Large Area Inkjet Printing for Organic Solar Cells and OLEDs using Non-Halogenated Ink Formulations

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Abstract

Transferring lab-scale processes of organic electronics to large area roll-to-roll production requires the use of up-scalable deposition techniques. Furthermore, industrial production demands the omission of halogenated and other harmful solvents. Here we discuss the solution processing of organic light emitting diodes (OLEDs) or organic photovoltaics (OPV) applying halogen free ink formulations that are compatible with large area inkjet printings. We demonstrate the inkjet printing of the emissive layer in smOLED devices and the photo-active layer in OPV. In both cases homogeneous layer thicknesses were obtained, yielding a uniform light emission from the printed smOLEd device. While in the case of the smOLED device the luminous output was slightly lower than that of a spin coated device, the photoactive layer printed for an OPV from the halogen free ink showed similar performance as a layer spin coated from chlorinated solvents.

Introduction

Roll-to-roll production on flexible substrates promises fast, cheap and large scale production of organic electronics.[1, 2] However, current lab-scale processes cannot directly be translated to larger scale industrial application. For example, chlorinated solvents are the common standard for the processing of a photo-active layer by spin coating for OPV. But spin coating is not a roll-to-roll compatible deposition method and chlorinated solvents are banned from industrial scale applications due their environmental and health risks. High class OLEDs with uniform light emitting layers are produced by thermal evaporation, while the wet chemical deposition by spin-coating from, e.g. toluene has also been introduced.[3] Currently, low cost, material efficient processing methods compatible to industrial roll-to-roll production need to be developed for both applications.

Inkjet printing is a non-contact deposition technique suitable for roll-to-roll production with a large versatility; it can be applied to a wide range of materials, such as metal nanoparticles and polymer dispersions as well as polymer and small molecule solutions.[4] Although it is often used for structured electronics, it can also be used for the deposition of large area thin films. It allows direct patterning, effectively structuring separate cells and modules during roll-to-roll production, as well as making economic use of materials. Most inkjet print apparatus used for smart materials printing have a limited number of nozzles, making the printing of larger areas slow. However, using the LP50 printing platform (Pixdro, OTB) equipped with an industrial printhead with 512 nozzles, 3.5 cm wide areas can be printed in a single pass with high speeds compatible to roll-to-roll web speeds (see Figure 1A).

In this work we report on inkjet printed organic solar cells and OLEDs using a printing platform compatible with roll-to-roll processing and excluding harmful halogenated organic solvents. We focus on the active layers in the device stacks as indicated schematically in Figure 1B. Recently, progress for ink formulations for OLED and OPV has been reported.[5-7] However active areas were limited and damaging interactions of the printed layer with the underlying layers were observed. There is a narrow window of operation for the development of ink formulations, as they have to fulfill several rheological requirements concerning viscosity, surface tension and boiling point to be printable. For most industrial printheads a viscosity ranging from 5-10mPa·s is preferred. Inks that can be printed by labscale printheads are therefore not always compatible with industrial size printheads needed for large are printing.

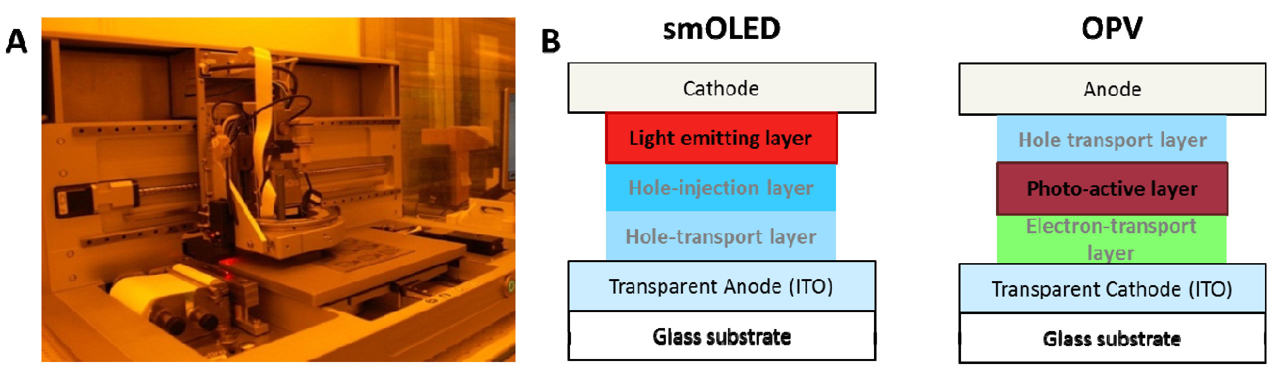

Figure 1. *(A) Pixdro LP50 printing platform equipped with industrial printheads capable of processing 20 by 30 cm sheets, and (B) schematic representation of OLED and OPV stacks with inkjet printed light emitting and photo-active layers, respectively.*

