

TOWARDS AN ALL-SOLUTION PROCESSED POLYMER SOLAR CELL

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ABSTRACT: To reduce the costs of polymer solar cells it is important to develop a fully solution processed route. Although several successful generic routes to solution processed hole collecting electrodes have been shown, this is not the case for the electron collecting electrode of polymer cells, as it is hard to find a solution processable low workfunction, low ohmic, electron collecting electrode. Here an efficient recombination layer is described formed by the combination of ZnO and PEDOT and applied in an electron collecting layer. The ZnO contacts the conduction band of the acceptor material to collect electrons from the absorber layer. Since ZnO is a wide bandgap material, it also acts as an exciton and hole blocking layer. Electrons collected by the ZnO layer easily recombine with holes from the highly doped, high conductive PEDOT layer. The performance of a device with a recombination layer is compared in a standard as well as inverted polymer solar cells. The performance of the device with the PEDOT/ZnO recombination layer deviates less than 10 % from similarly processed standard and inverted device structures.

1 INTRODUCTION

The growing interest in organic photovoltaics (OPV) is caused by their promise for low cost energy conversion. In order to have an impact on the power generation market on the longer term, OPV should combine high power conversion efficiency with low production costs, high speed production, short energy payback time, contain earth abundant materials and yield long device lifetimes.

A conventional polymer solar cell, consists of a glass substrate, a sputter coated and patterned ITO layer, a PEDOT:PSS layer, an absorber layer (typically a polymer:fullerene blend) and a thermally evaporated metal electrode (often: LiF/Al), see scheme 1. To fully exploit the benefits of OPV, glass needs to be replaced by a flexible substrate with sufficient barrier properties and both the ITO and LiF/Al electrodes should be substituted by stable, printable electrodes. Below, first alternatives for ITO are described followed by substitutes for LiF/Al.

Several groups reported on alternative device structures to circumvent the use of ITO as semitransparent hole collecting electrode. The most straightforward approach is to leave out ITO altogether and increase the conductivity of PEDOT by adjusting the PEDOT formulation.[1,2] This works well for narrow cells, so cells with a width below several millimetres. However, if the width increases, the sheet resistance of the PEDOT layer will reduce the device performance when measured under standard test conditions (1 sun illumination intensity).

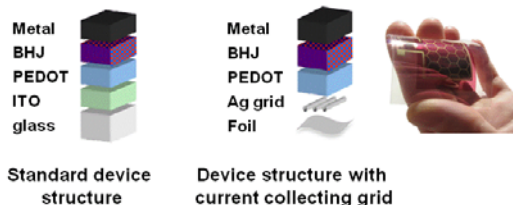
To reduce the sheet resistance one can apply a semi-transparent, highly conductive metal layer (stack) [3,4] or substitute ITO by another transparent conductive oxide [5] however, these layers are typically incompatible with solution processing. Alternatively, graphene as well as nanotubes based on carbon and silver have been applied to reduce sheet resistance losses.[6-8]

Instead of using a continuous sheet of a semitransparent material, one can also build a composite electrode consisting of a (metal) grid and a highly conductive polymer layer.[9,10] We have reported on a device concept based on a solution processed composite hole collecting electrodes consisting of a high conductive

PEDOT:PSS layer in combination with printed silver grids [11,12]. Apart from the cost saving aspects by replacing sputtered and post-patterned ITO it is demonstrated by modelling that the individual cell dimensions can be substantially larger without decreasing actually the cell performance.

These ITO-free solar cell architectures were fabricated both on glass substrates as well as on plastic foils with a size of 4 (2x2) cm². Maximum efficiencies of 1.93 % have been achieved using devices that are processed on PEN foil with embedded, screen printed Ag line causing a low sheet resistance. A blend of P3HT:[C60]PCBM was used as the photoactive layer and an evaporated LiF/Al contact as the cathode. A flexible 'standard' ITO-based cell with the same size and geometry reached an efficiency of only 0.95%. Please note, in the ITO reference device, or 'standard' device, the Ag grid and high conductive PEDOT:PSS layer are exchanged for an ITO on foil (60 Ohm □) and low conductive PEDOT:PSS layer.

