Inkjet Technology for Large-Area OLED and OPV Applications

Maosheng Ren, Harrie Gorter, Jasper Michels and Ronn Andriessen, Holst Center/TNO, PO Box 8550, 5605KN Eindhoven, the Netherlands

Abstract

The roll-to-roll manufacturing process is believed to significantly reduce the cost-price of flexible electronics. Inkjet printing of organic-based inks is a major research topic for flexible electronic applications because of its advantage of non-contact deposition and the ease for patterning for various industrial processes. We herein present a study on inkjet printing of homogeneous layers of Orgacon™ (Agfa-Gevaert, Belgium). Orgacon™ is a water-based dispersion of poly(3,4-ethylenedioxythiophene):poly(styrenesulphonic acid (PEDOT:PSS). This printed layer can be used as a transparent electrode for the Organic Light Emitting Diodes (OLEDs) and for Organic Photovoltaic (OPV). For OLED lighting applications, uniform light emission of large areas is required; the main challenge of using inkjet technology is the deposition of highly homogenous layers onto flexible non-porous foil substrates.

In this contribution, some of the fundamental aspects of inkjet ink and substrate interaction, and the resulting layer homogeneity of the active layer in relation to OLED and OPV-device performance are investigated. Combining both theoretical and experimental approaches, we studied the inkjet ink rheology and homogenous layer formation on a moisture barrier. We have enabled to deposit homogenous PEDOT and LEP using commercially available inkjet heads. Furthermore, we would like to demonstrate the ability of using inkjet printing for fabrication of 1"by 1"OLED devices, with Agfa high conductive PEDOT:PSS and Merck light emitting polymers dissolved in solution. The inkjet ink properties and the substrate pretreatment have been optimized in order to ensure a stable and robust printing and drying process. Moreover, inkjet printed OLEDs will be demonstrated and the resulting light emission uniformity, device performance and reliability on flexible substrates will be discussed.

Introduction

High efficient white OLEDs are typically manufactured using vacuum deposition techniques of small molecules onto glass substrates that are coated with a transparent conductive oxide, such as indium tin oxide (ITO). For high volume and low-cost OLED production for lighting applications, vacuum processing is comparatively expensive and roll-to-roll deposition techniques at ambient conditions are more appealing. The sequential deposition and curing of organic-based inks in a roll-to-roll (R2R) manufacturing process is believed to significantly reduce the cost-price per square meter. However, the substitution of traditional deposition techniques and applying well-known proven materials to a flexible moving substrate is not always trivial. Nevertheless, replacement of a 20 Ω/square transparent ITO layer by a high conductive PEDOT:PSS layer and printed metal structures in a thin film encapsulated flexible OLED with an active area of 150 cm^2 has previously been demonstrated [1], using spin-coating. We also reported that for three metal printing processes, inks/pastes based on silver nano-particles showed the best compliancy with our OLED device structure [2]. Our overall objective is a cost-efficient production method for lighting foils based on OLED technology, which have a comparable total cost of ownership to traditional lighting methods, such as fluorescent tubes. We are currently investigating high volume and roll-to-roll compatible solution-based deposition techniques, such as slot-die coating, screen printing, and inkjet printing. The general challenge is to develop deposition technologies and capabilities for processing thin and highly homogenous layers of functional polymers (such as PEDOT:PSS and light emitting polymers) on flexible substrates with a thin film moisture barrier.

One of our major research topics is inkjet printing of organic inks for printed electronics because of its advantage of non-contact deposition and the ease for patterning in various industrial processes. Over the past few years, with the development of reliable and robust inkjet print head technologies, ink jet technology is more and more used in the document/graphics productions. This development opens new opportunities for using industrial inkjet technology in the high-demanding OLED production, where uniform light emission on large areas is required. The main challenge of using inkjet technology is the deposition of highly homogenous layers of active materials onto flexible non-porous substrates.

