Photovoltaic Loss Analysis of Inkjet-Printed Polymer Solar Cells Using Pristine Solvent Formulations

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Summary: We have recently reported inkjet-printed organic solar cells with a record power conversion efficiency of 3.5%. In this contribution, we present our first trials to process a functional active layer of a polymer:fullerene bulk-hetero junction solar cell by inkjet printing using tetralene as a solvent. Solar cells with the inkjet-printed active layer based on pristine tetralene show calibrated AM1.5 power conversion efficiency (PCE) of around 1.3% over comparable doctor bladed cells with PCE of 3.3%. Analysis in terms of one-diode equivalent circuit combined with current-voltage characteristics of the devices as a function of light intensity and voltage were performed to reveal the dominant loss mechanisms of the inkjet printed solar cells using tetralene solvent formulation. The loss analysis described in this paper helps us to identify the device performance limitations and to design methods to improve the performance of inkjet printed organic solar cells.

Keywords: device loss analysis; fullerene; inkjet printing; morphology; organic photovoltaics; polymer solar cells; polymer; solvent formulations

Introduction

During the past decade, there has been an intensive search for cost-effective photovoltaics.[1,2] Among all alternative technologies to inorganic solar cells, polymer solar cells could provide the most significant cost reduction since their solution processability at low temperatures may ultimately allow for the printing of large area solar cells on flexible substrates with low fabrication cost.[2] At present, bulk heterojunction structures based on blends of polymer donor and a highly soluble fullerene derivative as acceptor have been the material system with the highest reported power conversion efficiencies.[3] We have recently reported the first highly efficient organic solar cells by inkjet printing.[4] By using a solvent mixture[4] and by adjusting the chemical properties of the polymer donor,[5] we have reported a record power conversion efficiency of 3.5% for inkjet printed organic solar cells.[5] In this contribution, we present our first trials to print organic solar cells based on pristine solvents. We discuss the losses of inkjet-printed polymer:fullerene solar cells using pristine tetralene as an organic solvent. A high power conversion efficiency reference device was fabricated by doctor blading, compared with the inkjet-printed device and the losses in the short circuit current density of the inkjet printed device were analyzed. The loss analysis described in this paper helps us to identify the device performance limitations and to design methods to improve the performance of inkjet-printed organic solar cells.[4,5]

Experimental Part

The devices were built on transparent indium tin oxide (ITO)-coated glass substrates, purchased from TFD. The glasses

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were cleaned 10 minutes in acetone and another 10 minutes in isopropyl alcohol using an ultrasonic bath, and, finally, a 10-minute ozone treatment. A thin layer of poly(3,4-ethylene dioxythiophene) doped with polystyrene sulphonic acid (PEDOT:PSS, H. C. Starck) was deposited by doctor blading on top of the ITO bottom electrode. The photoactive layer consists of an electron donor, a low-regioregular (RR, 93%) P3HT [poly(3-hexylthiophene)] blended with an electron acceptor, the fullerene $PC_{61}BM$ ([6,6]-phenyl C61 butyric acid methyl ester) in a ratio of 1:1, which was applied by a commercial piezoelectric-driven inkjet-printing tool (from Fujifilm Dimatix, Inc.) using tetralene as an organic solvent. Spreading and wetting on the substrate and, of course, the drying behavior of the inkjet-printed and doctor-bladed films are among other parameters influenced by the inkjet and doctor blading table temperature. Importantly, during the deposition of the active layer, the substrates were heated up to 60 °C and 40 °C for doctor-blading and inkjet-printing, respectively. In the case of inkjet-printing, we found that table temperatures above 40 °C can result in the accumulation of the RR-P3HT: $PC_{61}BM$ solvent mixture in the center of the substrate, causing strong thickness variations in the active layer: a very thick layer in the middle and a pile-up of very low concentrated formulation at the edges resulting in an ultra thin layer at the edges. Thus, inkjet table temperatures of 40 °C result in the most uniform film with less thickness variation within one printed area and a reliable printing regarding spreading and film formation. For the device fabrication by inkjet-printing, the glass/ITO/PEDOT:PSS-substrates were placed 1 mm below the inkjet print head. The temperature of the print head was set to 70 °C to prevent a viscosity increase or gelation of the solution in the nozzles due to a temperature drop. The thickness of the inkjet-printed and doctor-bladed active layer was measured via step height with atomic force microscopy (AFM) to be 200 nm. The devices were completed with a Ca-Ag electrode by thermal deposition. Prior to the evaporation of the top electrode, the devices were subjected to a thermal treatment at 140 °C for 10 minutes.

