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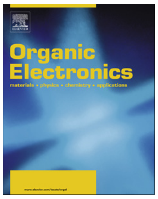

All-solution processed organic solar cells with top illumination

Bhushan R. Patil, Santhosh Shanmugam, Jean-Pierre Teunissen, Yulia Galagan *

Holst Centre – Solliance, P.O. Box 8550, 5605KN Eindhoven, The Netherlands

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ABSTRACT

All-solution processed organic solar cells with inverted device architecture were demonstrated. Devices contain opaque bottom electrodes and semitransparent top electrodes, resulting in top illuminated devices. Nanoparticles-based Ag ink was used for inkjet printing both top and bottom electrodes. Semi-transparent top electrode consists of high conductivity PEDOT:PSS and Ag current collecting grids. Printed electrodes were compared to evaporated Ag electrodes (both top and bottom) and to ITO electrode in terms of transmittance, roughness, sheet resistance and device performance. All-solution processed devices with top illumination have average PCE of 2.4%, using P3HT:PCBM as photoactive layer. Top-illuminated devices with inverted architecture and bottom-illuminated device with conventional architecture, containing the identical layers, but in the reverse sequence, were then compared. Performed studies have revealed an advantage of inverted cell architecture.

1. Introduction

Organic photovoltaics (OPVs) are a perfect complement to photovoltaic (PV) technology because of promising features such as low cost [1], high flexibility, and solution roll-to-roll processing [2–4]. One of the biggest challenges in roll-to-roll fabrication of OPVs is the replacement of Indium-Tin-Oxide (ITO) as a transparent bottom electrode. The main arguments to the replacement of ITO are the brittle nature and comparatively higher sheet resistance on flexible substrates. In addition to that a highly sophisticated vacuum fabrication processes and patterning of ITO are required. Owing to these bottlenecks, today enormous investigations are being made around the world to find an ideal replacement to ITO in OPVs.

In the past decade, a lot of alternatives have been proposed. Researchers have explored many of the potential conductive coatings of ultra-thin metal films [5,6], highly conducting polymers [7], carbon nanotubes (CNTs) [8], graphene [9], metal nano-wires [10,11] etc. However, most of the proposed alternatives have sheet resistance comparable to or higher than ITO. To reduce the sheet resistance of electrodes, current collecting grids were introduced as an integral part of transparent electrodes [12–15]. Disadvantage of this approach is a topology of the grids, however this issue can be overcome by embedding the current collecting grids into substrates [16,17].

An alternative approach, intensively presented in last few years, is manufacturing OPVs with top illumination, containing non-transparent bottom electrodes [18–25]. The advantage of this approach is very low sheet resistance of the electrodes, allowing to make large area devices [23]. Moreover, this approach does not have issues with topology of the grids and provide homogeneous surface for the deposition of subsequent layers. This approach has been intensively explored by the group from Fraunhofer ISE, where non-transparent bottom contact of Chromium/Aluminum/Chromium (Cr/Al/Cr) was evaporated through the shadow mask [18–21]. Janssen et al. have reported tandem polymer solar cells with non-transparent vacuum evaporated Chromium/Gold (Cr/Au) electrodes having top illumination [24]. Organic solar cells containing evaporated Al–Au bottom contacts with top illumination were demonstrated on stainless steel substrates by Chen et al. [22]. The device stack was electrically insulated from the conducting substrate by spin coating a photoresist. However, sometimes the electrical properties of the metal substrate were utilized and served as one of the electrodes in the OPV stack. Such type of OPV devices were demonstrated on stainless steel [23,25], titanium coated steel [25] or chromium coated aluminum [25]. Although direct deposition of OPV stack on metal substrates allows all-solution processing the following layers, this type of the devices is better suitable for the lab applications than for manufacturing large area modules, because of the interconnection issues and safety issues.

The upscaling of OPV modules with top illumination requires a Roll-to-Roll deposition of the non-transparent bottom electrode. Roll-to-Roll printing and coating is the most attractive deposition

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* Corresponding author.
E-mail address: yulia.galagan@tno.nl (Y. Galagan).

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method which can guaranty low cost manufacturing. Silver (Ag) is considered as a potential candidate for Roll-to-Roll solution processing, suitable for the application in OPV devices. Thin layer of printed Ag provides low sheet resistance, allowing large area devices and has high flexibility. Solution processed opaque bottom metallic electrode was demonstrated by doctor blading of organometallic silver precursor ink [26,27]. However, for the application of this silver coating as an electrode in the OPV devices, the post structuring either with laser ablation [26] or photolithography [27] was required. Krebs et al. [28] have demonstrated R2R processed semitransparent bottom Ag electrode with $\sim$25–30% transmittance at 550 nm. However, due to the low transmittance of such electrode, top illumination would be preferred. Later, the same group has demonstrated slot die coated non-transparent Ag film deposited from organometallic complexes and employed in the processing of top-illuminated ITO-free polymer solar cells in single-junction and tandem structures [29]. The usage of nanoparticles-based Ag inks as an opaque bottom electrode also was shown [30,31], however all-solution processed devices demonstrated efficiency below 1%.

Moreover, for top-illuminated devices a semitransparent top electrode is required. A lot of studies have been done on the optimization of thermally evaporated top contacts in the organic solar cells adapted for non-transparent substrates [23,32,33]. However, because the ultimate goal is all-solution processing, the investigation of printed alternatives are in the focus for many research groups. Combination of PEDOT:PSS with printed current collecting grids is considered as a promising alternative. However, as has been shown by Angmo et al., to prevent solvent penetration from the ink during solution processing of Ag, either thick PEDOT:PSS layer (that limits the transparency of the electrode) [34], or thick photoactive is required [29]. To overcome this problem aerosol jet printed grids have been demonstrated [19,35]. The advantage of this approach is that the most of the solvents were evaporated during the deposition, allowing to use relatively thin PEDOT:PSS. Recently our group has demonstrated PEDOT:PSS formulation with improved nature allowing to make only 40 nm layer of PEDOT:PSS which completely prevents the penetration of the solvents from Ag inks deposited either by inkjet or screen printing and provides high transmittance of the electrode [13].