The use of a current collecting grid combined with a high conductive PEDOT layer is attractive as a substitute for ITO. Due to the relative high work function of PEDOT, this composite anode forms a selective contact with the valence band of the polymer or donor material of the absorber layer. In other words it can only be used to collect holes from the photovoltaic device. Preparing a solution processed cathode to replace LiF/Al is more difficult.



Scheme 1 Layer stack of a conventional polymer solar cell (left). The layer sequence and picture of a device based on a composite electrode consisting of a Ag grid and high conductive PEDOT is shown on the right.

In inverted devices, metal-oxides like ZnO and TiO₂

are typically used to contact the conduction band of the fullerene acceptor material of the absorber layer.[13, 14] In thin film photovoltaic devices, these metal oxides are doped to decrease the sheet resistance. In this way transparent conductive oxides (TCOs) are prepared. However it is difficult to prepare these TCOs with low work functions from solution.[15] Here we make use of a recombination layer formed by the combination of ZnO and highly conductive PEDOT. The ZnO contacts the conduction band of the acceptor material to collect electrons from the absorber layer. Since ZnO is a wide bandgap material, it also acts as an exciton and hole blocking layer. Electrons collected by the ZnO layer easily recombine with holes from the highly doped, high conductive PEDOT layer. In addition, the high conductive PEDOT layer allows lateral charge transport of holes from a metal grid to the recombination site. Thus the combination of a metal grid, high conductive PEDOT and ZnO is expected to act as a semi-transparent, negative contact to the photovoltaic device which could be applied by solution processing methods only.

In this contribution, the photovoltaic properties of devices containing a PEDOT/ZnO recombination layer are evaluated and compared to commonly used device structures. By combining the recombination layer with the composite electrode described above, it is possible to develop an all solution processed polymer solar cell. It is noted that alternative approaches have been described elsewhere[8, 16-18]

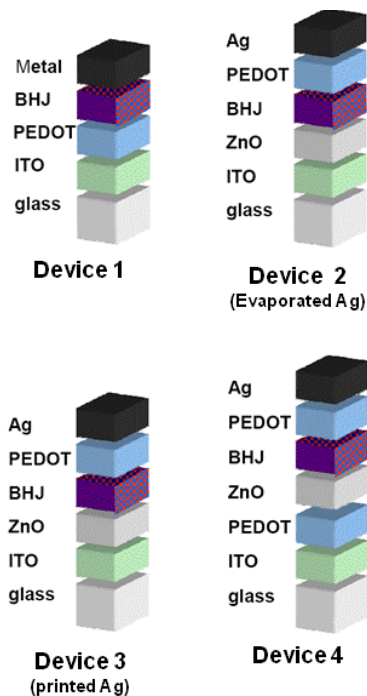
2 EXPERIMENTAL

An overview of the devices discussed in this paper is presented in scheme 2. Below a description is given how these structures are prepared and evaluated.

2.1 Standard devices (device 1)

Glass substrates with pre-patterned ITO electrodes (Naranjo substrates) have been applied. The substrates are carefully cleaned, dried, and treated with UV/O₃ prior to use. On the substrates, a 40 nm thick layer of PEDOT:PSS (Clevios P VP Al 4083, Heraeus) is spin coated. After PEDOT deposition, the samples are dried for 10 minutes at 120°C.

The P3HT:[C60]PCBM layer is spin coated from an *ortho*-dichlorobenzene solution containing 2.0 wt % P3HT (Plexcore OS2100, Plextronics) and 2.0 wt % [C60]PCBM (99.5%, Solenne B.V.). The spin-coating conditions were adjusted to give photoactive layers with the desired thickness (280-310 nm). Samples were annealed at 120°C for 5-10 min.



Scheme 2 Overview of the layer stacks of the different device configurations described in this paper. ‘BHJ’ abbreviates for bulk heterojunction. Device 1 is typically referred to as ‘standard device structure’; devices 2 and 3 are also described by ‘inverted devices’.