Results and Discussion

Figure 1 shows the AFM images of the RR-P3HT:$PC_{61}BM$ solution applied by inkjet-printing (Fig. 1a) and by doctor-blading (Fig. 1b). Due to the different substrate temperatures during layer deposition, a significant distinction in the grain size and surface roughness between doctor-bladed and inkjet-printed layers is visible. The AFM images display an extremely rough surface for the inkjet-printed active region. The root-mean-square (rms) roughness is calculated to be 26 nm for the inkjet-printed RR-P3HT:PCBM formulation while the rms roughness for the doctor bladed active layer was only 2.4 nm. A non-uniform surface roughness can affect the interfaces of the photo active layer and, therefore, the performance of the inkjet-printed device. The larger grain size of the RR-P3HT:PCBM inkjet-printed layer indicates morphological limitations due to a demixing phenomenon between the two components within the blend.

The plot in Figure 2a shows a typical current density- voltage (J-V) curve under illumination for the solar cells under study. The devices with an inkjet-printed active layer demonstrate a short-circuit current density (Jsc) of 4.73 mA cm^{-2}, an open-circuit voltage (Voc) of 0.45 Volts, and a fill factor (FF) of 63% under AM1.5 illumination with 100 mW cm^{-2}. This corresponds to a power conversion efficiency (PCE) of 1.29%, calculated using the formula $PCE = Voc \times Jsc \times FF/P_{light}$.[7] In contrast, the devices with doctor-bladed active layer reveal a much higher Jsc, Voc and FF, 7.87 Ma cm^{-2}, 0.6 Volts and 68% respectively. Thus, the doctor-bladed devices obtain a PCE of 3.3% under the same measured conditions to that applied for the inkjet-printed cells. The significantly lower values in Jsc (by 39%) and Voc (by 25%)

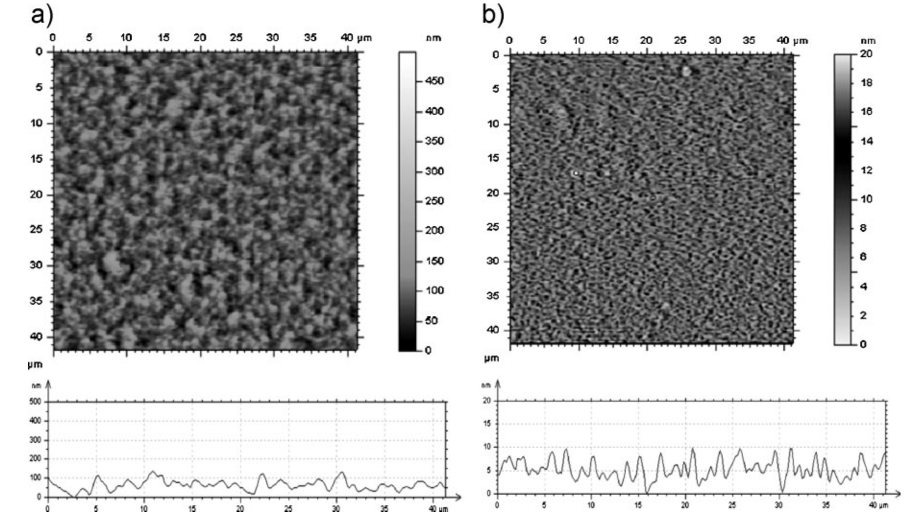

Figure 1.
Atomic Force Microscopy images of a 40 μm × 40 μm scanned area representing the surface topographies of the devices under study. a) Inkjet-printed RR-P3HT:PCBM based on tetralene; height scale is chosen to be 500 nm due to high surface roughness, b) Doctor-bladed RR-P3HT:PCBM based on tetralene. Due to the improved uniformity, the resolution is chosen to a 20 nm height scale.

for the inkjet-printed device indicate limitations in morphology for the inkjet-printed cells. We address this issue later in the text.

Figure 2b shows the dark current density/voltage (J/V) semi-logarithmic plot of the solar cell devices under study for the opening of the diode voltage range. The slope of the (log-linear) dark J-V curve between 0.2 V and 0.7 V represents the diode behavior of the solar cells as governed by the diode ideality factor (n) and saturation current (J_0).[6] From the dark J/V characteristics for voltages below 0.7 Volt, it can clearly be observed that the saturation current is higher and diode opens faster for the inkjet-printed solar cell compared to the doctor-bladed reference device. We have previously shown that for bulk heterojunction solar cells, the ideality factor correlates with the number of distributed interfaces within the blend, while the saturation current is related with the quality of the interfaces.[6] We interpret

