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Spray deposition of Polyethylenimine thin films for the fabrication of fully-sprayed organic photodiodes

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ABSTRACT

In the last years, a big effort has been put into the investigation of the scalability of deposition processes for organic optoelectronics to achieve large-scale and cost-effective fabrication of functional devices. One of the most prominent techniques that promises to obtain an easy-to-scale production is spray-deposition; however, so far, the feasibility of entirely spray-deposited optoelectronic devices has not yet been demonstrated. To fulfill this goal, in this work we investigate the spray-coating of Polyethylenimine (PEI) and the effect of the process parameters on the film characteristics, in terms of thickness, work-function and roughness. The achievement of thin layers of PEI (~10 nm) with full coverage is the last step towards the realization of lithography-free and vacuum-free organic electronic devices. For the first time, we show the fabrication of fully-sprayed organic photodiodes (OPDs), initially on patterned Indium-Tin Oxide, and subsequently on bare glass. The resulting photodiodes yield peak EQE above 65% and dark currents lower than 10–4 mA/cm^2 at a reverse bias of −4 V. Moreover, both the cathode and anode electrode of the OPDs fabricated with the described process-flow are semi-transparent, granting the simultaneous collection of two different light signals from the top and the bottom side.

1. Introduction

The recent interest in organic photosensitive devices is fully motivated by their extraordinary features, including the high tunability of their sensible spectrum [1–5], the facile deposition on flexible substrates [6–9] and the possibility of employing low-cost, large-scale fabrication techniques [10–12]. These peculiar aspects render the organic optoelectronic devices suitable candidates for substituting inorganic electronic parts in conventional systems, or even allowing the realization of novel concepts in highly innovative fields such as robotics and bioelectronics.

In order to take the biggest advantage from these appealing new technologies, a big effort has been put into the optimization of the material deposition techniques to achieve low material wastes and high-throughput fabrication. Among the many and well known fabrication techniques, spray-coating has recently been demonstrated effective for the fabrication of a wide spectrum of different devices. This technique is characterized by a high versatility in the choice of the usable materials, accurate thickness control [10], and the possibility of lithography-free patterning with means of shadow masking through a stencil. A short and non-exhaustive list certainly includes the spray-deposition of state-of-the-art Thin Film Transistors [10,13,14], OLEDs [15], organic solar cells [16,17], and organic photodiodes [6,18–21]. Nevertheless, all the works reported so far are bound to some process steps that are not scalable, not cost effective or not compatible with plastic substrates handling. In fact, once the spray-processing of the active materials is assessed, the major arising problems are linked to the fabrication of the electrodes. The common structure of an organic photodiode or solar cell implies the presence of two electrodes with different work functions aligned to the HOMO and LUMO of the active materials [5]. Moreover, one of these two electrodes must be transparent to allow the light to pass through and to reach the active area. The realization of transparent high-work-function electrodes, formerly delegated to the brittle and expensive Indium-Tin-Oxide [22], has been replaced by the spray deposition of materials such as CNT networks [6,23], silver nanowires [24] or blends of conductive polymers [6]. However, a cathode contact, typically realized with LiF/Al or Ca/Ag evaporated layers is always needed to complete the devices, leading to a reduced scalability of the process and increased cost and complexity. An interestingly evaporation-free approach was, however, presented by La Notte et al. [16], where the spray-pyrolysis of TiO_2 is exploited, and fully functioning spray-deposited organic solar cells are produced. While the need of vacuum steps is avoided, the need

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of FTO substrates and the high temperatures needed by the spray-pyrolysis (above 300 °C) compensate the cost effectiveness of the spray coating, and exclude the employment of most of the commonly used flexible substrates.

Nevertheless, a possible and particularly promising solution to this issue has been proposed by Zhou and coworkers [25], which investigated the effectiveness of Polyethylenimine (PEI) and Polyethylenimine ethoxylated (PEIE) as universal work function modifier. Due to the induction of a permanent dipole at the interface with a conducting material, the workfunction of the latter is reduced by more than 1 eV, converting typical p-type conductors such as ITO or PEDOT:PSS in n-type conductors. This finding has then been applied in the realization of spin-coated organic solar cells [25,26], TFTs [25] and OLEDs [27]. Moreover, a remarkable work by Azzellino et al. [28] shows how PEIE can be used as a workfunction stabilizer into silver-based ink-jet printed organic photodiodes. In all these reports, however, the PEI and PEIE layers are obtained solely by spin-coating technique, which leads to a process bottle-neck.

In this work, we first demonstrate the feasibility of smooth, reliable and effective spray-coated thin PEI layers that exhibit performances comparable to analogous spin-coated films, and then we apply the gained know-how towards the realization of fully sprayed OPDs. In a first stage, the feasibility of fully-spray-coated OPDs onto ITO-coated glasses is shown, and then OPDs are realized onto a substrate of bare glass throughout the successive spray-deposition of all the active materials, leading to the first ITO-free, fully-sprayed OPDs realized entirely with low temperature and vacuum-free processes.