Devices are completed by vacuum deposition of the counter electrode. This electrode is formed by 1 nm layer of LiF and 100 nm of Al. The electrode layers are vacuum deposited at 1×10^{-6} mbar through a shadow mask. In this way, 4 cells are obtained with areas of 0.10 cm², 0.15 cm², 0.33 cm², and 1.0 cm² on a single substrate.

The thicknesses of the layers constituting the device are PEDOT (30 nm)/BHJ (297nm)/ LiF (1 nm)/ Al (100 nm).

2.2 Inverted devices (devices 2 and 3)

The ZnO layer of inverted devices is prepared from ZnO nanoparticles dispersed in acetone as described elsewhere.[19, 20] The ZnO dispersion (~10 mg/ml in acetone) is spin coated on top of the ITO substrate and subsequently annealed at 120°C for 10 minutes. The BHJ layer is deposited as described under 2.1.

High conductive PEDOT (Orgacon 5015, Agfa) is applied by spin coating followed by annealing at 120°C for 10 minutes. Note, the original Orgacon 5015 formulation is adjusted by diluting (1:1 by volume) with 2-propanol.

The Ag electrode is either applied by vacuum deposition (device structure 2) or screen printing (device structure 3). The thickness of the layers of device 2 are: ZnO (30)/BHJ (315 nm)/PEDOT (500)/Ag (100 nm). The layers of device 3 have the following thicknesses: ZnO (40)/BHJ (296 nm)/PEDOT (500)/Ag (16 micrometer). The silver ink (Toyo Rexalpha 018) used for screen printing is converted by a UV curing step.

2.3 Inverted devices with recombination layer (device 4)
 Samples with device structure 4 are prepared following the description of device structure 3, except for the first PEDOT layer. This layer is formed by spin coating a PEDOT:PSS (Clevios P VP AI 4083, Heraeus) followed by annealing for 10 minutes at 120°C. The following layer thicknesses were measured on device 4: PEDOT/ZnO (159 nm) (the individual layer thicknesses were not determined) /BHJ (262 nm)/PEDOT (392 nm)/Ag (16 micrometer).

2.4 Characterization

Film thickness measurements were performed with a Dektak 8 surface profilometer (Veeco).

Current density-voltage (JV) measurements were done in a setup (MiniSunSim) of our own design, containing a Keithley 2400 SourceMeter wired to a sample holder in a nitrogen-filled glove box. The sample was illuminated by a halogen lamp. The intensity of the halogen lamp corresponds to approximately 0.85 sun.

An automated rotating filter wheel was used to record the current densities at various wavelengths for external quantum efficiency (EQE) measurement. A silicon reference cell with known spectral response was used for calibration purposes. This enabled the measurement program on the computer to calculate the short-circuit current of the organic solar cell under 1000 W/m², AM1.5 illumination ($J_{sc,SR}$). Using this calculated short circuit current we estimated the power conversion efficiency (calc. eff.) by: $\text{calc. eff.} = V_{oc} * FF * J_{sc,SR}$. In general, the thus calculated efficiency is within 10% of the measured efficiency using a properly calibrated, high-end solar simulator. Exceptions are observed if the short circuit current density does not increase linearly with illumination intensity.

Samples were illuminated through an illumination mask with a well defined aperture area. To reduce systematic errors caused by cells having different cell dimensions, only cells with an active area of 0.15 cm² are reported here.[21] These cells were illuminated through an aperture of 0.09 cm².

3 RESULTS AND DISCUSSION

Figure 1 presents the JV-curves of all four device structures; table 1 provides the JV-parameters of the curves presented in figure 1.

The black curve is recorded on a standard device structure based on ITO/PEDOT/BHJ/LiF/Al. This device structure represents our reference system. The performance of the device is typically for our baseline process on standard devices (average maximum power point = 2.7 mW/cm² for cells with an active area of 0.17 cm²; aperture area 0.09 cm²) although the open circuit voltage is rather low. It is noted that a rather large spread in open circuit voltages is observed for similarly processed devices.