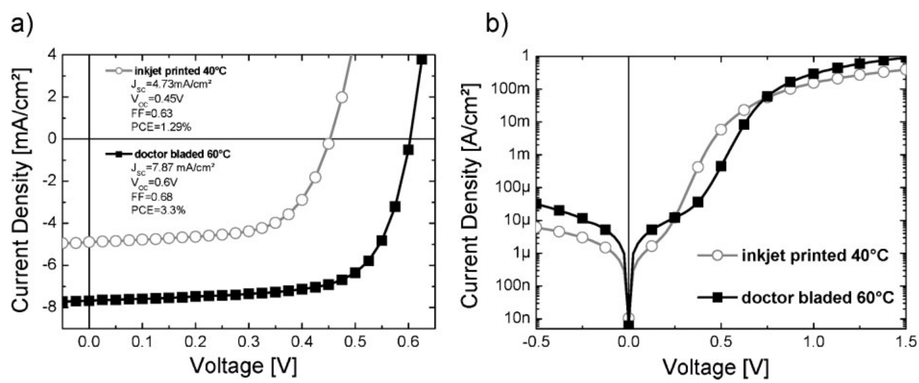

Figure 2.
Current-voltage characteristics of inkjet-printed (gray open dots) and doctor-bladed (black filled squares) P3HT:PCBM devices based on tetralene under AM1.5 spectra with 100 mW cm^{-2} (Figure 2a) and in the dark (Figure 2b).

the differences in the saturation current and ideality factors between the inkjet-printed and doctor-bladed cells to different morphologies arising from the different processing conditions.

The morphological differences between the inkjet-printed and doctor-bladed cells are reflected in the absolute values of n and J_0. The ideality is 1.63 and 1.34 for the doctor bladed and inkjet printed samples, respectively. The saturation current is $2.4 \times 10^{-9}\,\mathrm{A\,cm^{-2}}$ and $6.6 \times 10^{-9}\,\mathrm{A\,cm^{-2}}$ for the doctor-bladed and inkjet-printed samples, respectively. The difference in ideality between inkjet-printed and doctor-bladed cells provides an indication that there is a difference in the molecular distribution of PCBM within the P3HT. The ideality factor for the inkjet-printed cells shows a value of less than 1.4, while for the doctor-bladed cells the ideality factor presents a value of 1.63. Ideality factors below 1.4 indicate low intimate mixing of RR-P3HT and PCBM within the blend, resulting in reduced bulk heterojunction interfaces and, therefore, reduced charge separation efficiency. These limitations in the morphology of inkjet-printed cells are expected to lead to increased geminate recombination which can be the main reason for the limited Jsc of the inkjet-printed cells. We have previously shown that lower absolute values of J_0 typically lead to a higher Voc.[7] In this study, the higher value of J_0 combined with a rough active layer for the inkjet-printed cells can be invoked to explain the lower value of the Voc for the inkjet-printed cells in comparison to the higher Voc (600 mV) achieved with the doctor-bladed cells.

To further assess the losses in the short-circuit current of the inkjet-printed cells, the inkjet-printed and doctor-bladed devices were subjected to an illumination intensity and voltage dependence measurement. The light intensity measurement is presented in Figure 3a. The tetralene doctor-bladed cell is demonstrated by the black filled squares and the linear fit exhibits a slope of 0.98 (typical value for a fairly optimized device), which is significantly higher compared to the slope of 0.93 for the equivalent tetralene inkjet-printed cells depicted by the gray open dots. The smaller slope results in a 22% loss in the J_{SC} ($100^{0.926}/100^{0.981}$) of the inkjet-printed devices compared to the doctor-bladed device over the measured two decades in light intensity. Further indications for recombination losses can be seen in the voltage dependence measurement (presented in Figure 3b). Fitting the linear regime in reverse direction, where the sample is dominated by the parallel resistance, and

