

Spray-coating deposition for large area organic thin-film devices

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ABSTRACT

We report the implementation and testing of an airbrush coating system for the fabrication of a variety of organic electronic and optoelectronic devices using a commercially available airbrush unit. Our setup was implemented inside a glove box in order to allow the entire fabrication process of the test devices to be performed under nitrogen atmosphere. Several devices such as organic photodetectors, organic light-emitting diodes and organic thin-film transistors were fabricated using commercially available polymers (such as MEH-PPV, P3HT and PCBM). IV-characteristics, as well as film morphology and roughness of spray coated devices were compared to those of spin coated devices with similar architecture. Although films deposited by spray coating showed a considerably higher surface roughness, the corresponding devices are capable of achieving performances comparable to those of spin coated devices.

Keywords: spray-coating, organic photovoltaics, organic light emitting diodes, organic photodetectors, organic thin-film transistors.

1 INTRODUCTION

Organic electronic devices based on solution-processable polymers are among the most promising applications of organic semiconductors. Low-cost fabrication by means of simple coating and printing techniques is surely one of their greatest advantages. Although several possible deposition techniques are mentioned in literature [1, 2], spin-coating seems to be the method of choice in many research activities presented so far. Despite the simplicity and effectiveness of this technique in producing high quality thin films, it lacks several aspects necessary for large-scale production. One very promising, yet little examined, alternative deposition technique is spray-coating, which would offer much a higher suitability and flexibility with respect to large-area industrial-scale application processes [3, 4].

Other advantages of spray-coating as an alternative deposition technique for organic thin-film devices are an easier thickness control over wider ranges, the capability of deposition on non-flat surfaces and lower material losses during deposition, which are of great value for industrial-scale and lab-scale applications likewise. On the other hand, some of the significant disadvantages of this technique are the lower overall layer homogeneity and the extremely high surface roughness when compared to spin-coated layers. Nevertheless, it can be shown, that these

issues do not have a significant effect on device performance. Previously, a special spray deposition method called evaporative spray deposition was specially designed in order to obtain smooth polymer layers [5]. This method however involved a vacuum process, which makes it less practical for the implementation in large area deposition systems. In this article we demonstrate the suitability of spray-coating for different classes of organic thin-film devices while comparing them with spin-coated devices of similar architecture.

2 EXPERIMENTAL DETAILS

For the deposition of the organic layers by spray-coating, a commercially available airbrush unit (Gabbert Triplex) was used. All ink-containing parts of the airbrush are resistant to organic solvents, such as toluene, and are therefore suitable for the desired application. Our test setup was implemented inside a glove box in order to ensure well controlled environmental conditions throughout the entire fabrication process. Figure 1 shows a schematic drawing of the airbrush coating system, indicating the atomizing gas and material inlets as well as the vertical arrangement of airbrush unit and substrate.

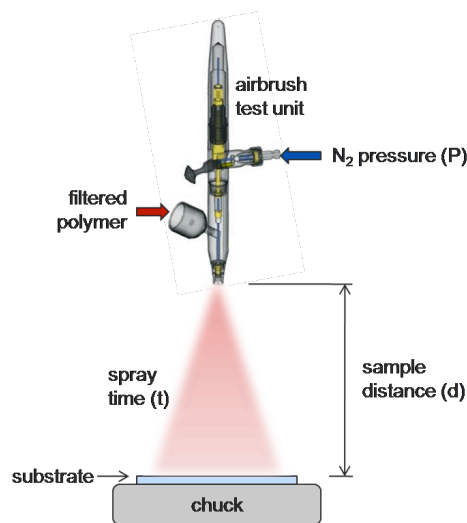


Figure 1: Illustration of the implemented airbrush coating system. All experiments were carried out inside a glove box under nitrogen atmosphere.

The most important process parameters were found to be atomizing gas (N_2) pressure, nozzle-to-sample distance and spray time. Atomizing gas pressure directly affects the beam profile and the mean drop size. In all our experiments

this pressure was fixed to 2 bar, which allowed us to achieve a suitable beam profile. Depending on the solution to be deposited, i.e. polymer and solvent type, the nozzle-to-sample distance can only be varied in a certain range. One can distinguish between three regimes: wet, intermediate and dry [3]. In the wet regime, the nozzle-to-sample distance is low resulting in the formation of a wet polymer layer on top of the substrate, hence producing inhomogeneous layers with no real thickness control. On the other hand, in the dry regime, when the nozzle-to-sample distance is high, the entire solvent evaporates before reaching the sample and a polymer powder is formed. The intermediate regime is the one suitable for the deposition of organic thin films. In this regime, homogeneous layers can be formed and the thickness can be precisely controlled by adjusting the spray time. The general device architectures for the organic optoelectronic devices and the thin-film transistors fabricated are illustrated in Figure 2.

