Inkjet Technology for Large-Area OPV Applications

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Abstract

The roll-to-roll manufacturing process is believed to significantly reduce the cost-price of large area organic photovoltaic systems. Therefore, we build up knowledge base concerning the influence of process conditions on the performance of polymer solar cells. Inkjet printing has been a major research in processing photoactive materials because of its advantage of non-contact deposition and the ease for patterning for various industrial processes. A large area solar cell module, with inkjet printed PEDOT:PSS Orgacon™ (Agfa-Gevaert, Belgium)and photoactive layers (based on P3HT:[C60]PCBM blend) on a flexible substrate, has been demonstrated. Both the PEDOT:PSS and photoactive layer were deposited by inkjet printing. A non-chlorinated solvent was used for the deposition of the photoactive blend. 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 OPV-device performance are investigated. Combining both theoretical and experimental approaches, we studied the layer formation on a moisture barrier. We have enabled to deposit homogenous PEDOT and OPV using commercially available inkjet heads. Furthermore, we would like to demonstrate the ability of using inkjet printing for fabrication of OPV devices, with Agfa high conductive PEDOT:PSS and Merck and Plextronics P3HT 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. The flexible solar cell module illustrated a power conversion efficiency of 3.2% under AM 1.5 conditions.

Introduction

The growing interest in organic photovoltaics (OPV) can be explained by the promising low cost approach for the energy conversion. In order to reach an impact on the high power market on the longer term, the organic photovoltaics should provide high power conversion efficiency, low production costs and long term stability. The low cost potential is based on the use of low-cost materials and substrates and the very high production speeds which can be reached by roll-to-roll printing and coating techniques [1-2]. Photovoltaic devices require either a transparent anode or cathode. Generally a transparent conductive oxide (TCO) like indium tin oxide (ITO) is used as a transparent electrode. However, to obtain a highly conductive ITO film with improved crystallinity, a high temperature is required. Such a high temperature process can be realized on glass substrates. In such case the sheet resistance of a typical ITO film is about 5-15 Ω/□. Due to a limit in processing temperature, the conductivity of a thin ITO film on flexible substrates like PET or PEN is significantly lower. Typical reported sheet resistance for ITO on flexible supports is in the order of 30-60 Ω/□. Scaling up of the dimensions of OPV devices with ITO electrodes leads to the efficiency drops. Additionally, high mechanical flexibility is an important requirement for all layers in flexible photovoltaic devices. Under numerous bending cycles, the brittle ITO layer can be easily cracked, leading to a decrease in conductivity and as a result degradation of the device performance. Finally, the price of ITO and the requirement of expensive post-patterning demonstrate the necessity to look for alternatives for ITO as an electrode. Different types of transparent electrodes, which are mainly based on carbon nanotubes or different types of high conductive PEDOT:PSS, have been reported [3]. In general such kinds of electrodes do not provide high efficiency with large scale devices due to the limited conductivity. The sheet resistance of these materials is typically in the range of 200-800 Ω/□. Further increasing of the conductivity is possible with integration of metal grids, which are either thermally evaporated through micro structured shadow masks or deposited by a lithographic method. Deposition of an Ag grid by diffusion transfer reversal has been reported. Screen printed silver grids [4] were demonstrated in a roll-to-roll processed OLED device.

One of our major deposition technique 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. The main challenge of using inkjet technology is the deposition of homogenous layers of active materials onto flexible substrates. In this paper we demonstrate the fabrication of flexible OPV device with the substitution of the ITO electrode by a combination of an inkjet printed high conductive PEDOT:PSS and inkjet printed photo-active layers. For these purposes we designed OPV devices on foils with a moisture barrier. Our fabrication method can potentially be scaled up high volume Roll-2-Roll production.

Device fabrication procedures

OPV were fabricated on 6" by 6" flexible foil substrates, as shown in Figure 1, 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

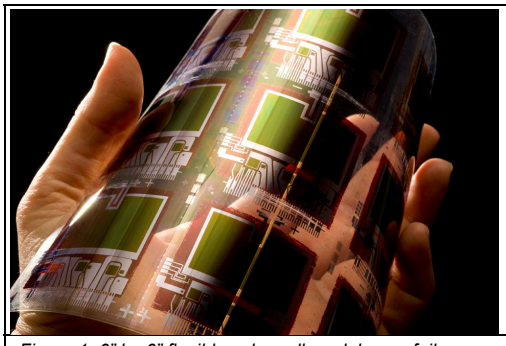


Figure 1: 6" by 6" flexible solar cell modules on foil.

