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# Digital fabrication of organic solar cells by Inkjet printing using non-halogenated solvents

T.M. Eggenhuisen<sup>a</sup>, Y. Galagan<sup>b</sup>, E.W.C. Coenen<sup>c</sup>, W.P. Voorthuijzen<sup>b</sup>, M.W.L. Slaats<sup>a</sup>, S.A. Kommeren<sup>a</sup>, S. Shanmuganam<sup>b</sup>, M.J.J. Coenen<sup>a</sup>, R. Andriessen<sup>b</sup>, W.A. Groen<sup>a,d,\*</sup>

<sup>a</sup> Holst Centre, High Tech Campus 31, 5656AE Eindhoven, the Netherlands

<sup>b</sup> Solliance – Holst Centre, High Tech Campus 31, 5656AE Eindhoven, the Netherlands

<sup>c</sup> TNO Science and Industry, P.O. Box 6235, 5600HE Eindhoven, the Netherlands

<sup>d</sup> Faculty of Aerospace Engineering, Delft University, Kluyverweg 1, 2629 HS Delft, the Netherlands

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## ABSTRACT

Inkjet printing offers versatility and flexibility for the sequential deposition of functional layers for the production of large area organic photovoltaics (OPV). Four layers of an OPV cell are inkjet printed, comprising an ITO-free semi-transparent front electrode (a metal current collecting grid, inkjet printed PEDOT:PSS and ZnO nanoparticle layers), and the photo-active layer combined with PEDOT:PSS as hole transport layer. To render the process R2R compatible, large area printing is performed using a 3.5 cm wide printhead and non-halogenated ink formulations only. Similar performance is achieved for the inkjet printed cells as for cells with only spin coated layers and ITO. For the P3HT/PCBM bulk-heterojunction, a mixture of non-halogenated solvents ensured good solubility, proper printing behavior and a blend morphology that yields similar performance to a layer spin-coated from chlorinated solvents. The potential of inkjet printing for large area OPV was demonstrated by the fabrication of a module with 92 cm<sup>2</sup> active area, which showed an efficiency of 0.98%. Losses due to front and back electrode resistances are modeled and used to explain the recorded I-V curve. Combining these functional layers with inkjet printed electrodes lays out the roadmap toward fully roll-to-roll compatible digital fabrication of OPV.

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## 1. Introduction

Organic photovoltaics (OPVs) have several benefits over conventional silicon PV, such as freedom of shape, semitransparency, light weight, flexibility and the possibility of high volume production with a favorable energy payback time. Currently, OPV appear in selected applications such as portable electronic devices. However, large area OPV films are foreseen to contribute to energy harvesting when integrated in facades, buildings, greenhouses or in public transportation. For these applications, roll-to-roll (R2R) production will facilitate the high production throughput at reduced costs. In a lab environment, efficiencies of polymer single junction solar cells of up to 9.2% have been reported [1], while in industrial environments polymer-based OPV cells and modules have reached 10.3% and 8.2%, respectively [2,3]. Nevertheless, a fully R2R processed OPV module with ITO-free electrode, free of evaporation steps and processed under ambient conditions yielded 1.8% [4]. Hence, research into

transferring current lab-scale processes to large area R2R production of OPV with minimized efficiency losses is still of importance.

On lab scale, solution processing of OPV is commonly performed by spin coating with halogen containing solvents as the main deposition technique for the functional layers. However, R2R production requires alternative deposition techniques and industrially compatible synthetic procedures using halogen-free solvents to reduce the environmental impact. Several R2R compatible technologies are available to deposit one or multiple layers of OPV [5], for example, slot die coating [6], gravure printing [7], screen printing [8], spray coating [9] or inkjet printing. Inkjet printing has shown its versatility in the past decades, and is an industrial production technique in the graphical, textile and ceramics industry. In the field of organic electronics, it can be used for the deposition a variety of functional materials, such as inorganic and metal nanoparticles, polymer dispersions and solutions of polymers or small molecules [10,11]. Often it is applied for printing microelectronics at high resolution, but here we focus on its application for the deposition of large area (> 1 cm<sup>2</sup>), uniform, thin films. Being a drop-on-demand deposition technique it has an economic use of materials and allows for direct patterning of separate cells and modules during R2R production, making

\* Corresponding author at: Holst Centre, High Tech Campus 31, 5656AE Eindhoven, the Netherlands.

