



ELSEVIER

Contents lists available at ScienceDirect

## Solar Energy Materials &amp; Solar Cells

journal homepage: [www.elsevier.com/locate/solmat](http://www.elsevier.com/locate/solmat)

## Repair of defects in photoactive layer of organic solar cells

A. Jolt Oostra<sup>a,\*</sup>, Paul W.M. Blom<sup>b,c</sup>, Jasper J. Michels<sup>b,d</sup><sup>a</sup> Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands<sup>b</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany<sup>c</sup> King Abdulaziz University, Abdullah Sulayman, 22254 Jeddah, Saudi Arabia<sup>d</sup> Holst Centre/TNO, High Tech Campus 31, 5656 AE Eindhoven, The Netherlands

## ARTICLE INFO

## Article history:

Received 22 September 2014

Received in revised form

24 November 2014

Accepted 7 December 2014

Available online 30 December 2014

## Keywords:

OPV

Damage

Repair

Hypochlorite

Short circuit prevention

## ABSTRACT

Defects occurring during printing of the photoactive layer in organic solar cells lead to short-circuits due to direct contact between the PEDOT:PSS anode and metallic cathode. We provide a highly effective repair method where the defected zone with bare PEDOT:PSS is treated with aqueous sodium hypochlorite to locally disrupt the conductivity of PEDOT:PSS by over-oxidation. We demonstrate that even macroscopically large defects with a surface area of 10 mm<sup>2</sup> can be repaired, restoring solar cell performance. In contrast, untreated defected solar cells exhibit a significantly increased leakage current and corresponding decrease in light-to-power conversion efficiency.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Organic photovoltaic (OPV) devices have gained considerable interest as an attractive alternative to conventional, inorganic solar cells owing to compatibility with the large-scale roll-to-roll production methods involving flexible substrates [1]. An optimized bulk heterojunction OPV (BHJ-OPV) device contains a photoactive layer in which an electron donor (e.g. poly(3-hexylthiophene-2,5-diyl) (P3HT)) and an acceptor (e.g. phenyl-C61-butyric acid methyl ester (PCBM)) [2] component are intimately phase separated. In this way the formation of free charge carriers by dissociation of photo-generated excitons at the donor–acceptor interface is maximized, while at the same time providing sufficiently pure phases to allow for high carrier mobilities and efficient charge collection [3].

A typical BHJ-OPV device in conventional geometry consists of four functional layers: (i) a transparent anode, typically Indium Tin Oxide (ITO), (ii) a hole transport layer of poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS), (iii) the photoactive layer (e.g. P3HT:PCBM), and (iv) a low work function cathode. The spin-coated PEDOT:PSS layer improves the alignment of the energy levels of the anode and the highest occupied molecular orbital (HOMO) of the donor-material, and planarizes spikes created during ITO sputtering, that would otherwise penetrate the thin photoactive layer and decrease device efficiency [4–6]. In some cases the ITO anode can even be fully replaced by high conductive (HC) grades of PEDOT:PSS [7,8]. Two

examples of cathode systems compatible with the conventional OPV stack geometry are lithium fluoride/aluminum (LiF/Al) and barium/aluminum (Ba/Al). These cathodes, of which the Al phase (~100 nm) forms the bulk, are typically applied by thermal evaporation.

Most fundamental studies on organic solar cells (OSCs) are performed on devices with limited lateral dimensions (<1 cm<sup>2</sup>) [9], facilitating reproducible manufacture of statistically relevant numbers of robust test vehicles for investigations into e.g. the influence of material properties and stack geometry/design on the OSC's photo-physical performance [1]. It should however be realized that in a wet-chemical production environment for large area OPV devices, more aspects that influence cell performance and lifetime should be taken into consideration. For instance, flaws in the production process may result in areas where PEDOT:PSS is left uncovered by the photoactive material. One can for example think of print head failure or substrate misalignment during the deposition of the photoactive layer. Subsequent evaporation of the cathode would then result in flawed, short-circuited OSCs. Another problem is the occurrence of damage to the organic layer stack after printing or coating due to handling issues. To maintain a high production yield despite these issues [10], repair procedures are desired which guarantee the final performance of flawed OSC precursors to be comparable to that of un-faulted ones.

