen@uhasselt.be (J. Drijkoningen).

http://dx.doi.org/10.1016/j.orgel.2014.02.025
1566-1199/© 2014 Elsevier B.V. All rights reserved.

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:$PC_{71}BM$ (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/O_3 treatment. Subsequently, the ITO substrates were covered by a 30 nm thick layer of PEDOT–PSS (poly (3,4-ethylenedioxythiophene)–poly(styrene-sulfonic acid)) (Heraus 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-octylnonyl)-9*H*-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]) donor polymer was obtained from SolarisChem ($M_n = 79$ kDA, $D = 2.4$) and used without further purification. The active layer consisting of PCDTBT:$PC_{71}BM$ ([6,6]-phenyl C_{71} 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

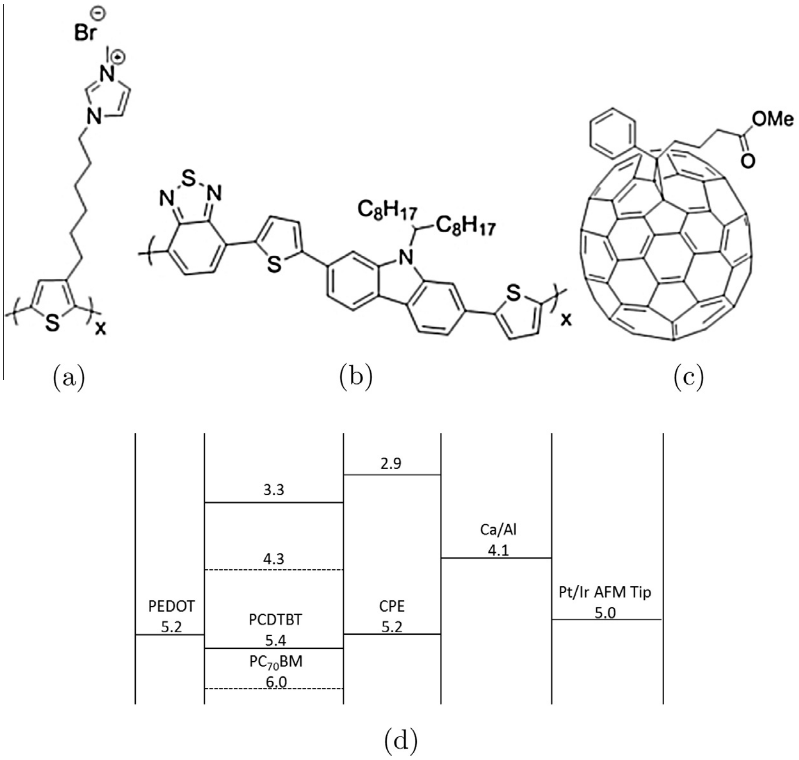


Fig. 1. Imidazolium-functionalized polythiophene interlayer polymer (a), the PCDTBT donor polymer (b) and $PC_{71}BM$ acceptor (c). The energy levels as determined from [13] (d).