2. Materials and methods

The blend for the active layer has been obtained dissolving solid-phase regioregular poly(3-hexylthiophene-2,5-diyl) (Rieke Metals Inc.) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) (Solenne B.V.) in o-DCB (Sigma–Aldrich) with a 1:1 wt% ratio and stirred overnight (>12 h) at 60 °C. The PEDOT:PSS (CLEVIOS P VP CH 8000) solution was sprayed in a dilution of 1:3 in isopropyl alcohol (Sigma–Aldrich). The highly conductive PEDOT:PSS utilized for the top electrodes was a mixture of PEDOT:PSS (CLEVIOS PH 1000). The electrodes have been patterned throughout a shadow-masking technique, which was proved accurate in a previous work for the definition of the desired active area of 9 mm^2. Finally, the Polyethylenimine solutions for spin coating and spray coating were obtained dissolving in ethanol 0.4 and 0.1 wt%, respectively. Where the sheet resistance was measured, it was done using a custom-made four-points probe and a Keithley 4200 semiconductor parameter analyzer. The topography, average thickness and uniformity of all the spray-coated layers (PEDOT:PSS, highly conductive PEDOT:PSS, PEI and P3HT:PCBM) were evaluated with means of AFM imaging (JEOL JSPM-5200), mechanical profilometer (Veeco Dektak 150) and white light interferometry (Veeco NT9080). For the WLI measurements, a thin layer of aluminum (15 nm) was evaporated on the deposited material, in order to guarantee the reflection of white light. The work-function was measured with respect to a highly ordered pyrolytic graphite (HOPG) through a Kelvin Probe with a golden reference electrode (KP Technology Ltd., KP020). The EQE of the fabricated devices and the transmittance of the single films were evaluated using a 300 W xenon arc lamp chopped at 210 Hz, passing through an Oriel Cornerstone 260¼ m monochromator and a calibrated photodiode with a transconductance amplifier connected to an Oriel Merlin digital lock-in amplifier. Finally, the IV-characterization of the OPDs were performed by means of a Keithley 2602 sourcemeter, dark current measurements were performed inside a dark chamber, and photocurrent measurements were performed under a sun simulator at AM1.5.

3. Results and discussion

As previously discussed, the first part of the work consisted in the optimization of the spray deposition of the PEI layer. The parameters considered here were the thickness of the fabricated layer, the roughness, and the work-function of the electrodes modified through the spray deposition of PEI. In order to have a benchmark, a spin-coated layer of PEI was first deposited and it was taken as a reference for the successive measurements. The obtained layer on glass had a thickness of 11 nm (as deter) and an RMS roughness of 7 nm and substantially reduced the work-function of several materials, as reported in Table 1, leading to results comparable to the ones previously reported in literature [25].

The optimization of the spray-coated layer, passes through the choice of several parameters, among which the most important ones are nozzle-to-sample distance, heat-plate temperature, atomization pressure, spraying time, choice of the solvent and material concentration [29]. In our case, since ethanol is a solvent with a particularly low boiling point (78 °C), and after atomization easily evaporates even at ambient temperature, the heat-plate was set to the minimum stable point guaranteed by the setup, which was 40 °C. The nozzle-to-sample distance and the atomization pressure were set to the maximum distance that was still guaranteeing the formation of wet droplets on the substrate (15 cm and 1.5 bar, respectively). Since the choice of most of the parameters was forced by the spray set-up and the choice of the solvent, the residual degrees of freedom are the spraying time and the material concentration only. Hence, several spray coated layers were fabricated on ITO-covered glass with different concentrations of PEI in ethanol (0.4, 0.2, 0.1 and 0.05 wt%) and with different spraying times (5, 10, 15, 20 s).

As shown by Fig. 1, for a fixed concentration, the thickness is linearly increasing with the spraying time. Particularly, the thickness goes from a minimum of 5 nm achieved with 5 s spraying time and a PEI concentration in ethanol of 0.05 wt%, to a maximum of 55 nm achieved with 20 s spraying time and a PEI concentration in ethanol of 0.4 wt%. Some interesting information can be, however, extrapolated combining the AFM images in Fig. 2 and the roughness reported in Fig. 1. The layers obtained with a spraying time of 5 s, besides from the case with 0.4 wt% PEI in ethanol, were characterized by a high roughness, presented several non-homogeneities and a low coverage. Not surprisingly, Fig. 3 shows how these layers led to a relatively small variation of Work Function with respect to the bare ITO (which presents a measured work-function of 4.78 eV). Even if in the last case, namely when the PEI concentration is brought to 0.4 wt%, a spraying time equal to 5 s guarantees a lower work-function, the fabricated layer resulted to present a partial coverage, factor that could lead to faulty final devices. A sub optimal coverage might result into local hot spots where the work function is higher, issue which could reduce or compromise the performances of any kind of stacked device.

Table 1
Work-function measured for the pristine material and the same material modified with a 11 nm thick layer of PEI.

Material	Pristine WF (eV)	WF with spin-coated PEI (eV)
Au	5.05	4.0
Al	4.15	3.6
Ag	4.4	3.9
ITO	4.7	3.9
PEDOT:PSS	4.7	4.05

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