Recently, we have demonstrated a highly effective procedure to decrease the leakage current of organic light-emitting diodes (OLEDs) by treating the stack of PEDOT:PSS and light-emitting polymer (LEP) with aqueous sodium hypochlorite (NaClO<sub>(aq)</sub>) prior to cathode deposition [11]. The reduction in leakage current results from over-oxidation of exposed areas of microscopic dimensions of PEDOT:PSS

\* Corresponding author.

E-mail address: [a.j.oostra@rug.nl](mailto:a.j.oostra@rug.nl) (A.J. Oostra).

by hypochlorite, thereby locally interrupting the conductivity [12]. The lifetime of the devices appeared not to be affected by the treatment. From an application point-of-view, this procedure is attractive owing to its compatibility with the wet-processing techniques [13].

In this article we show that the oxidative treatment applied to improve OLED performance can also be utilized to repair precursors of conventional OSCs containing macroscopic defects in the photoactive layer. The effectiveness of both the maltreatment and the repair procedure is studied and compared for devices containing LiF/Al and Ba/Al cathodes. If left untreated, the defects lead to high leakage currents and considerable loss in device performance. We show however that for both cathode types upon treatment device performance levels are reached that are comparable to those of devices containing non-violated photo-active layers. In order to arrive at an optimized repair procedure, we also quantitatively study the consequences of exposing the pristine blend surface to aqueous sodium hypochlorite.

## 2. Materials and methods

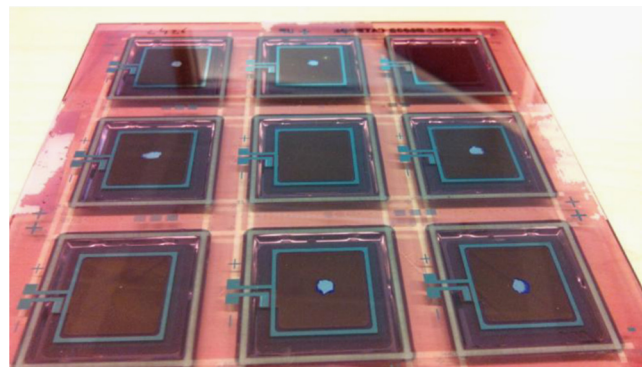
Glass substrates ( $152 \times 152 \text{ mm}^2$ ) containing nine ITO ( $22 \times 23 \text{ mm}^2$ ) pixels were cleaned according to our previously reported method [11]. HC PEDOT:PSS (0.84% solids,  $\sim 500 \text{ S/cm}$  in-plane conductivity) was provided by AGFA Gavaert, Mortsel, Belgium and used as received. P3HT (Plexcore<sup>®</sup> OS 2100) was purchased from Sigma-Aldrich. Technical-grade PCBM ( $> 99\%$ ) was purchased from Solenne B.V., the Netherlands. P3HT:PCBM blend solutions for spin-coating were prepared by dissolving both P3HT and PCBM in 1,2-dichlorobenzene with a 1:1 ratio by weight at  $80 \text{ }^\circ\text{C}$  and subsequently allowed to cool down to room temperature.

OSC active stacks with lateral dimensions of  $19.0 \times 20.4 \text{ mm}^2$  were prepared as follows. HC PEDOT:PSS was spin-coated on the substrates after which PEDOT:PSS in-between the ITO pixels was removed with a damp cleanroom wipe to avoid parasitic currents. The patterned plates were subsequently annealed for 10 min at  $200 \text{ }^\circ\text{C}$  in vacuum, giving dry layers of PEDOT:PSS on top of ITO with an average thickness of 100 nm. The PEDOT:PSS-covered plates were then allowed to cool down to room temperature. P3HT:PCBM-based photoactive layers (90 nm) were spin-coated on the PEDOT:PSS-covered substrates and annealed for 10 min at  $130 \text{ }^\circ\text{C}$  under nitrogen after which the plates were allowed to cool at  $20 \text{ }^\circ\text{C}$ .