In this study, we have investigated the potential of inkjet printed silver layer, deposited from Ag nanoparticles ink, as a non-transparent bottom electrode and inkjet printed Ag grids as a top electrode for organic solar cells with top illumination. All-solution processed ITO-free organic solar cells with inverted architecture were demonstrated.

2. Experimental

The substrates for fabricating OPV devices were either 30 × 30 mm glass slides (Eagle XG, Corning Inc., USA) or ITO covered glass substrates (sheet resistance of $10\,\Omega/\square$) patterned by photolithography (Naranjo, the Netherlands). Substrates were cleaned with several rinsing steps including ultrasonic treatment with Extran industrial detergent, deionized (DI) water and isopropanol (IPA).

Bottom Ag electrode was made either by thermal evaporation or inkjet printing of Ag nano-particles ink. Evaporation was carried out using a shadow mask in a vacuum thermal evaporation chamber at base pressure below 2×10^{-6} mbar inside N_2 environment. Ag slug for evaporation was purchased from Sigma–Aldrich Corporation. The Ag nano-particles ink (SunTronic U5603) was purchased from Sun chemicals, UK. The Ag ink was inkjet printed by DMP-2800 (Dimatix-Fujifilm Inc., USA) printer, equipped with a 10 pL cartridge (DMC-11610, Dimatix-Fujifilm Inc., USA). Printing was performed with a drop space of 20 μm, a voltage of 20 V, a print head temperature of 30 °C, a frequency of 10 kHz and a customized waveform. After printing, the samples were sintered for 30 min at 130 °C in an hot air oven. Alternative annealing for the printed Ag electrode can be photonic flash sintering, which can provide the resistance of the electrode even lower [36], than after 30 min of thermal annealing. The thicknesses of bottom electrodes: ITO, evaporated Ag and ink-jet printed Ag layers were 135, 100 and 250–300 nm, respectively.

To fabricate electron transport layer (ETL), a zinc oxide (ZnO) nanoparticles (np) solution in acetone was used. Synthesis of ZnO np was performed using a modified hydrothermal condensation process [37] where nano-particles (diameter of $\sim$1–5 nm) were re-dispersed in acetone at a concentration of 10 mg/ml. The solution was spin coated in air at 1000 rpm for 1 min with 5000 rpm/s acceleration. Thickness of ZnO layer was measured in the range of 30–40 nm.

Photoactive layer (PAL) solution was prepared by mixing poly(3-hexylthiophene) (P3HT, Plexcore 2100, Plextronics Inc., USA) and [6,6] phenyl-C61-butyric acid methyl ester (PC$_{60}$BM, 99%, Solenne B.V., The Netherlands) with weight ratio of 1:1 and at a concentration of 26 mg/ml in ortho-dichlorobenzene (oDCB). Solution was prepared in ambient conditions and kept stirring for 16 h at 90 °C. PAL was fabricated by spin coating the solution at 1000 rpm for 1 min with 1000 rpm/s acceleration inside nitrogen (N_2) glove box and annealed at 130 °C for 10 min. The measured PAL thickness was approximately of 240 nm.

A highly conductive PEDOT:PSS (Orgacon S315, Agfa-Gevaert N.V., Belgium) was used as an hole transport layer (HTL). PEDOT:PSS (approx. 120 nm) was spin coated at 1000 rpm for 1 min with 1000 rpm/s acceleration and dried in air for 2 min at 120 °C. Then, PEDOT:PSS layer was annealed inside N_2 glove box at 120 °C for 8 min.

A top electrode was either thermally evaporated or inkjet printed, using the same method and materials as for preparation of bottom Ag electrode. The top electrode has a current collecting grids pattern. The thicknesses of evaporated and inkjet printed top grids electrodes were 200 and 250–300 nm, respectively. Sintering of top electrode was done for 20 min at 130 °C in an hot air oven. Longer sintering time might increase conductivity of inkjet printed Ag electrode. However, it can lead to a degradation of the photoactive and PEDOT:PSS layers, because sintering is performed in air. As a result, the performance of the photovoltaic devices decreases. The optimal sintering condition has been found to be between 10 and 20 min at 130 °C [13].

The grid electrode consists of three lines with a pitch size of 2 mm. The width of evaporated grids was exactly 150 μm, providing the grids surface coverage of 7.5%. While, the width of inkjet printed grid lines was in average of 250 μm, providing the grids surface coverage of 12.5%. Because a top PEDOT:PSS/Ag-grid electrode does not have a well-defined area, an illumination mask was used to have precise active area of 0.25 cm^2.

Current–density voltage (JV) characteristics and external quantum efficiency (EQE) measurements were performed in a N_2 glove box with a source meter (Keithley 2400) between -2 and 2 V using simulated AM 1.5 global solar radiations (100 mW/cm^2) with a halogen lamp. Power conversion efficiencies were calculated using the short-circuit current density obtained from the EQE measurement. The average performance of at least 8–10 identical devices is reported.

The layers thicknesses were measured with an optical profilometer Wyko NT9100 (Veeco, Mannheim, Germany). The surface roughness was analyzed with optical interferometry. The measurements were performed with a Bruker NPFlex 3D Optical Profiler, using the phase-shifting interferometry mode with green light. AFM analysis was performed with Park NX10 system.

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