In this paper we demonstrate the use of inkjet technology in the fabrication of flexible OLEDs, where the active organic layer is applied by inkjet printing. As a benchmark, the device performance will be compared with spin coated reference devices. We will investigate several process requirements for the deposition of homogeneous electro-active layers, such as pre-treatment of the substrate to modify the surface energy, and ink formulations to yield stable inkjet inks with concentration, wetting behavior and rheological behavior determined by the boundary conditions for a robust deposition process.

For these purposes we designed OLED devices on foils with a moisture barrier. Our fabrication method can potentially be scaled up wider flexible and active OLED lighting tiles using a suitable metal support structure on the thin film barrier for the current distribution. The ambition is that, with sufficient reproducibility and reliability, our processing techniques may be applied to the fabrication of flexible OLED lighting tiles, but also for systematic moisture barrier analysis of thin film encapsulated foil-based OLEDs [3].

Ink and substrate characterizations

Organic light-emitting diodes were fabricated on 6" by 6" flexible foil substrates, onto which a silicon nitride-based moisture barrier was applied. The transparent barrier was based on low-temperature plasma deposited amorphous hydrogenated silicon nitride films as the intrinsic moisture barrier and was stacked with planarization layers to spatially separate defects in these films. To limit the ingress of water and oxygen, the above mentioned moisture barrier was also applied as encapsulation stack on top of the manufactured OLEDs, as sketched in Figure 1.

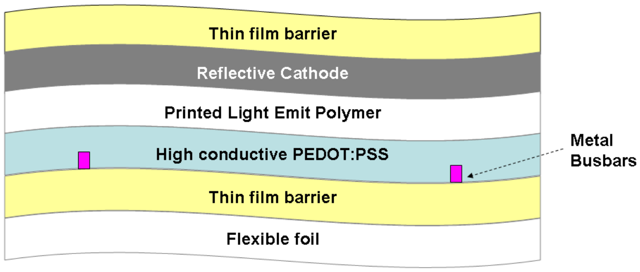

Figure 1. Schematic representation of a bottom-emitting (ITO-free) OLED on foil.

The (ITO-free) OLED layer stack consisted of a highly conductive PEDOT:PSS (Agfa Orgacon™ HILHC5 IJ) that served simultaneously as the transparent anode and as the hole injection layer. PEDOT:PSS is basically a (99%) water-based polymer dispersion. Because of the polymer intrinsic high molecular weight, the ink viscosity is not linear as function of shear rate (measured with a Anton Paar Physica MCR rheometer), as shown in Figure 2. For most inkjet heads, the shear rate is in the order 10^5-10^6 s^{-1}. The shear thinning effect in the high shear regime is demonstrated. In order to obtain a single droplet formation without any satellites and a short ligament, we have optimized the waveform of the print head.

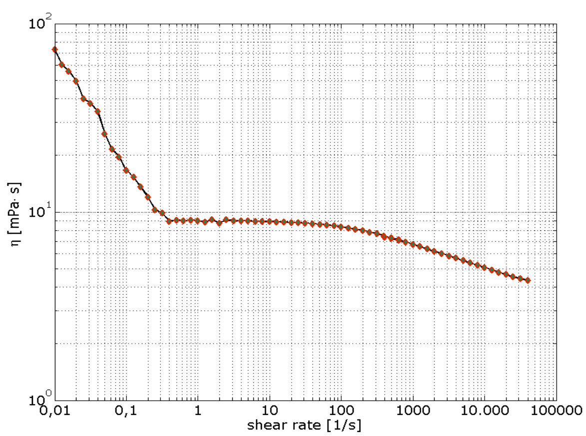

Figure 2: PEDOT:PSS ink viscosity as function of shear rate, measured with a Anton Paar Physica MCR rheometer.

