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Combining solvents and surfactants for inkjet printing PEDOT:PSS on P3HT/PCBM in organic solar cells

Sander Kommeren[a], Michiel J.J. Coenen[a], Tamara M. Eggenhuisen[a], ThijsM.W.L. Slaats[a], Harrie Gorter[a], Pim Groen[a,b,*]

[a] *Holst Centre, High Tech Campus 31, 5656, AE Eindhoven, the Netherlands*
[b] *Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629, HS Delft, the Netherlands*

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ABSTRACT

A commonly used strategy in the fabrication of organic electronics involves the use of orthogonal solvents, *i.e.* the alternating use of organic solvents and water for the application of consecutive layers to prevent dissolution of previous layers. This strategy therefore requires the deposition of sequential layers with a large mismatch in surface energy. In case of organic photovoltaics (OPV) a particularly challenging deposition is that of the aqueous Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate (PEDOT:PSS) on the hydrophobic Poly(3-hexylthiophene-2,5-diyl/Phenyl-C61-butyric acid methyl ester (P3HT/PCBM) layer. The mismatch in surface energy causes dewetting and inhomogeneous layer formation. In inkjet printing individually placed droplets should spread sufficiently far to form a homogeneous closed layer before the solvents in the droplet evaporate. A formulation for the aqueous PEDOT:PSS layer has been developed in which the combination of solvents and surfactants is essential for achieving a homogenous layer on the timescales needed for inkjet printing. Homogenous layers of PEDOT:PSS on P3HT/PCBM were achieved for layer thicknesses from 400 nm to 50 nm. The efficiency of the OPV's fabricated with the new formulation were comparable with reference devices, where evaporated molybdenum oxide (MoO_x) was used as a topelectrode. This shows that by the addition of solvents and surfactants a hydrophilic solution can be inkjet printed successfully to form homogenous layers on hydrophobic surfaces and achieve good efficiencies in an inverted organic solar cell.

1. Introduction

In the field of organic electronics or printed electronics the making of devices like organic photovoltaics, OPV, including the more recent perovskite based solar cells and organic light emitting diodes, OLED, by solution processing by roll-2-roll (R2R) production of devices on flexible substrates, at ambient temperatures and at low costs in large quantities [1–6]. Organic solar cells have been fabricated using a broad range of R2R compatible techniques including slot-die coating [1,3,7,8] and gravure printing [4,9]. We recently published the fabrication of partially and fully inkjet printed solar cells [10–12]. These papers mainly focused on the fabrication and characterization of inkjet printed OPV devices rather than on the development of the used inks. In this paper we will address the development of an aqueous solution on a hydrophobic surface which can be a coated and cured layer of the light absorbing layer in case of OPV or the light emitting layer in case of an OLED. In our case we report on research on a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) ink specifically designed for the deposition on the hydrophobic surfaces, like the poly(3-hexylthiophene)/phenyl-C61-butyric acid methyl ester (P3HT/PCBM) photoactive layer in OPVs. A problem that frequently arises with R2R solution processing techniques is that they require the deposition of sequential layers with large mismatches in surface energy. In case the surface energy of the previous layer is much higher than the surface tension of the desired ink, this ink will spread uncontrollably while in the opposite case, the ink will not wet and no uniform closed layer will be formed. The latter situation occurs when applying a hydrophilic layer of PEDOT:PSS on top of a hydrophobic P3HT/PCBM film. The mismatch between the low surface energy of P3HT/PCBM (24.2 mN/m) and the high surface tension of the used aqueous PEDOT:PSS solution (72.8 mN/m) causes dewetting and inhomogeneous layer formation which makes it difficult to coat PEDOT:PSS properly on the P3HT/PCBM layer [13,14]. P3HT/PCBM is not the only photoactive layer that shows such low surface energy. Other materials such as poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PCDTBT) give similarly low surface energies [15].

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[*] Corresponding author. Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629, HS Delft, the Netherlands.
E-mail address: w.a.groen@tudelft.nl (P. Groen).

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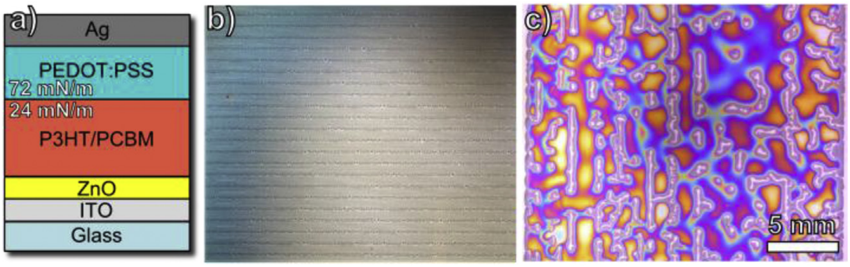

Fig. 1. A schematic representation of the inverted OPV stack (a), A picture of an inkjet printed layer of our standard CH8000 based, inkjet printing formulation (b) and a printed layer of CH8000 + 0.1 wt% Capstone FS-3100 (c). Both printed layers show inhomogeneous layers due to dewetting of the ink in the substrate.

Hydrophobic surfaces are often treated with UV-ozone to improve wetting of hydrophilic solutions, however, this method is undesirable and detrimental for the photoactive layer [9,16]. Although the surface energy of the photoactive layer can be raised by using UV-ozone or plasma treatments, this practice might affect the surface chemistry of the layer [9,14,17]. The use of a plasma treatment can also require several minutes of treatment, rendering it very expensive in R2R processes operating at speeds of several tens of m/min.