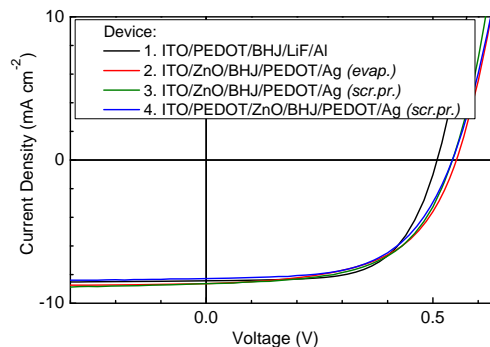


Figure 1 Current-density versus voltage curves of polymer solar cells with various device structures as described in the legenda. In these devices the bulk heterojunction (BHJ) is formed by a P3HT:[C60]PCBM layer.

The JV-curve measured on device structure 2, the inverted device structure with an evaporated Ag electrode, is shown in red. Besides an increase in open circuit voltage, which is compensated by a lower fill factor, the device performance is very similar compared to the standard device structure (device structure 1). The larger short circuit current is understood as the overall result of various factors influencing this PV parameter. These factors include, (a) the replacement of a weakly absorbing PEDOT layer between the ITO and bulk heterojunction layer by a nearly transparent ZnO layer; (b) this ZnO layer will influence the optical field distribution within the layer stack of the devices, note that interference effects are important in these thin devices; (c) the slight differences in the layer thicknesses of the bulk heterojunctions; (d) the relatively thick Orgacon 5015 layer in device 2; (e) the rough Orgacon 5015 layer resulting in a less mirror-like metal back contact and thus increasing the optical path of reflected light and influencing the interference effects.

Replacing the evaporated Ag electrode (red line) by a screen printed Ag electrode (green line) does not affect device performance significantly. This is an important observation for the development of solution processed polymer solar cells. Apparently, the UV exposure to convert the Ag ink is not very harmful for the polymer solar cell.

Table 1: Overview of the JV-characteristics of the JV curves given in figure 1. Device structure refers to device architectures presented in scheme 2.

JV-parameter	unit	Device Structure			
		1	2	3	4
V_{oc}	mV	509	551	543	543
J_{sc}	mA/cm ²	8.43	8.63	8.63	8.27
$J_{sc,SR}$	mA/cm ²	9.46	9.76	9.40	8.80
FF	%	63.1	55.7	57.2	57.7
MPP	mW/cm ²	2.71	2.65	2.68	2.59
$calc. eff.$	%	3.04	3.00	2.92	2.76

Finally, the blue line reveals the JV-curve of the polymer solar cell containing the recombination layer

consisting of PEDOT and ZnO. The *JV*-curve closely resembles the curves of the inverted devices, referred to as device structure 2 and 3. From table 1 it is clear that the short circuit current density of device 4 is slightly lower (4 %) compared to devices 2 and 3. Tentatively, this reduced current density is attributed to a combination of higher absorption losses in the recombination layer (with an overall layer thickness of 159 nm) and an altered optical field distribution within the device caused by the relatively thick PEDOT/ZnO layer and relatively thin bulk heterojunction layer.

From the fact that the measured current density of device 4 is only 4 % lower compared to the measured current densities of cell 2 and 3, it is concluded that the introduction of a recombination layer does not cause important losses to the device performance. This is in agreement with similar recombination layers applied in polymer tandem solar cells. [22]

5 CONCLUSIONS

A solution processed PEDOT/ZnO layer is successfully applied in the electron collecting electrode of a polymer solar cell. The inclusion of this recombination layer results in a power conversion efficiency loss less than 10% relative. It is anticipated that the ITO layer in device 4 could be replaced by a printed metal grid thus opening a route to high performing, high-throughput, fully solution processed polymer solar cells.

6 ACKNOWLEDGEMENTS

This work has been supported by the European Commission as part of the Framework 7 ICT 2009 collaborative project HIFLEX (Grant agreement no. 248678), the Dutch Polymer Institute (DPI Project No. 678) and by Agentschap NL within the project OZOFAB grant no. EOSLT1002. The authors are grateful to HiFlex partners Frederik Krebs (DTU Denmark), Birger Zimmermann (ISE Fraunhofer, Germany), Dirk Bollen (Agfa, Belgium), Stefan Gritsch (Dr. Schenk, Germany) and Stephen Ryley (MATRI, United Kingdom) for providing materials (PEDOT formulations) and valuable discussions within the consortium.