Figure 3 shows wetting envelopes of the substrate: silicon nitride and metal busbars/lines before and after plasma treatment. The polar and disperse coordinates of water, the main component in the PEDOT:PSS inks, show the relation between the ink and the substrate. If, as for the untreated substrates, the surface energy of the substrate is much lower than the surface tension of the ink the wetting, spreading, and layer formation will be poor. Large differences in the surface energy will cause inhomogeneous layer formation or even de-wetting spots. By applying a plasma treatment the low surface energies of both substrate materials increase and the difference between the two different materials becomes smaller, as shown in Figure 3. In such a way, the layer formation can be controlled and stabilized. Further improvement of the wetting behavior can be obtained by lowering the surface tension of the ink by additives, e.g. surfactants or alcohols.

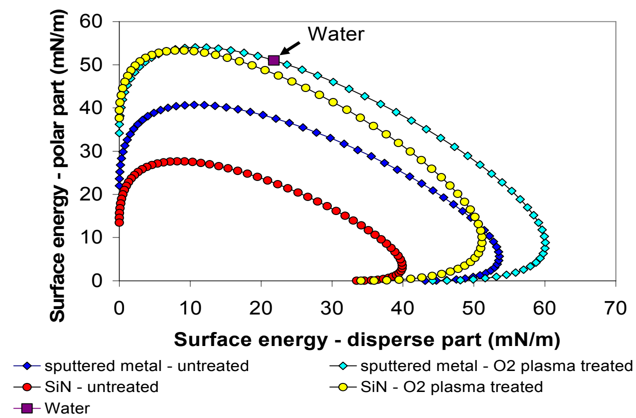

Figure 3. Wetting envelopes for untreated and pretreated substrate.

Adding surfactant to the PEDOT:PSS may influence the jetting behavior. Depending on surfactant type and concentration, the equilibrium surface tension of the PEDOT:PSS dispersion ranges from 20 to 40 mN/m. Figure 4 shows the effect of different surfactants in a graph in which surface tension is plotted as a function of time, measured by a Bubble Tensiometer. By adding certain percentage of surfactant, the surface tension of the PEDOT:PSS can be reduced and be suitable for the inkjet printing.

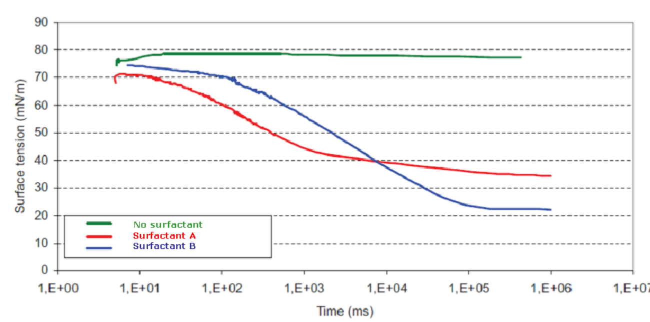

Figure 4: Effect of surfactant, measured surface tension as function of time.

Inkjet printed PEDOT layer

For most of the experiments, a commercially available Spectra Galaxy PH 256/50 AAA inkjet printhead was used. It has 256 individually nozzles with a nozzle diameter of 42 µm and nozzle spacing of 0.254 mm. The distance between individual inkjet deposited droplets is denoted as dot pitch, which can be varied by the printing speed and jetting frequency. At a very low dot pitch the cap of a line contains too much ink, which leads to uncontrolled spreading. With decreasing the dot pitch, a smooth line can be created. If the dot pitch becomes too small, wetting instability occurs [4]. Capillary effects lead to a regular pattern of wider and smaller parts in the line. At a still larger dot pitch the drops will not merge anymore into a continuous line [5]. For narrow and thin single lines (within the capillary length scale), the line width can be calculated as a function of droplet size (R_{drop}), equilibrium contact angle (θ_e) and dot pitch (dp) using Equation (1).

$$w = 2R_{\mathrm{drop}} \frac{\sin\theta_e}{\sqrt{\theta_e - \frac{1}{2}\sin 2\theta_e}} \sqrt{\frac{4}{3}\pi \frac{R_{\mathrm{drop}}}{dp}} \tag{1}$$

The cross-sectional area (volume per unit length) of a single inkjet printed line can be adjusted by means of the printing speed. The width of a single printed line is dependent of the ink-substrate contact angle as illustrated in Figure 5.