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 OPV, as sketched in Figure 2.

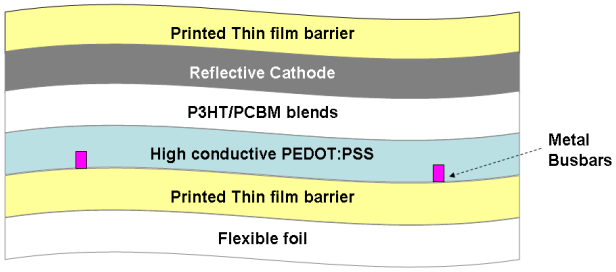


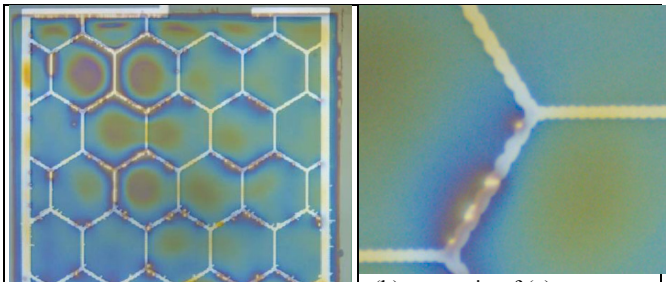
Figure 2: Schematic of a (ITO-free) OPV module on foil.

The samples were prepared in ambient atmosphere, excluding deposition of the cathode, which was evaporated under vacuum. Flexible devices were made on PEN substrates with a thin film barrier produced with Holst Centre technology. Cabot AG-IJ-G-100-S1 silver nano particle ink has been used for the inkjet printing of the conductive grids. Immediately after printing the substrates are placed in a temperature controlled oven for 30 minutes at 135°C. The resulting current collecting grid lines are visually inspected with a microscope, followed by measuring the sheet resistance (Keithley 2400 Source Meter) and cross section area (Veeco Dektak Profilometer) of the lines on 5 different places of the grid. For the inkjet experiments a FujiFilm Dimatix Materials Printer (DMP 2831) with 10 pl drop size print heads is used. The drop spacing was set to 30 µm, while the chuck temperature was fixed at 20°C. Using inkjet printing, the silver grids are covered with high conductive OrgaconTM PEDOT:PSS from Agfa-Gevaert.

The bulk heterojunction solar cells have been produced using a[C60]P3HT:PCBM solution with non-chlorinated solvents. P3HT was purchased from both Merck and Plextronics, Plexcore OS 2100 and [C60]PCBM (99%) from Solenne BV. The mixing ratio was 1:1 by weight. The solution contained 2 wt % of polymer. Both PEDOT:PSS and OPV layers were applied with layer thickness of 100 and 200 nm respectively. The metal cathode (1 nm LiF, 100 nm Al) was thermally evaporated in a vacuum chamber through a shadow mask. The finished OPV devices were encapsulated with stainless steel lids using Huntsman Araldite® 2014-1 sealer as well as using the Holst Centre thin film encapsulation technology. Current–voltage curves were measured using simulated AM 1,5 global solar irradiation (100 mW/cm2), using a WXS-300S-50 solar simulator (WACOM Electric Co.) The active area of the devices was 4 cm2. Schematic representation of the ITO based and ITO-free devices used in this study are shown on Figure 1. Life time tests were done by measuring the performance of the devices over time. The life time conditions for the samples were the following: dark at room temperature, dark at 45°C and illuminated using a G2 light engine combined with a S-bulb (Solaronix), at 1 sun, at 45°C.

Inkjet printed PEDOT layer

Shunt lines/grid were introduced to increase the conductivity in the absence of ITO, see Figure 3 (a). However, sometimes when high conductive PEDOT:PSS were deposited on top of the metal grid, a lot of pin-holes occurred and the Ag grids are not fully covered with PEDOT:PSS, as shown in Figure 3 (b). These pin-holes lead to direct contact with anode and cathode, significantly reduce the device efficiency and life time.



(a) (b): zoom-in of (a)

Figure 3. Photography of inkjet printed PEDOT:PSS on top of Ag grid.