7 REFERENCES

- [1] Y. Zhou, F. Zhang, K. Tvingstedt, S. Barrau, F. Li, W. Tian, O. Inganäs, *Appl. Phys. Lett.* 92 (2008) 233308.
- [2] E. Ahlswede, W. Muhleisen, M. Wahinuddin bin Moh Wahi, J. Hanisch, M. Powalla, *Appl. Phys. Lett.* 92 (2008) 143307.
- [3] J. Meiss, M. K. Riede, K. Leo, *Appl. Phys. Lett.* 94 (2010) 013303.
- [4] B. O'Connor, C. Haughn, K.-H. An, K. P. Pipe, M. Shtein, *Appl. Phys. Lett.* 93 (2008) 223304.
- [5] J. Hanisch, E. Ahlswede, M. Powalla, *Eur. Phys. J. Appl. Phys.* 3 (2007) 261.
- [6] J. Wu, H. A. Becerril, Z. Bao, Z. Liu, Y. Chen, P. Peumans, *Appl. Phys. Lett.* 92 (2008) 263302.
- [7] J. van de Lagemaat, T. M. Barnes, G. Rumbles, S. E. Shaheen, T. J. Coutts, C. Weeks, I. Levitsky, J. Peltola, P. Glatkowski, *Appl. Phys. Lett.* 88 (2006) 233503.
- [8] W. Gaynor, J.-Y. Lee, P. Peumans, *Nano*, 4 (2010) 30.
- [9] T. Aernouts, P. VanLaeke, W. Geens, J. Poortmans, P. Heremans, S. Borghs, R. Mertens, R. Andriessen, L. Leenders, *Thin Solid Films*, 451-452 (2004) 22.
- [10] J. Zou, H.-L. Yip, S. K. Hau, A. K.-Y. Jen, *Appl. Phys. Lett.* 96 (2010) 203301.
- [11] Y. Galagan, J.-E.J.M. Rubingh, R. Andriessen, C.-C. Fan, P.W.M. Blom, S.C. Veenstra, J.M. Kroon, *Sol. Energy Mater. Sol. Cells*, 95 (2011) 1339.
- [12] Y. Galagan, R. Andriessen, E. Rubingh, N. Grossiord, P. Blom, S. Veenstra, W. Verhees, J. Kroon, ISBN 978-3-00-029955-1, p. 88-91, *Lope-C* 2010, May 31 - June 2, Messe Frankfurt, Germany.
- [13] F.C. Krebs, *Sol. Energy Mater. Sol. Cells*, 92 (2008) 715.
- [14] C. Waldauf, M. Morana, P. Denk, P. Schilinsky, K. Coakley, S. A. Choulis, C. J. Brabec, *Appl. Phys. Lett.* 89 (2006) 233517.
- [15] H. Oh, J. Krantz, I. Litzov, T. Stubhan, L. Pinna, C. J. Brabec, *Sol. Energy Mater. Sol. Cells*, 95 (2011) 2194.
- [16] B. Zimmermann, M. Glatthaar, M. Niggemann, M. K. Riede, A. Hinsch, A. Gombert, *Sol. Energy Mater. Sol. Cells*, 91 (2007) 374.
- [17] F. Krebs, *Organic Electronics*, 10 (2009) 761.
- [18] S. K. Hau, H.-L. Yip, J. Zou a, A. K.-Y. Jen, *Organic Electronics* 10 (2009) 1401-1407.
- [19] C. Pacholski, A. Kornowski, and H. Weller, *Angew. Chem., Int. Ed.* 41, (2002) 1188.
- [20] W.J.E. Beek, M.M. Wienk, M. Kemerink, X. Yang, and R.A.J. Janssen, *J. Phys. Chem. B* 109 (2005) 9505.
- [21] M.-S. Kim, I M.-G. Kang, L. J. Guo, J. Kim, *Appl. Phys. Lett.* 92 (2008) 13330.
- [22] J. Gilot, M. M. Wienk, R. A. J. Janssen, *Appl. Phys. Lett.* 90, (2007) 143512.