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All-solution-processed organic solar cells with conventional architecture

Jacobus J. van Franeker [a,b], W.Pim Voorthuijzen [a], Harrie Gorter [a], Koen H. Hendriks [b], René A.J. Janssen [b], Afshin Hadipour [c], Ronn Andriessen [a], Yulia Galagan [a,*]

[a] Holst Centre—Solliance, PO Box 8550, 5605 KN Eindhoven, The Netherlands
[b] Eindhoven University of Technology—Solliance, PO Box 513, 5600 MB Eindhoven, The Netherlands
[c] IMEC—Solliance, Kapeldreef 75, B-3001 Leuven, Belgium

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ABSTRACT

All-solution processed organic solar cells with a conventional device structure were demonstrated. The evaporated low work function LiF/Al electrode was replaced by a printed high work function silver electrode combined with an additional electron transport layer (ETL). Two electron transport layers were tested: (I) zinc oxide (ZnO) nanoparticles and (II) poly[(9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)] (PFN). Devices with printed silver nanoparticle inks on top of the ZnO electron transport layer lead to crack formation in the silver layer during the drying and sintering. The crack formation was avoided by using PFN as electron transport layer. The sputtered high work function ITO electrode was substituted by a printed composite electrode containing inkjet-printed silver grids in combination with high conductivity poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS). All-solution processed solar cells demonstrated a power conversion efficiency of 1.94%.

1. Introduction

The worldwide energy production is currently undergoing a shift towards the use renewable energy sources. The annual growth rate of the photovoltaic industry is about 30% per year [1]. Alternative energy technologies have great potential for further development and aim to further reduce the production cost of energy. The development of organic photovoltaics could further decrease the production cost of solar energy because organic materials can be fully processed from solution on flexible substrates using high-speed roll-to-roll printing and coating processes [2–7]. The potential for fully solution-processed solar cells is not often realized because the required electrodes are still processed by sputtering or vacuum deposition. Previously at Holst Centre a solution processed roll-to-roll compatible transparent electrode has been developed [8–10]. This transparent electrode is based on a current-collecting grid (CCG) in combination with high-conducting poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (HC-PEDOT) and is an alternative to vacuum deposited indium tin oxide (ITO). Printed top electrodes have been demonstrated for inverted configurations of organic solar cells, where a silver electrode was screen printed [11–13]. All-solution processed solar cells with an inverted cell architecture have already been demonstrated [5,14], however, solution processing of conventional solar cells requires substitution of the low work function LiF/Al or Ca/Al electrodes by their printable analogs. The alternative printable metal is silver, which can be processed in the form of nanoparticle inks [15,16]. However, its work function is not optimized for electron collection in combination with the fullerene acceptors that are commonly used in organic solar cells. Conventional organic solar cells with a silver electrode for electron collection show a drop in open-circuit voltage (V_{oc}), which can be explained by the higher work function of Ag vs. LiF/Al or Ca/Al [17–19]. To circumvent these effects it is possible to insert an electron transport layer (ETL) [19–21] in between the photoactive layer (PAL) and the silver electrode. Typical electron transport layers used in organic solar cells consist of zinc oxide (ZnO) [22,23], titanium oxide (TiO*x*) [24,25], or poly[(9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene) (PFN)] [26,27].

In this study, we demonstrate a solution processable top electrode for organic photovoltaic (OPV) devices with a conventional cell architecture. The evaporated LiF/Al electrode is replaced by a solution processed electron transport layer (PFN) and printed silver. Together with replacing the transparent ITO front electrode by a solution processable hole collecting electrode, consisting of printed silver grids and HC-PEDOT, the novel printable top

* Corresponding author. Tel.: +31 40 4020 447; fax: +31 40 4020 699.
E-mail address: Yulia.galagan@tno.nl (Y. Galagan).

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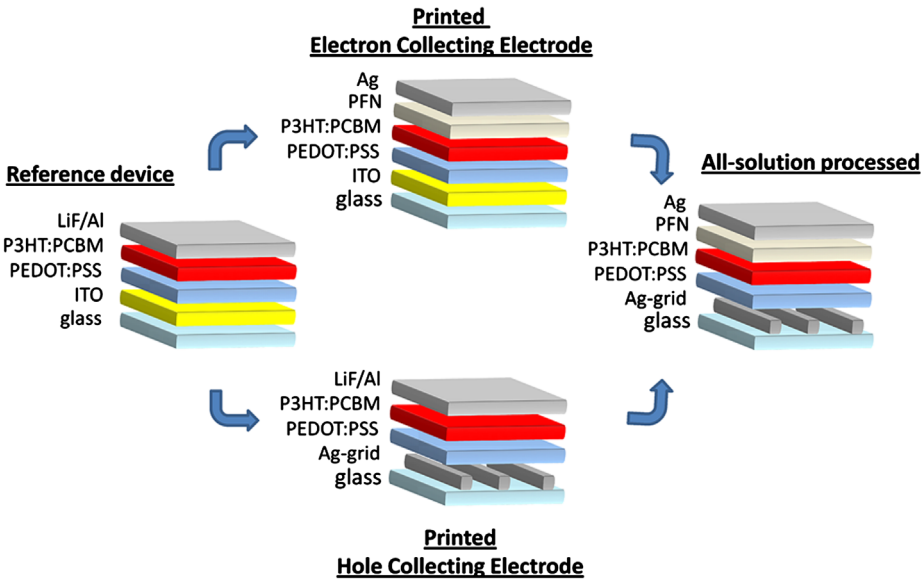