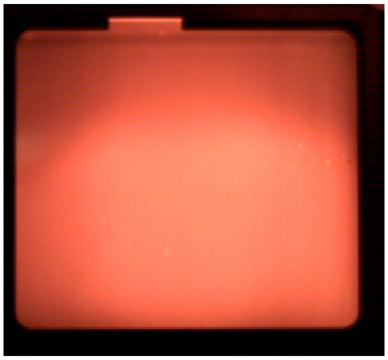

***Figure 2**. Photograph showing 3.75 cm^2 working smOLED with a highly uniform inkjet printed light emitting layer using a non-halogenated ink formulation.*

Inkjet printed smOLED

Homogeneous light emission over a large area is one of the selling points of OLED. For this, uniform thickness and composition of the light emitting layer is essential. Layer thickness variations in the order of nanometers will be detected rapidly as bright spots or darker areas. Uniform large area OLEDs were fabricated by first inkjet printing an aqueous HTL layer, followed by a toluene-soluble, thermally crosslinkable HIL layer. Using a halogen free ink formulation, a light emitting layer containing phosphorescent small molecules was finally printed as a ~80 nm layer on top. The halogen free ink formulation had a viscosity of only 1.5 mPa·s, below the specifications of the printhead. Indeed during jetting satellite formation was observed, which resulted in decreased sharpness of the printed areas edge. Nonetheless, the photograph in Figure 2 shows that the layer emits red light with a homogeneous intensity, confirming the uniformity of the layer thickness of the emissive layer as well as the two underlying functional layers. After jetting the individual ink droplets have merged into a wet layer of uniform thickness, while during drying only a limited coffee stain effect occurred. In fact the light emission was of similar homogeneity as that from a smOLED with the same light emitting layer produced by spin coating from toluene.

In addition to the layer uniformity, a homogeneous mixing of the different light emitting layer components should ensure good performance of the devices. The performance of devices with a green phosphorescent small molecule in the emitting layer was tested by IVL. The luminescence and current density in the inkjet printed device was slightly lower than a spin coated reference

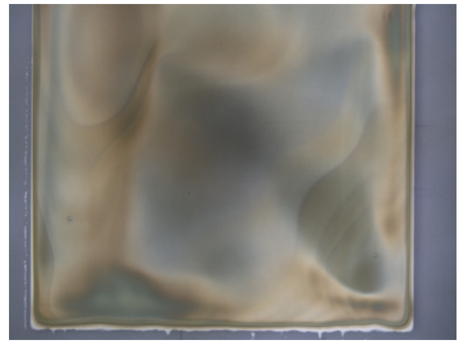

***Figure 3**. Optical micrograph of inkjet printed photoactive layer (area of 2 by 2 cm).*

device. However, the relative layer thicknesses in the inkjet printed device (see Figure 1) were not yet optimized for maximal light emission, but for optimal layer homogeneity. Even though functional device were obtained, the IVL response of the inkjet printed devices indicate that layer thickness variations, barely noticeable by eye, in the three printed layer may accumulate to cause local defects. Future optimization of the halogen free ink formulation and printing parameters will therefore focus on the increase in luminous output and reliable printing and device performance.

Inkjet printed organic solar cells

The layer thickness of the photoactive layer in organic photovoltaics mostly affects the device performance and balances increased efficiency by increased light absorption with a decrease in charge extraction due to longer percolation pathways. A homogeneous thickness in the active area will ensure optimum yield from the full device. The halogen free ink formulation showed good and stable jetting, even though the viscosity was 1.9 mPa·s. Thus, the slightly higher viscosity as compared to the smOLED ink already improved the jetting, even though it is still below the printhead specifications. The photograph in Figure 3 shows a printed area of 2 by 2 cm, and layer thickness variations can be observed as changes in the color intensity. Slight variations in the phase separation and P3HT crystallization cause differences in light interference, which is observed in the body of the printed area. The outer rim shows difference in color intensity, indicating a coffee stain. To determine the size and extend of the coffee stain, white light interferometry was performed, and a 3D height profile