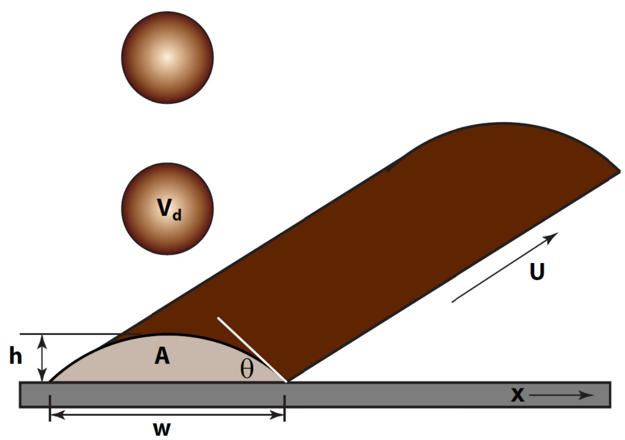

Figure 5: Definition of inkjet droplet impact on a non-porous substrate to form a single line.

Inkjet printed line widths are measured either using a microscope image or a Dektak profilemeter. Figure 6 shows the theoretical as well as measured line widths of inkjet printed PEDOT on silicon nitride. The graph shows good agreement between the theoretical and experimental values.

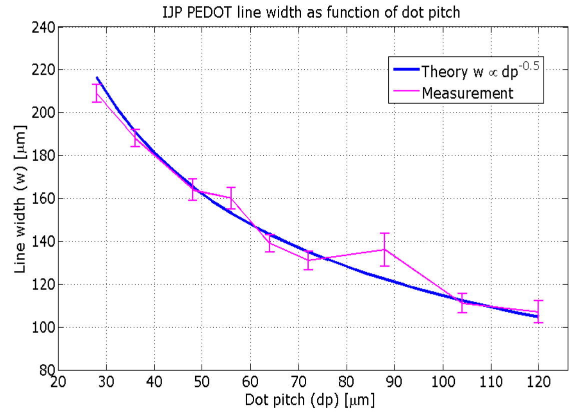

Figure 6: Line width of printed PEDOT:PSS as function of dot pitch, comparison between experimental measurements and theoretical predicted values.

Printed OLED

Our glass-based (ITO-free) OLED device typically consists of a transparent anode, a hole-injection layer (PEDOT:PSS), a white light-emitting polymer (LEP, Merck Livilux™) and barium (5 nm)/ aluminum (100 nm) as the cathode. A highly conductive PEDOT:PSS (Agfa Orgacon™ HILHC5 IJ) served simultaneously as the transparent anode and as the hole-injection layer. Metal busbars around and within the active area were obtained by screen printing or RF sputtering. The metal structure within the active area had a honey-comb shape, as shown in Figure 7. The width of the metal lines was in all cases in the order of 200 µm. The height of the metal was ~200 nm for sputtered metal and ~1.5 µm in case of screen-printed metal flakes. The PEDOT:PSS and the light-emitting polymer were deposited from solution by inkjet printing under ambient conditions.

Typical dry layer thicknesses were 100 nm for PEDOT:PSS and 80 nm for the light-emitting polymer. After thermal evaporation of the cathode, the devices were sealed by applying a metal lid with a UV curable epoxy adhesive. Figure 7 shows the photographic image (a) the inkjet printed PEDOT (b) inkjet printed LEP (on top of PEDOT) under UV illumination and (c) light output of OLED device driven at a voltage of 8V.