Fig. 1. Device structures for the solar cells with different electrodes.

electrode allowed fabricating all-solution-processed organic solar cells with a conventional device structure. This structure uses the smallest possible amount of layers (two metal electrodes, two interfacial layers, and an active layer). This is in contrast to the recently developed inverted all-solution processed devices [5,14], where either no metal electrode is used (limiting the conductivity and thus current generation) or extra layers are necessary. Also, in the above mentioned inverted devices a PEDOT:PSS layer is situated on both sides of the active layer, which often leads to processing issues and shorted cells. This is not necessary in our devices with a conventional device architecture. An overview of the mentioned device structures is shown in Fig. 1.

2. Experimental

For the ITO-based devices 30 × 30 mm glass substrates covered with an ITO layer (sheet resistance 10 Ω/sq), patterned by photolithography, were obtained from Naranjo. Clevios PVP Al 4083 PEDOT:PSS, from Heraeus, was filtered and then spin coated at 3000 rpm (acceleration 1000 rpm/s, with closed lid for 60 s) on cleaned substrates, resulting in a layer thickness of around 30 nm.

Silicon nitride coated glass plates with a thickness of 0.7 mm and size of 30 × 30 mm were used as the substrates for ITO-free devices. Current collecting grids were inkjet printed using a Dimatix DMP-2800 with Suntronics U5714 silver ink (Ag content: 40 wt%) and a drop spacing of 40 μm. Sintering was done for 30 min at 190 °C, resulting in grid lines with a width of 150 μm and a height of 300 nm. The grid spacing was 2 mm and lengths of the grids were 4, 5, 7 and 11 mm for A–D devices, respectively. Then, high conductivity PEDOT:PSS (OrgaconTM from Agfa-Gevaert) was inkjet-printed using a Spectra Galaxy printer, resulting in an average layer thickness of 200 nm.

Poly(3-hexylthiophene) (P3HT, Plextronics Plexcore OS 2100) and [6,6] phenyl-C_{61}-butyric acid methyl ester (PCBM, 99%, Solenne BV) in weight ratio of 1:1 were dissolved in a concentration of 26 mg/mL of each in ortho-dichlorobenzene (oDCB). The solution was stirred for 16 h at 65 °C and filtered before usage. Before spin coating of the photoactive layer (PAL) the PEDOT was dried for 10 min at 130 °C. The PAL was spin coated in air at 1000 rpm for 60 s (acceleration 1000 rpm/s, with closed lid) and the resulting layer thickness was about 240 nm. Annealing of the photoactive layer was done in nitrogen at 130 °C for 10 min for devices with an evaporated electrode and was performed after deposition of the ETL but before evaporation of the metal. For the devices with printed silver electrode the annealing was performed after the fabrication of the whole device, initially 5 min in air at 120 °C in an oven for the drying and sintering of silver, and then 5 min in nitrogen at 130 °C.

Zinc oxide (ZnO) nanoparticles (diameter: 5–10 nm) were prepared using a modified sol–gel process [28,29] and dispersed in acetone at a concentration of 10 mg/mL. Spin coating was done at 1000 rpm (acceleration 5000 rpm/s, with open lid) for 60 s. This resulted in a layer thickness of 20–40 nm. PFN was synthesized following the method described in [30] and dissolved in ethanol. The best results were obtained with a concentration of 0.5 mg/mL with 0.01 mL of added acetic acid to facilitate dissolving. Spin coating was done at 1000 rpm (acceleration 5000 rpm/s, with open lid) for 60 s. The layer thickness is below 10 nm but cannot be determined exactly by the available experimental equipment.

Metal electrodes (either 100 nm Ag or 1 nm LiF/100 nm Al) were thermally evaporated in a vacuum chamber through shadow masks at a base pressure below 2×10^{-6} mbar. For the inkjet-printed silver electrodes Suntronics U5714 silver ink was printed using a Dimatix DMP-2800 and a drop spacing of 20 μm. The printed silver was sintered in air for 5 min at 120 °C.

Current density–voltage (*J–V*) characteristics were measured in nitrogen with a Keithley 2400 source meter between −2 and +2 V using ~100 mW/cm^2 white light illumination from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter to approximate sunlight. Sometimes S-shaped *J–V* curves where observed, which could be resolved with UV-illumination. Measurements were done with a mask to have well-defined illuminated areas of 0.04, 0.09, 0.25, and 0.81 cm^2 for respectively the A–D cells which have active areas of approximately 0.09, 0.16, 0.36 and 1.00 cm^2, respectively. The size of the active area is determined by the geometrical overlap of both electrodes, which is not accurately determined for the devices with printed electrodes. Therefore the masks are used to be certain of the incident light power. The external quantum efficiency (EQE) was determined using a 50 W Philips focusline tungsten halogen lamp in combination with an Oriel Cornerstone 130 monochromator. A lock-in amplifier (Stanford research Systems SR830) was used to measure the response as a voltage over a 50 Ω resistance. These