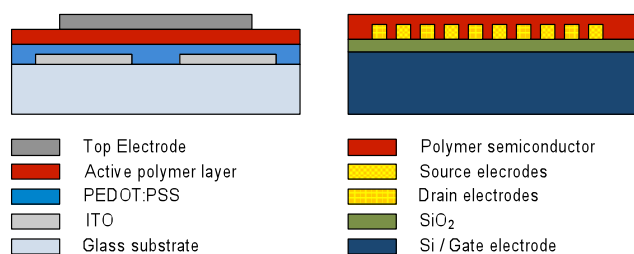


Figure 2: Schematic drawing showing a general layout of the fabricated OPD/OLED (left) and OTFT (right).

2.1 Organic Photodetectors

For the fabrication of the organic photodetectors ITO electrodes with the desired structure were formed on glass by conventional photolithography. The structured ITO-glass substrates were then cleaned by sonication in acetone and isopropanol in sequence. PEDOT:PSS aqueous dispersion (CLEVIOS™ P VP CH 8000) was deposited by spin coating and then dried on a hot plate. The active layer of the device consisted of a blend of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) as donor and acceptor materials, respectively. The P3HT:PCBM (1:1) blend was deposited from a solution of 1wt% concentration in toluene for both, spin-coated as well as spray-coated samples. All samples were then placed again on a hot plate for annealing. Finally, a LiF(1nm)/Al(100nm) cathode was evaporated on top.

2.2 Organic LEDs

Structured ITO-glass substrates were prepared as described in the previous section. The PEDOT:PSS layer (CLEVIOS™ P VP AI 4083) was deposited by spin coating and then dried on a hot plate. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) was

used as the light emitting polymer. The MEH-PPV layer was then deposited from a solution of 0.5wt% concentration in toluene, again using the two different deposition techniques described above. A LiF(0.8nm)/Al(100nm) cathode was evaporated on top.

2.3 Organic TFTs

Organic TFTs were fabricated on highly p-type doped Si wafers, on which an 80nm thick SiO₂ layer was thermally grown. An interdigitated electrode structure consisting of a 2nm thick Ti layer (to promote Au adhesion on Si) followed by a 45nm Au layer was evaporated on top of the SiO₂. The spacing formed between the source and drain contacts of this interdigitated structure was chosen to be 50μm. Regioregular P3HT was used as a semiconductor for the channel of our p-type TFT and was deposited on top of the sample from a solution of 1wt% concentration in toluene. Again, both deposition techniques mentioned before were applied.

3 RESULTS AND DISCUSSION

In this section we will discuss the measurement results obtained for the different device classes. Our main aim is to compare device performance with respect to the applied deposition technique, in order to evaluate the feasibility of spray-coating for the fabrication of different organic thin-film devices.

3.1 Organic Photodetectors

Figure 3 shows a comparison of the IV-characteristics of a spin-coated and spray-coated organic photodetector, each measured once under dark and illuminated conditions. State of the art OPD characteristics with on/off-ratios of more than 4 orders of magnitude at -1V and dark current density levels of around 10⁻⁴ mA/cm² were achieved using both deposition techniques. Note that the processing conditions for spray-coating the P3HT:PCBM layer were only marginally optimized as opposed to the well optimized spin-coating parameters.

When comparing the film quality produced by the two deposition techniques, a much higher surface roughness is observed for spray-coated layers. Nevertheless, microscopic images show pinhole free films over an area of few square centimeters. Examining the film topography by atomic force microscopy confirmed the inferior quality mentioned above at the micrometer scale. At the sub-micrometer scale, however, a surface roughness as low as 4.5nm (rms) could be measured, which is comparable with typical values of spin-coated films. We suggest this to be one of the reasons for comparable device performance despite lower film quality. Figure 4 shows two AFM images of the spray-coated film at the micrometer and sub-micrometer scale.

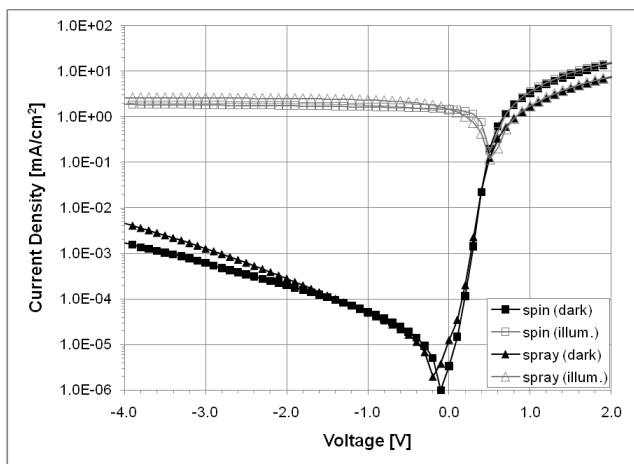


Figure 3: IV-characteristics of a spray coated and a spin coated organic bulk heterojunction photodetector (BHJ OPD) under dark and illumination conditions.