E-mail address: [pim.groen@tno.nl](mailto:pim.groen@tno.nl) (W.A. Groen).

post-processing patterning steps unnecessary. Furthermore, when using digital fabrication altering the cell or module layout does not require (often) expensive replacement of hardware. Therefore, it offers flexibility and cost-effectiveness needed to facilitate this stage of OPV product development and prototyping. Most print-heads in lab scale inkjet printing equipment have a limited number of nozzles, making the printing of large areas slow and causing printing artifacts [12,13]. Here we use an industrial print-head with a printing width of 3.5 cm, allowing printing of large areas in a single pass at speeds compatible to R2R web speeds.

Thus far, in the field of OPV inkjet printing has mostly been applied for the photo-active layer. In 2007 and 2008, the applicability of inkjet printing was demonstrated for a photo-active layer containing a blend of poly(3-hexylthiophene) (P3HT) and phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) using inks containing (*ortho*-)dichlorobenzene [14,15]. Devices with performances comparable to a spin-coated reference cell were fabricated using inks containing chlorinated solvents, reaching efficiencies of up to 3.5% [16]. However, using inks based on only halogen-free solvents significantly decreased the cells performance. Later, more reports followed showing good performance of the devices with inkjet printed photo-active layers from formulations still containing at least one chlorinated solvent [17–19]. Recently, OPV devices with a PFDTBTP photo-active polymer inkjet printed from halogen-free formulations reached a maximum performance of up to 2.7% efficiency, comparing to 3.5% reached for a cell printed from a halogenated solvent [20]. Besides the polymer:fullerene blend, printing of other layers and layer combinations for OPV have been reported as well. For example, regular devices with a printed PEDOT:PSS (PEDOT) hole transport layer and P3HT:PCBM using non-halogenated solvents showed performance equal to a device with the photo-active layer spin-coated from *ortho*-dichlorobenzene [21]. Furthermore, a composite electrode, such as an inkjet or screen printed Ag grid and inkjet printed PEDOT, has been demonstrated to yield performance comparable to devices with an ITO front contact [22,23]. The combination of PEDOT/Ag was also used for the back electrode, for example, by inkjet printing a Ag grid on top of PEDOT [24].

We here demonstrate the feasibility of inkjet printing for four layers of the digital fabrication of OPV. Although the inkjet printing of one or two layers in an OPV has been reported, we here evaluate the effect of printing successively four electro-active layers in an inverted OPV stack. Also, harmful halogenated solvents are replaced by more benign halogen-free solvents in all inkjet ink formulations. First a printed ZnO electron transport layer in combination with a printed high conductive PEDOT is tested. The performance of printed ZnO on ITO as well as the additive effect of printing ZnO on top of printed PEDOT is reported. For cells with 1 cm<sup>2</sup> active area, up to four functional layers are inkjet printed (PEDOT/ZnO/P3HT:PCBM/PEDOT) on a metal current collecting grid, resulting in ITO-free cells. Three inkjet printed layers are combined for a large area module with 92 cm<sup>2</sup> active area. The I-V characteristics of the module are explained by a theoretical model incorporating performance losses due to resistance in the current collecting grid and interconnections.

## 2. Material and methods

Solvents were acquired from Sigma-Aldrich and used as received. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Agfa, Orgacon-IJ 1005) was provided by Agfa and used as received. Poly(3-hexylthiophene) (P3HT, Merck, Lisicon SP001, Mw ~ 19 kg/mol), and [6,6] phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM, 99%, Solenne BV) were used as received.