Other methods to improve the wetting of PEDOT:PSS on the photoactive layer is the addition of solvents, usually isopropanol or dimethyl sulfoxide and/or surfactants, usually Zonyl FS-300 or Capstone FS-31, which improve layer formation in several coating techniques but are not effective for inkjet printing on hydrophobic surfaces [9,14,18–27]. Most techniques for the wet-chemical fabrication of organic electronics such as spin coating, wire bar coating, slot-die coating and slide coating deposit the layer as one continuous wet film [7]. With inkjet printing the deposition of the ink is different as many small droplets are deposited on the surface and which have first have to flow together and merge to form a homogenous, closed film, before the solvent in the droplets evaporates. Given that such processes only take milliseconds to seconds, one must consider not only the static, equilibrium surface tension, but also the dynamic surface tension. Here, we report on the influence of a co-solvent and a surfactant on the dynamic surface tension and how these can be combined to inkjet print uniform PEDOT:PSS layers on top of hydrophobic P3HT/PCBM photoactive layers. After evaluation of the starting formulation, the dynamic surface tension of different PEDOT:PSS ink formulations was investigated using bubble tensiometry. Suitable combinations were subsequently evaluated using high speed camera imaging. Finally, devices in which the several PEDOT:PSS inks based on the newly developed formulations were inkjet printed on top of P3HT/PCBM were fabricated, evaluated and compared a reference device made with a conventional top electrode made from Molybdenum oxide (MoO_x).

2. Experimental methods

P3HT/PCBM samples were made with 2 wt% solution of both P3HT (Merck Lisicon SP001) and PCBM (99% Solenne BV) in Chlorobenzene (99.9%, Sigma Aldrich). Upon mixing, the solution was stirred overnight at 70 °C and filtered through a 0.45 μm filter before use. Glass plates with sizes of 3 × 3 cm^2 or 15 × 15 cm^2 were cleaned using multiple ultrasonic cleaning steps at elevated temperature in baths containing Teepol soap, followed by extensive rinsing in deionized water and drying in an oven at 80 °C. Substrates were treated with UV/ozone for 5 min prior to spincoating. Approximately 0.5 mL of solution for the 3 × 3cm^2 or 4 mL of solution for the 15 × 15 cm^2 substrates was then spincoated on the glass plates at 550 rpm with an acceleration of 2000 rpm/s for 95 s. This yielded P3HT/PCBM layers with thickness of 250–300 nm, as measured with a Dektak 8 M profilometer (Veeco). The spincoated layers were annealed at 130 °C for 10 min.

2.1. Ink formulation and characterization

Inkjet inks were based on either low conductive PEDOT:PSS (Clevios CH8000 from Heraeus) or high conductive HILHC5i (Agfa Gevaert N.V.). To these dispersions various surfactants such as Capstone FS-3100 (DuPont), 4-dodecylbenzenesulfonic acid (DBSA, Sigma Aldrich), Sodium dodecylbenzene sulfonate (SDBS, Sigma Aldrich), N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDAPS, Sigma Aldrich)) and alcohols (Ethanol (Biosolve BV), 1-propanol (Sigma Aldrich), isopropanol (Fluka), 1-butanol (Merck), 2-butanol (Sigma Aldrich), 1-pentanol (Sigma Aldrich)) were added. Inks were stirred for several hours prior to use. The contact angle measurements were made on an Easydrop Standard (Krüss), with 2 μL drops. The equilibrium surface tension measurements were made on the same apparatus using the pendant drop method. These contact angle and pendant drop measurements were performed at room temperature (22 °C). Dynamic surface tensions were measured on a Krüss Bubble Tensiometer (BP2) with a glass capillary (KR SH2031, Krüss) with an inner diameter of 0.2 mm and a hydrophobic silane coating. These measurements were performed over a range of 5 m s to 10000 ms at a temperature of 20 °C.

2.2. Inkjet printing and jetting evaluation

The jetting experiments were performed on a LP50 platform (OTB, Roth&Rau) with a Konica Minolta KM-512LN printhead having 512 nozzles with a nominal drop volume of 42 pL. Prior to inkjet printing the PEDOT:PSS ink formulations were filtered with a 0.45 μm hydrophilic PVFE filter. To calculate the dry layer thickness of the PEDOT:PSS ink the following formula is used:

$$T_{dry} = \frac{V_d \cdot f_{wt}}{DP \cdot LP}$$

Here, DP is the dotpitch, LP is nozzle spacing which on a KM-512LN printhead is 70 μm, Vd is the volume of an individual droplet (42 pL) and f_{wt} is the weight fraction of the dispersed PEDOT:PSS. In this research the expected dry layer thickness for the PEDOT:PSS layer are shown for ink formulations with several dotpitches.

2.3. High speed imaging

The landing and spreading of individually jetted droplets was performed using a phantom v310 high speed camera equipped with a long-range microscope objective capturing at 15600 frames per second, a resolution of 512 × 384 pixels and an overall magnification of 0.22 μm/pixel. Individual droplets were jetted from disposable Fujifilm Dimatix DCM-11610 cartridges with a nominal droplet volume of 10 pL. The droplets landed on spincoated films of P3HT/PCBM on glass which were prepared as described above.

2.4. Device preparation

The solar cells were made on 30 × 30 mm^2 glass/indium tin oxide