For a high efficiency OPV, the layer homogeneity of the active layer demands a high standard smoothness. Fundamental understanding of the wetting behavior of PEDOT:PSS on the heterogeneous substrate is demanded in order to yield a more homogeneous layer [5-6]. Experiments were designed and performed in order to study the spreading and wetting behavior of PEDOT on the printed silver shunt lines to distinguish between the effect of topology versus chemical heterogeneity (and differences in surface energy). We deposit PEDOT with patterns on Ag and Silicon Nitride (SiN) substrate.

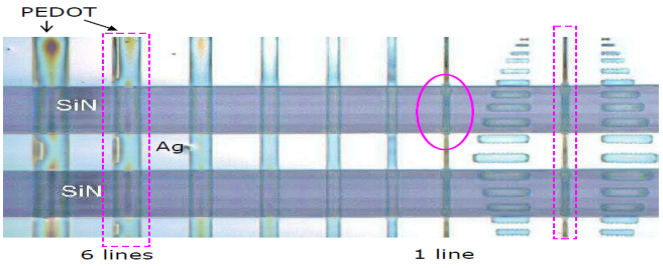


Figure 4: inkjet printed PEDOT:PSS (HILHC5 IJ) on heterogeneous substrate.

Figure 4 shows the effect of PEDOT wetting over an array of silver lines (white area in the picture) on SiN (grey area in the picture). It shows that a difference occurs in wetting due to the nature of surface energy variations. This lines become significantly broader on the better wetting SiN and near the interface a very broad patch of PEDOT can be observed. This implies that PEDOT ink is depleted from the surface of the silver and the layer thickness on silver will be less near the transition to SiN.

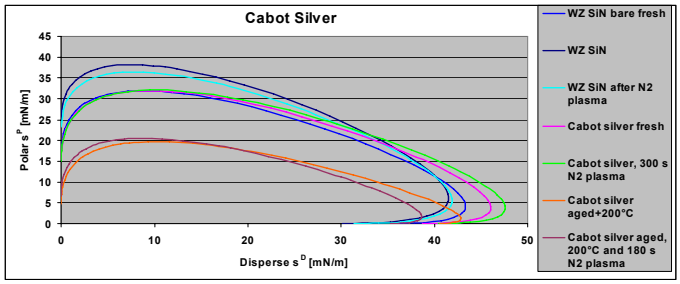


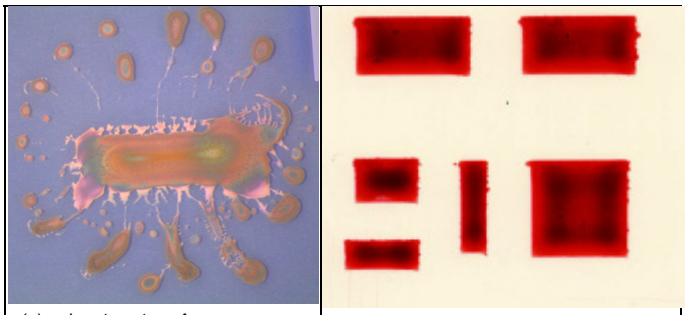
Figure 5: Measured surface energy of WZ SiN and Cabot silver ink.

Figure 5 shows wetting envelopes of the substrate: silicon nitride and metal 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 4. 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. For inkjet printing a finite but low contact angle is desirable. The difference in surface energy between the ink and the substrate is the determining factor with respect to spreading of PEDOT on top of the silver and SiN. As a first order estimate one can compare the PEDOT ink to water. For water the disperse part is approximately 22 mN/m and the polar part is about 51 mN/m. With plasma pre-treatment, the wetting envelope can be brought closer to the surface energy of water and thus wetting is improved. The difference in the line width is mainly caused by the difference in the polar part of the surface energy between silver and SiN, as the wetting envelop shown in Figure 5. 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. By adding certain percentage of surfactant, the surface tension of the PEDOT:PSS can be reduced and be suitable for this purpose[6].

Inkjet printed OPV layer

The bulk heterojunction solar cells have been produced using a[C60]P3HT:PCBM solution with non-chlorinated solvents. P3HT was provided from both Merck and Plextronics. The photoactive layer (PAL) consists of a P3HT/PCBM donor-acceptor blend is deposited on top of the PEDOT:PSS layer and covered with LiF/Al as a reflective cathode. A typical dried PAL thickness is about 200 nm.