### 2.1. Device fabrication

All device fabrication steps were performed under “clean room, class 1000” conditions. Glass with ITO or Mo/Al/Mo (MAM, 20/100/20 nm thickness) current collecting grids prepared by sputtering and patterned by photolithography were used as substrates. A grid length was 1 cm and a grid spacing was 2.5 mm. Substrates were cleaned in several rinsing, ultrasound treatment and scrubbing with Teepol industrial detergent steps. The following stack was used: glass/ITO/ZnO/P3HT:PCBM/MoO<sub>x</sub>/Ag, and ITO was replaced by MAM/PEDOT for inkjet printed devices. ZnO nanoparticles were synthesized according to Ref. [25] using the hydrothermal condensation of Zn(acetate). After several rinsing steps, the nanoparticles were redispersed in acetone and applied by spin coating (1000 rpm, 5000 rpm/s, 60 s). ZnO nanoparticles for inkjet printing were redispersed in veratrole:*o*-xylene mixture with concentration of 17.5 mg/ml. The photo-active layer was spin coated from a 2 wt%/2 wt% P3HT:PCBM solution in chlorobenzene (550 rpm, 2000 rpm/s, 95 s). The resulting ZnO and P3HT:PCBM layer thicknesses were approximately ~50 and 220 nm, respectively. Inkjet printing of all layers (PEDOT:PSS, ZnO and P3HT:PCBM) was performed on an LP50 printing platform (Pixdro, OTB) using an industrial printhead (KM512L, 3.5 cm width, 360 DPI) and non-halogenated solvents only. For the photo-active layer an ink consisting of *o*-xylene, indan and tetraline (1:1:1) was used with a 1.3 wt% concentration of both P3HT and PCBM, yielding a layer with ~240 nm thickness. On top of the inkjet printed photo-active layer a 200 nm thick PEDOT layer was printed using an adjusted S315-IJ (Agfa) formulation. The Orgacon PEDOT:PSS from Agfa-Gevaert (conductivity of 200 S/cm) was used for the front electrode with a thickness of 100 nm. The drying conditions for three inkjet printed layers were the following: PEDOT:PSS was dried on a hotplate at 130 °C for 6 min, the ZnO was dried by placing on a hot plate at 130 °C for 1 min and the photo-active layer was dried on a hotplate at a temperature of 80 °C for 30 s. Prior to evaporation of the back electrode, the devices were annealed for 10 min in a N<sub>2</sub> atmosphere. A MoO<sub>x</sub>/Ag or Ag back electrode was applied by thermal evaporation with 10+100 or 100 nm thickness, respectively.

### 2.2. Characterization

Layer thicknesses were obtained by Dektak profilometry. Cross sections for analysis with scanning and transmission electron microscopy (SEM and TEM) were prepared using a Nova 200 Nanolab Small Dual Beam. Before preparation, a thin Pt layer is deposited on the entire sample in a sputter coater to avoid charging. Subsequently, a 500 nm Pt layer is deposited using electron beam induced deposition and a 1.5 μm Pt layer is deposited using ion beam induced deposition on the region of interest to protect the sample during preparation. As a final cleaning step, a 5 kV milling step was performed. TEM studies were performed using a TECNAI F30ST TEM operated at 300 kV. Non-contact atomic force microscopy (NC-AFM) measurements were performed on a NX-10 AFM (Park Systems) using a PPP-NCHR non-contact cantilever (Park Systems), having a nominal resonance frequency of 330 kHz and a force constant of 42 N/m. Current–voltage (J–V) curves were measured using simulated solar light in a home built set-up with a halogen lamp (100 mW/cm<sup>2</sup>) calibrated with a Si reference cell and using a shadow mask for 1 cm<sup>2</sup> devices and with AM 1.5 global solar irradiation using a WXS-300S-50 solar simulator (WACOM Electric Co.) for the large area modules. For 1 cm<sup>2</sup> devices the average J–V for at least 8–10 devices is reported. Four identical large area modules were fabricated and the average parameters are presented.

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