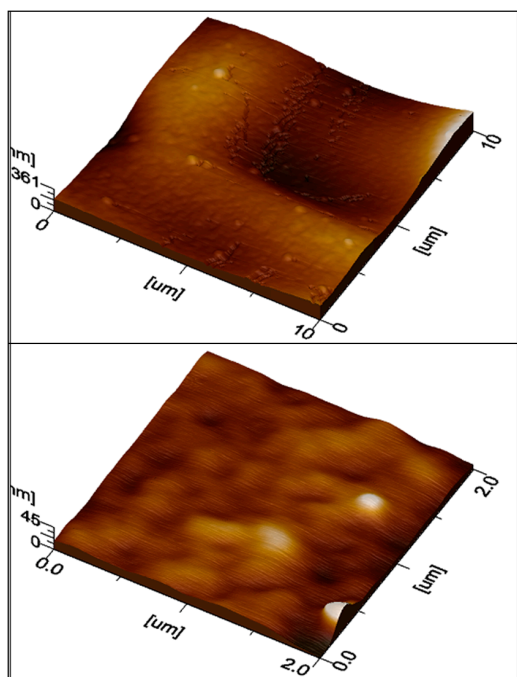


Figure 4: AFM images showing the spray-coated P3HT:PCBM film topography at the micrometer scale (top) and at the sub-micrometer scale (bottom).

3.2 Organic LEDs

In Figure 5 the IV-characteristics and the current efficiencies of a spin-coated and a spray-coated OLED are plotted. Both devices showed an optically uniform illumination distribution over the 5mm² device area. Current levels and efficiencies were comparable. The difference observed in the current densities of the two devices can be attributed to a difference of active layer thickness. As mentioned in the previous section, a very high

surface roughness, which can easily reach 100nm (rms), is obtained when using spray-coating. This makes a direct comparison of the layer thickness not very meaningful. Furthermore, measuring the layer thickness of such rough layers is rather complicated. One way to overcome this problem could be the definition of an effective layer thickness for spray-coated films, which still has to be investigated in the future. A similar approach has already been introduced by another group [3]. The OLED design discussed in this article was not optimized and serves just as a basis for the comparison of both deposition techniques for OLED fabrication, hence the low efficiencies of both devices.

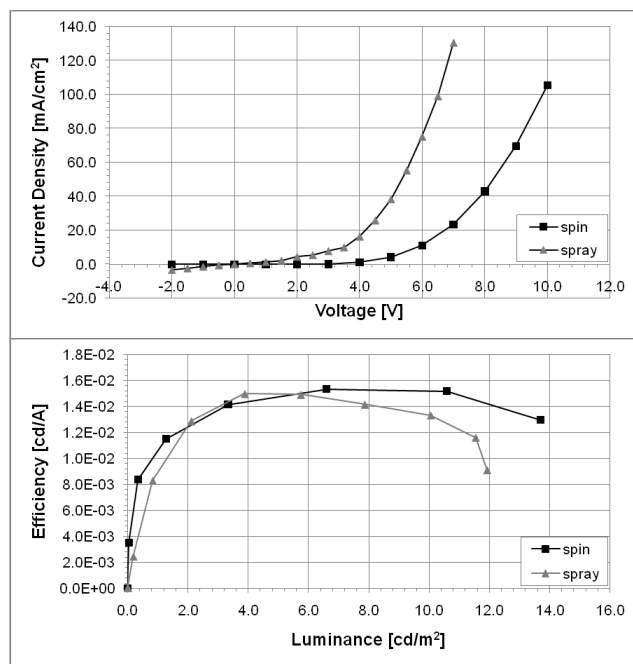


Figure 5: IV-characteristics of a spray coated and a spin coated MEH-PPV OLED (top) and their corresponding current efficiency plots (bottom).

3.3 Organic TFTs

The measured output characteristics ($I_D V_{DS}$) of the two fabricated devices are shown in Figure 6 along with the corresponding transfer characteristics ($I_D V_{GS}$). Upon examination of these plots, one can clearly observe a transistor-like behavior with saturating drain current for both devices. It is however obvious that the drain current of the spray-coated OTFT is lower than the spin-coated one by almost one order of magnitude. This is also reflected in the calculated mobility of both devices, being approx. $1.0e^{-3}$ cm²/Vs for the spin-coated device and $2.4e^{-4}$ cm²/Vs for the spray-coated one. The lower mobility is not surprising if the process of layer formation is taken into account. As described before, a large portion of the solvent in the solution is evaporated on its way to the substrate. If the nozzle-to-sample distance is high, but still within the

intermediate regime, the droplets arriving at the sample will dry faster thereby forming coarse grains. This introduces higher impedance for charge carrier movement along the channel. By decreasing the nozzle-to-sample distance, the drying time of the droplets could be increased thereby introducing more time for reorganization. This issue is still to be examined in future work.

different classes of organic thin-film devices exhibiting performances comparable to their spin-coated counterparts as for the OPDs/OLEDs and inferior performance in case of the OTFTs. The results presented here should be regarded as preliminary results promoting spray-coating as a promising alternative for the large-area deposition of organic thin-films. For further investigation of the important process parameters and the development of an optimization framework for the different organic electronic and optoelectronic devices, the reproducibility of the fabrication process has to be assured. Therefore, an automated spray-coating system featuring good control of the different process parameters is to be constructed.