To investigate the resilience of pristine P3HT:PCBM blend films to the oxidizing environment required for the repair procedure, glass-based PEDOT:PSS-P3HT:PCBM stacks were fully submerged for various times in 5% aqueous sodium hypochlorite, after which the layers were rinsed with distilled water and blown dry with nitrogen gas. Static water contact angles were then measured by means of a Dataphysics OCA 15 plus. Reported contact angles are average values each obtained from five independent measurements.

Cathodes (LiF/Al or Ba/Al, lateral dimensions of  $19.0 \text{ mm} \times 20.4 \text{ mm} = 3.876 \text{ cm}^2$ ) were applied by either depositing (nominally) 1 nm lithium fluoride or 5 nm barium, followed by 100 nm aluminum under high-vacuum conditions ( $P < 5 \times 10^{-7} \text{ mbar}$ ). The cathode was carefully positioned within the borders of the ITO pixel, thereby defining the exact area of the solar cell. After cathode deposition, the substrates were encapsulated with a metal lid to prevent speedy degradation.

Defects in the photoactive layer with sizes of approximately  $10 \text{ mm}^2$  (see Fig. 1) were created prior to cathode deposition by locally removing P3HT:PCBM with a swab stick soaked with xylene. A statistically relevant number of defected devices were treated by depositing a droplet of  $\text{NaClO}_{(\text{aq})}$  (5%, purchased from Sigma-Aldrich) on top of the wiped areas in the photoactive layer. After 30 s the drop was removed using a syringe. The treated area was subsequently



**Fig. 1.** Glass plate hosting nine OSCs ( $19 \times 20.4 \text{ mm}^2$ ); some of the OSCs contain a defect with a surface area of  $\sim 10 \text{ mm}^2$  (light blue regions). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

rinsed with distilled water to remove any  $\text{NaClO}$  residues. Treated devices were thoroughly dried in a vacuum.

## 3. Results and discussion

Fig. 2 shows magnified microscopic images of various defects, either intentionally or unintentionally inflicted to the active photolayer (P3HT:PCBM) of conventional OSCs having the device structure as outlined above. We obtained these images by taking the photographs through the glass substrate of fully processed and encapsulated devices whilst illuminating in reflection. Each defect is identified as a roughly-edged light yellow colored area surrounded by a darker orange shade indicating the intact photoactive layer. The defects in Fig. 2A–C were intentionally created by locally removing a  $\sim 10 \text{ mm}^2$  patch of P3HT:PCBM according to the method described in Section 2. Fig. 2D shows a non-intended spin-coating defect (a so-called “comet tail”) created during depositing the photoactive layer due to the presence of the contaminant particle apparent on the right side of the image.

The defects in Fig. 2B–D were subsequently treated with aqueous hypochlorite (see Section 2) to disrupt the conductivity of the locally exposed PEDOT:PSS [12] in order to prevent the crater to cause a short circuit upon cathode deposition [11]. Fig. 2A images an untreated defect. Comparing 2A with 2B–D clearly shows that the aqueous treatment, in combination with the drying procedure applied after the final aqueous rinse, causes the PEDOT:PSS layer to buckle. The conception that the buckled film represents the PEDOT:PSS layer is supported by the observation in Fig. 2C that the residual film inside the defect has locally ruptured and flipped over due to accidental contact damage with the glass pipette, leaving the ITO uncovered. For such a defect the hypochlorite treatment is not expected to result in short circuit prevention once the cathode is applied.

In our previous work on OLEDs [11] we carried out the PEDOT passivation procedure by fully submersing the LEP/PEDOT:PSS stacks in hypochlorite solution, during which the exposed PEDOT regions react via thiophene oxidation and ring opening, as proposed by Yoshioka et al. [13]. The LEP, typically not a polythiophene and more difficult to oxidize, remained unaffected at least for short treatment times. Thus, repaired OLEDs behaved similar to reference devices in terms of optoelectronic performance and life time [11].

Full submersion into aqueous hypochlorite may however not be suitable for P3HT:PCBM-based devices, as P3HT, a polythiophene itself (!) and usually forming a relatively pure region at the top interface of the blend film [14], is likely to react in much the same way as PEDOT, which might negatively affect device performance. For this reason we investigate to what extent submersion

Download English Version:

<https://daneshyari.com/en/article/77925>

Download Persian Version:

<https://daneshyari.com/article/77925>

[Daneshyari.com](https://daneshyari.com)