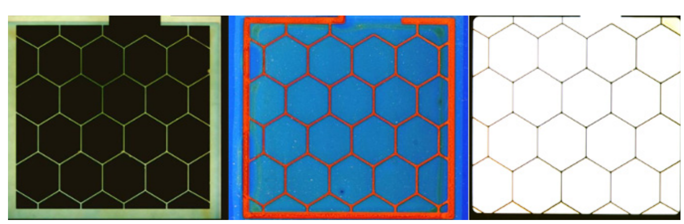

Figure 7: Photographs of (a) inkjet printed PEDOT on a glass substrate with sputtered metal, (b) inkjet printed Livilux™ LEP onto the device, under UV illumination and (c) electroluminescence, after cathode evaporation and encapsulation with a metal lid, of the device is driven at a voltage of 8 V.

The current-voltage-light (IVL) characteristics of the OLED devices were measured using a Keithley 2400 general-purpose source meter. During the IVL cycle the brightness was monitored by a photodiode calibrated with a Konica Minolta LS-100 luminance meter. The luminance meter was mounted orthogonally to the OLED that was connected to a Keithley 6517A electrometer/high-resistance meter. The systematic error in these measurements is estimated to be ±10%.

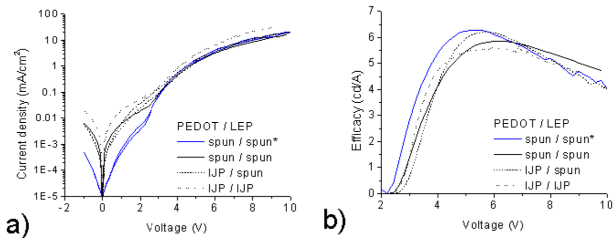

Figure 8. IVL measurement of 1"by 1" OLEDs on glass with benchmark of spin-coated and inkjet printed HILHC5 PEDOT:PSS and LEP layers.

All PEDOT:PSS layers were formed from the same Orgacon inkjet printing formulation (HILHC5 IJ) with exception of the OLED of which the IVL is indicated in blue (HILHC5 for spin coating version), as indicated in Figure 8. In general, the current-voltage-light cycles of the 1"by 1" OLEDs nearly overlap. The OLED with the inkjet printed LEP layer does exhibit a somewhat higher IV profile, stemming from local layer thickness variations. Also in the lower voltage regime, before turn-on, the parasitic current is higher than for the spin-coated samples. Although such leakage currents may arise from defects (dust, scratches, etc) in the active area, the use of high conductivity PEDOT:PSS does require homogeneous coverage by the LEP to avoid the formation of soft shorts.

Deposition of the white LEP by inkjet printing is again posing a challenge: homogeneous film formation on a hygroscopic PEDOT:PSS surface of some organic solvent systems [3]. In Figure 7, we have demonstrated a uniform light emission with optimal droplet formation, compatibility with the substrate, coalescence, leveling and drying to form a homogeneous 80 nm dry LEP layer. Despite this complexity, the brightness and efficacy levels were found to be in the same range as the OLEDs manufactured by spin-coating, as shown in Figure 8.

Printed OPV device

The OPV device stack is very similar the OLED stack, as sketched in Figure 9. Instead of using a light-emitting polymer, a P3HT/PCBM donor-acceptor blend is deposited on top of the PEDOT:PSS layer and covered with LiF/Al as a reflective cathode. Metal busbars/lines around or within the active area can be deposited by screen printing metals. The metal structure within the active area has a honey-comb shape or consisted of one or more evenly spaced lines. Typical dry layer thicknesses were 100 nm for high conductive PEDOT:PSS and 200 nm for the P3HT/PCBM blends.