The challenge of inkjet formulation of photoactive layers (based on P3HT:[C60]PCBM blend) lies on the ink jettability and solubility. Particles precipitate from the solution and these aggregate in time and eventually block the inkjet nozzles. Observed is that an ink of PCBM/P3HT (Merck) shows sufficient stability for 24 hours. This time span is sufficient for the small scale process on a Dimatix DMP2831 printer, but it is insufficient to scale up towards large volume production, which demands high robustness and reliability.



(a) solvent system A *(b) solvent system B*

Figure 6: inkjet printed Photo-Active Layer with various solvents systems.

Using the Dimatix DMP2831 printer, we vary the solvent system in order to study the layer formation. By selecting the proper solvents system, the PAL layer formation can be influenced, as shown in Figure 6. Using of non-chlorinated solvent system B, we are able to deposit PAL with no pin-holes. The solvent system B shows reasonable stable droplet formation and reproducible results with respect to layer formation with an area of 30 mm x30 mm, see Figure 6 (b).

OPV devices were fabricated with P3HT polymer from Plextronics with non-chlorinated solvent systems and deposited with inkjet printing on a substrate with inkjet printed PEDOT:PSS. The deposited PAL with 100 nm in thickness.

Figure 7 shows the OPV devices fabricated with P3HT polymer from Plextronics. Solvent systems and deposition techniques (SC vs. IJ OPV blend) were varied, in order to distinguish the device efficiency. The current density-voltage (JV) characteristics of the OPV devices were measured using a simulated AM 1.5 global solar irradiation (100 mW/cm2).

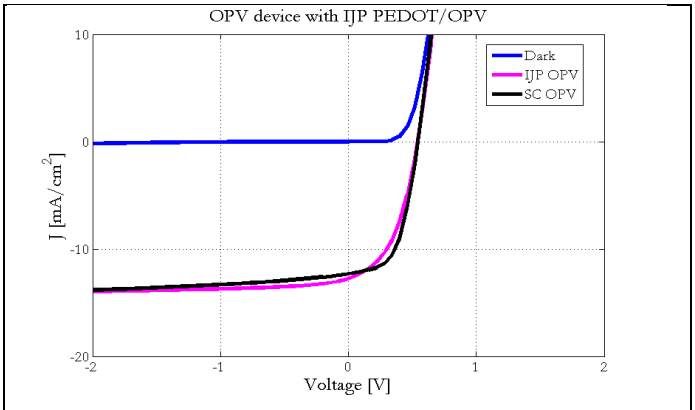


Figure 7. Device performance of OPV devices with benchmark of spin-coated and inkjet printed PEDOT:PSS and inkjet printed PAL layers.

For Plextronics P3HT polymer, it can be seen, in Figure 7, that the OPV devices with inkjet PAL (inkjet printed OPV indicated as red line in Figure 7) show efficiency of MPP=3.2%, although the

device with spin coated PAL has a slightly higher MPP=3.6% (black line).

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 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 demonstrated the ability of using inkjet printing for the fabrication of 3cm solar cell modules, with inkjet printed Agfa high conductive PEDOT:PSS Orgacon™ and photoactive layers (based on P3HT Merck:[C60]PCBM blend) dissolved in solution on a flexible substrate.

A non-chlorinated solvent was used for the deposition of the photoactive blend. Both the PEDOT:PSS and photoactive layer were deposited by inkjet printing. The properties of the inks, as well as substrate pretreatments have been optimized in order to ensure a robust printing and drying process.

Moreover, OPV device with inkjet printed PEDOT:PSS and PAL shows a comparable performance with respect to the spin coated one. The inkjet processed flexible solar cell module illustrated a power conversion efficiency of 3.2% under AM 1.5 conditions.

Acknowledgement

Holst Centre is an open innovation research centre founded by TNO and IMEC that is developing roll-to-roll production techniques for foil-based organic electronics and wireless autonomous transducer solutions, in cooperation with industry and universities. This research has been funded by the Dutch Ministry of Economic Affairs, Philips Research, Merck KGaA and Agfa-Gevaert. The authors would like to thank Harrie Gorter, Julia Galagan, Nadia Grossiord for their helps in preparing and measuring of devices.

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