REFERENCES

- [1] Stephen R. Forrest, "The path to ubiquitous and low-cost organic electronic appliances on plastic," *Nature*, Vol. 428, 911, 2004.
- [2] M. Fahlman and W.R. Salaneck, "Surfaces and interfaces in polymer-based electronics," *Surface Science* 500, 904–922, 2002.
- [3] Doojin Vak, Seok-Soon Kim, Jang Jo, Seung-Hwan Oh, Seok-In Na, Juhwan Kim, and Dong-Yu Kim, "Fabrication of organic bulk heterojunction solar cells by a spray deposition method for low-cost power generation," *Appl. Phys. Lett.* 91, 081102, 2007.
- [4] R. Green, A. Morfa, A. J. Ferguson, N. Kopidakis, G. Rumbles, and S. E. Shaheen, "Performance of bulk heterojunction photovoltaic devices prepared by airbrush spray deposition," *Appl. Phys. Lett.* 92, 033301, 2008.
- [5] Takamasa Ishikawa, Makiko Nakamura, Katsuhiko Fujita, and Tetsuo Tsutsui, "Preparation of organic bulk heterojunction photovoltaic cells by evaporative spray deposition from ultradilute solution," *Appl. Phys. Lett.* 84, 2424, 2004.

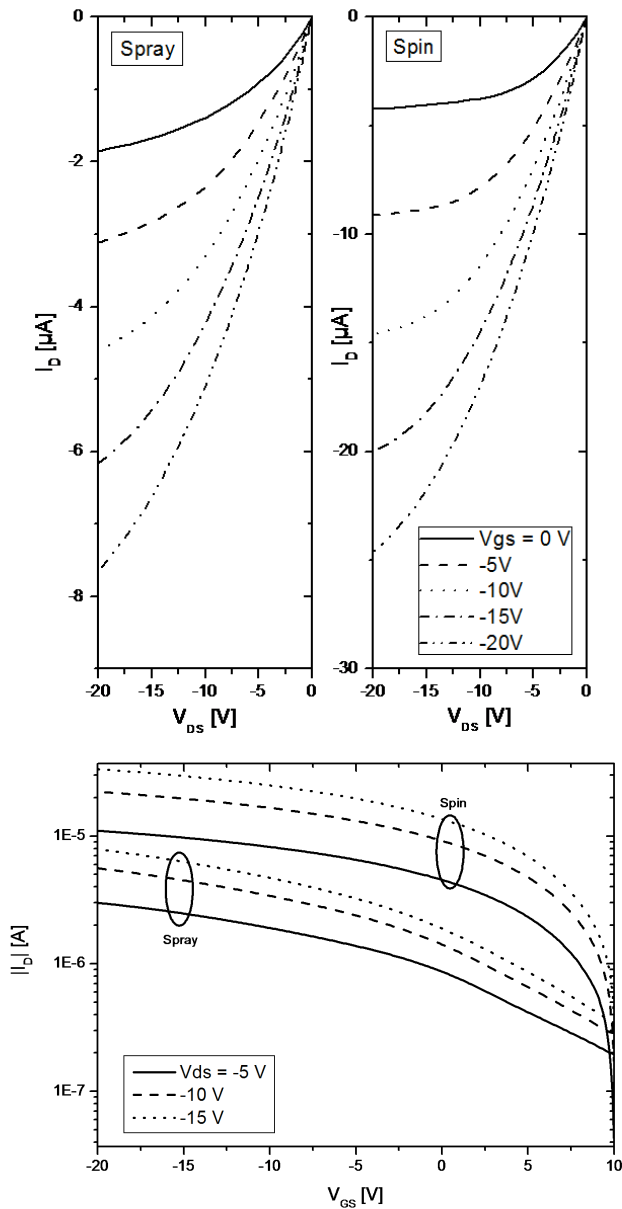


Figure 6: Output characteristics ($I_D V_{DS}$) of a spin-coated and spray-coated device (top) and the corresponding transfer characteristics (bottom).

4 CONCLUSION

In conclusion, we implemented a simple and low-cost spray-coating test setup using a manually operated airbrush unit. Using this setup we could successfully fabricate