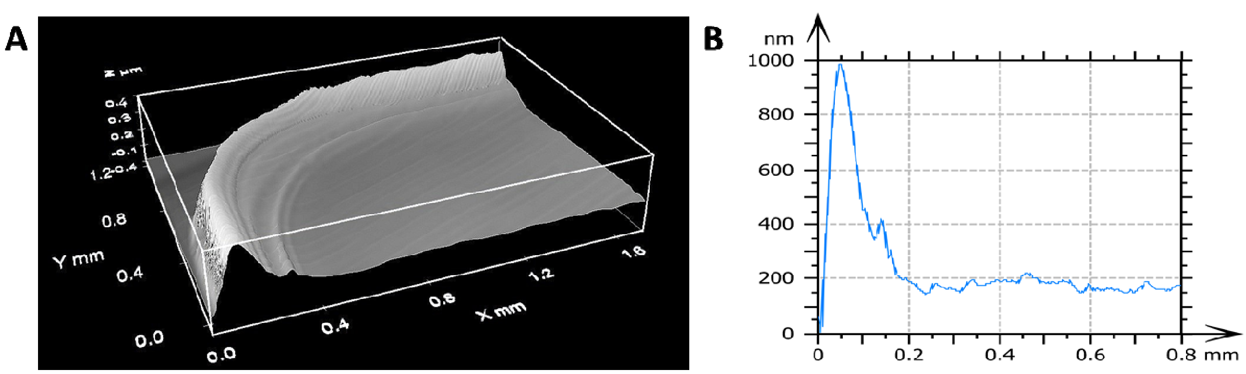

***Figure 4.** (A) 3D Height profile of the corner of an inkjet printed photo-active layer obtained by white light interferometry, and (B) 2D height profile showing extend of coffee stain.*

is shown in Figure 4. The coffee stain encompasses ~500% of the layer in height, while it extends over ~0.2-0.4 mm in width. This is significant and leaves room for optimization of the ink formulation or printing parameters. As can be observed from the line plot, the average layer thickness in the center of the printed area is ~200 nm, which corresponded to thickness measurements with profilometry. Overall, taking the coffee stain into account, 36 to 64% of the printed area consists of a homogeneous thickness, and this percentage increases for larger areas (e.g. up to 77% for a 10 by 2 cm long device).

Control over the blend morphology of the photo-active layer in OPV is essential to reach high performances. Best results reported in literature are usually for spin-coated layers from ortho-dichlorobenzene, and for small active areas (<1 cm^2). Here we demonstrate the use of non-halogenated ink formulations for the inkjet printing of OPV leading to cells with performances similar to that of a spin coated reference.[8] Ink formulations were developed for the current workhorse photo-active polymer, poly(3-hexylthiophene) (P3HT) blended with phenyl-C61-butyric acid methyl ester (PCBM). A uniform layer thickness is most critical for the light emitting layer in OLEDs. However, for OPV the phase separation in the photo-active layer blend is also critical and is largely affected by the processing parameters such as solvent system, drying procedures and thermal annealing. The target for halogen free ink formulations is to reach the performance of a large area cell (3.75 cm^2) with inverted device architecture with a spin-coated photo-active layer from ortho-dichlorobenzene. Due to the sheet resistance of the large area ITO bottom electrode, the cell maximum power point is limited to approximately 2 mW/cm^2. The IV curves in Figure 5 show that by inkjet printing the PAL from halogen free solvents similar performance is reached. Further optimization of the processing parameters, such as layer thickness is expected to improve the devices fill factor.

Conclusions

Here we demonstrate the use of inkjet printing using industrial printheads for both OLED and organic solar cells. For industrial scale production, halogen free ink formulations were developed to print the light emitting layer in OLED as well as the photo-active layer in OPV. A red OLED with light emission over 3.75 cm^2 as uniform as a spin-coated device was thus inkjet printed. For OPV, the inkjet printed layer reached similar performance as a layer spin-coated from chlorinated solvents. Both achievements demonstrate the power of inkjet printing for large area production of organic electronics.

Experimental Methods

All devices were processed on glass/ITO, which was cleaned in several scrubbing and rinsing steps. The smOLED devices consist of three solution processed layers, the smOLED emissive layer, PEDOT:PSS as HIL and a thermally crosslinkable HIL layer and an evaporated Ba/Al cathode. OPV devices consist of an inverted cell stack with a ZnO electron transport layer and an evaporated MoO_x/Ag anode. The photo-active layer consists of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM). The inkjet printing was performed on a Pixdro LP50 printing platform with an industrial printhead with 512 nozzles.

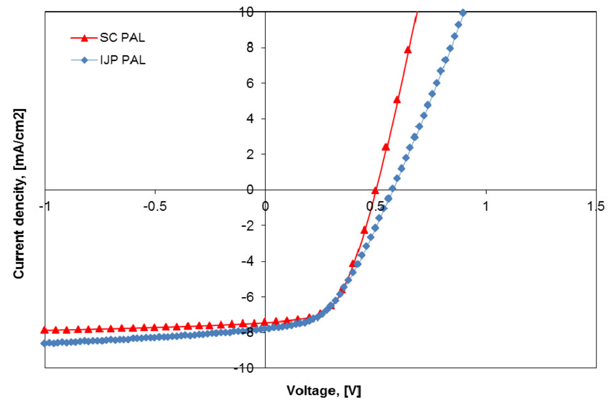

Figure 5. JV curves of OPV with spin-coated photo-active layer using ODCB (SC PAL) and inkjet printed photo-active layer using non-halogenated solvents (IJP PAL), active area is 3.75 cm^2.

All areas were printed in a single pass at 2 cm/s. The active device areas were limited by the electrode masks at 3.75 cm^2. Performance of the smOLED devices was measured using a home built IVL setup. The height profile of the PAL was determined using white light interferometry (Leica DCM3D) and the layer thickness was verified using profilometry. The OPV efficiency was measured under AM1.5 illumination.

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