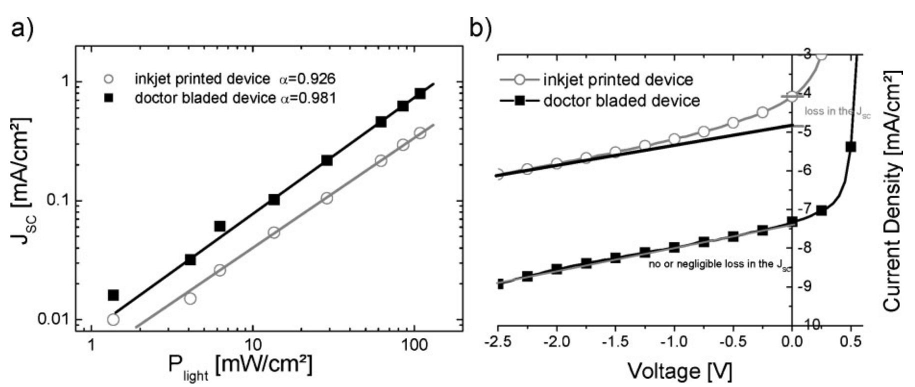

Figure 3.
a) The light intensity of the short-circuit current for the inkjet-printed device (gray open circles) and the doctor-bladed cell (black solid squares) in a double-logarithmic representation. The lines represent a linear fit with slope = 0.981 and 0.926 for the doctor-bladed and inkjet-printed cell, respectively. b) The voltage dependence of the illuminated photocurrent for extended reverse bias. The lines represent a linear fit of the JV-curves for the linear regime under reverse bias, where the current is dominated by the parallel resistance.

extrapolating this regime to zero volts, the loss in the Jsc due to recombination is visible. Recombination issues[8,9] can, therefore, explain losses in the Jsc of the inkjet-printed device compared to the doctor-bladed device.

The higher surface roughness together with the low diode ideality *n*, which represents the shape of the distributed pn-interface in the bulk-heterojunction or their morphology, indicates too large phases and, therefore, a loss in the charge separation for the inkjet printed solar cell. The phases of the P3HT and/or PCBM are significantly larger than the exciton diffusion length and, therefore, some of the excitons do not reach the P3HT-PCBM interface when the active layer is deposited by inkjet-printing using a pristine organic solvent (tetralene). We note that the drying behavior and the film uniformity of the inkjet-printed layer are also influenced by the inkjet table temperature. As we also discussed above in the text, for the RR-P3HT:PCBM we have found that inkjet table temperatures of 40 °C result in the most uniform film within one printed area and more reliable printing regarding the wetting behavior and film formation. Higher inkjet table temperatures result in a suppressed film formation and, therefore, a dewetting of the inkjet-printed layer due to an unfavorable surface behavior of the substrate. The limitation in the performance of inkjet-printed cells based on pristine solvent can be attributed to the low deposition temperatures (40 °C) of the inkjet table for the comparatively high-boiling solvent, such as tetralene (b. p. 207 °C, vapor pressure 0.18 mm Hg at 20 °C) used in this study. According to the above-mentioned, pristine tetralene ink formulation negatively affects the P3HT:PC_{61}BM morphology and surface roughness due to demixing phenomenon of the materials within the blend during the drying process and film formation. The poor morphology of the inkjet-printed RR-P3HT:PCBM device together with a significantly lower value of the built-in voltage Vbi (inkjet-printed device Vbi = 0.51 V) compared to the control doctor-bladed device (doctor-bladed device Vbi = 0.71 V) can also be the reason for the low value of the Voc: the ideality factor *n* is inversely proportional to the slope in the semi-logarithmic representation – the higher the *n*, the lower the slope. Thus, with the low value of the ideality factor *n*, injection currents are equal to the photo-generated current for relatively smaller voltages.

The higher surface roughness together with the low diode ideality factor *n* indicates too large phases and, therefore, a loss in the charge separation for the inkjet-printed device. The phases of the P3HT and/or PCBM are significantly larger than the exciton diffusion length and, therefore, some of the excitons do not reach the P3HT-PCBM interface when the active layer is deposited by inkjet-printing using pristine tetralene. Thus, unfavorable morphology can be the major reason for the lower Jsc of the inkjet-printed device from tetralene compared to the controlled doctor-bladed solar cell. We argue that the much lower values of J_{SC} for the inkjet-printed solar cells are related to morphological limitations, reduced charge separation efficiency and increased recombination.

Conclusion

Device loss analysis of inkjet-printed solar cell using tetralene solvent formulation indicates losses in the Jsc and Voc, which could be identified as losses due morphological issues and recombination mechanisms within the inkjet-printed active layer. We suggest that the limitation in the performance of inkjet-printed cells can be attributed to the low deposition temperature for the comparatively high-boiling solvents, such as tetralene used in this study, resulting in an inhomogeneous drying and, therefore, a non-uniform film formation with high surface roughness. One possibility to enhance the morphology of inkjet-printed polythiophene (P3HT) and methanofullerene (PCBM) and, thus, the device performance is to monitor the film formation and drying of the wet bulk by adjusting the solvent formulation. We have recently improved the morphology of inkjet-printed P3HT:PCBM blends by adjusting the regioregularity of the poly(3-hexylthiophene) polymer donor[5] and by using a solvent mixture.[4] Thus, we have developed new methods to gain control over the nanomorphology of poly(3-hexylthiophene):fullerene active layers during the printing process.[4,5]

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