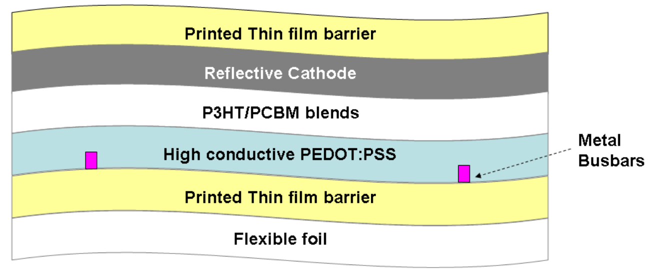

Figure 9. Schematic of a (ITO-free) OPV on foil.

The current density-voltage (JV) characteristics of the OPV devices were measured using a simulated AM 1.5 global solar irradiation (100 mW/cm2). A Xenon lamp-based solar simulator was used as the light source. The lamp was calibrated with a standard silicon photodiode detector. Figure 8 shows the performance (JV curve) of a 1" by 1" OPV device.

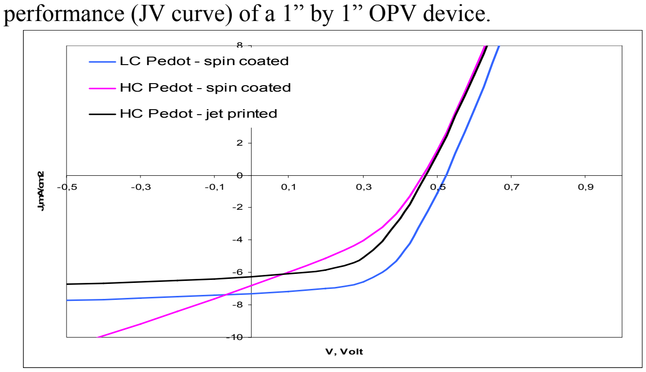

Figure 10. Device performance of 1"by 1" OPV on glass with benchmark of spin-coated and inkjet printed PEDOT:PSS and spin coated OPV layers.

Both the PEDOT:PSS ink formulations (conductive variations) and the deposition techniques (spin coating vs. inkjet printing) were varied. Inkjet printed PEDOT:PSS shows an equivalent quality compared to spin coating, with respect to layer homogeneity and device performance. When using the same PEDOT:PSS, the inkjet printed OPV device shows slightly better performance (less leakage current) than the spin coated version, as indicated in Figure 10. The reason for this is that the inkjet printed device, removal of PEDOT:PSS from undesired area (to prevent shorts) will be not necessary. This may increase OPV production yield as it omits an extra structuring step.

Conclusion

Some of the fundamental aspects of inkjet ink and substrate interaction have been addressed. The resulting homogeneity of the active layer (PEDOT:PSS) related device performance of OLED and OPV are investigated. Combining both theoretical and experimental approaches, we have optimized the inkjet ink formulation and homogenous layer formation on a moisture barrier. With commercially available print heads, we have deposited PEDOT:PSS and LEP to give homogeneous layers. Furthermore, we have demonstrated the ability of using inkjet printing for the fabrication of 1”by 1”OLED devices, with Agfa high conductive PEDOT:PSS and Merck light emitting polymers dissolved in solution. The properties of the inks, as well as substrate pretreatments have been optimized in order to ensure a robust printing and drying process. Moreover, inkjet printed OLED and OPV devices have been demonstrated. The resulting light emission uniformity and the device performance have been addressed. ITO-free OLEDs on glass containing inkjet printed PEDOT:PSS and inkjet printed LEP layers were found to have comparable performance to the spin-coated reference devices. With industrial inkjet printing technology, it is feasible to upscale the manufacture OLEDs for lighting and signage application and OPV foil production.

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Author Biography

Maosheng Ren received his B.S. from Beijing University of Aerospace Engineering in China (1999) and his Ph.D. in Mechanical Engineering from Eindhoven University of Technology, the Netherlands (2005). After his graduation, he was involved in product development of new wide-format inkjet color printers for Océ Technologies. He joined Holst Centre/TNO (NL) in 2009 where he is currently responsible for the development of R2R ink jet printing technologies and processes for large area OLED lighting and OPV devices and modules that should enable future mass production.