

Poly-(3-hexylthiophene)/[6,6]-phenyl-C61-butyric-acid-methyl-ester bilayer deposition by matrix-assisted pulsed laser evaporation for organic photovoltaic applications

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Thin films of polymers are normally prepared by solvent-based methods, such as spin coating, dip-coating, and drop-casting which are quick and inexpensive, but not effective in finely controlling the homogeneity and tailoring the final thickness. Multilayer structures are hardly realizable also with the ink jet printing technique, another conventionally used method for depositing organic materials.

A modified laser-based approach, which could be more suitable for soft materials than PLD, is that obtained by matrix-assisted pulsed laser evaporation (MAPLE).[1] In fact, in this case, the material of interest is dissolved or suspended in a volatile solvent and then frozen at the liquid nitrogen (LN) temperature, forming the target to be laser irradiated. The laser energy is mainly absorbed by the solvent, which vaporizes, thereby entangling the solute material and promoting its deposition onto the desired substrates. Since the laser energy is principally absorbed by the solvent, lower energy densities (few or few tenths of mJ/cm^2) respect to PLD can be used, and therefore, the laser-solute interaction is minimized. Moreover, the MAPLE technique, as a derivative of the PLD method, represents an interesting alternative for the deposition of single and multilayer structures onto plastic and other thermo-labile substrates, as well as on rough, tri-dimensional and flexible supports at room temperature. These peculiarities make MAPLE an appealing technique in the field of organic photovoltaic (OPV) devices. Few attempts of MAPLE deposited polymeric multilayers have been already reported in the literature.[2–4] Nevertheless, they always consist of two-steps processes, which require breaking the vacuum conditions inside the deposition chamber, result-

ing in the problems of contamination, oxidation, and waste of time. This procedure is due to the high difficulty in having a rotating multitarget system holder working at LN temperature. Here, we report the first single step MAPLE (ss-MAPLE) deposition of a bilayer structure consisting of the most-studied donor-acceptor combination for polymer solar cells, namely, the electron-donating polymer [regioregular polymer poly-(3-hexylthiophene) (P3HT) and the electron-accepting fullerene [6,6]-phenyl-C61-butyric-acid-methylester (PCBM). Furthermore, the same solvent has been used for both polymers, thus overcoming the typical drawback of re-dissolution of the bottom layer occurring in the conventional solution-based deposition techniques. A polymeric solar cell based on the ss-MAPLE deposited P3HT/PCBM heterojunction has been fabricated and characterized. The two polymers, P3HT and PCBM (Sigma Aldrich), were both dissolved in toluene with the weight concentration of 0.3 wt.%. The obtained solutions, after sonication, were poured in a double-section target holder, suitably fabricated to allow the switch of the laser-irradiation between the two frozen solutions under the same vacuum deposition conditions. The target holder was a copper cup consisting of two concentric cylindrical sections, separated each other, thus allowing both solutions to be frozen simultaneously at the liquid nitrogen temperature (77 K) without intermixing. The composite target, containing the two frozen solutions, was placed inside the vacuum chamber, on a refrigerated target holder (77 K), which was evacuated down to 5×10^{-4} Pa by a combined system of rotary and turbomolecular pumps. The target was rotated at the frequency of 3 Hz to allow uniform erosion, and its temperature was monitored

during the deposition and kept constant (77 K). The substrate holder, placed in front of the target at the distance of 45 mm, was heated at 60 °C and translated during the process in order to improve the thickness uniformity of the layers. MAPLE depositions of each material were performed using a pulsed Lambda Physik (LPX-305i) KrF excimer laser ($\lambda=248$ nm, $t=20$ ns, pulse rate=10 Hz). The laser beam was focused (rectangular spot of 0.075 cm 2) and attenuated to obtain the fluence value of 250 mJ/cm 2 . Before starting the MAPLE deposition, 500 pulses were used to remove the surface layer of frozen water vapor formed on the target surface of the two polymer solutions. It is important to stress that the surface of the second polymer was cleaned after the deposition of the first one in order to remove also eventual contamination by the first solution evaporation. All these procedures were performed while screening the substrate with a shutter. To deposit P3HT and PCBM layers, 6000 and 4000 laser pulses were applied obtaining a corresponding final thickness of 68 nm and 25 nm, respectively. These numbers of pulses were used to deposit both single polymer and bilayer structures, on silica slabs and $< 100 >$ Si substrates. UV-Vis absorption spectra were acquired for the single polymer layers and for the bilayer structure, deposited on silica slabs, using a Perkin Elmer spectrophotometer in the wavelength range 350-750 nm with a resolution of 2 nm. Atomic force microscopy (AFM), scanning electron microscopy (SEM), and energy dispersive x-ray spectrometry (EDS) were used to characterize the morphological and compositional properties of the deposited samples. In particular, SEM and EDS analyses were performed by using a NVISION 40 Focussed Ion Beam (FIB) system equipped with a high resolution SEM-Field Emission Gun (FEG) Gemini column and an Inca Energy 350 X-ACT Oxford EDS spectrometer. Morphological and chemical investigations were carried out both in plan view and cross-sectional geometry. AFM measurements were performed in non contact mode (Park XE 70 instrument). Finally, a bilayer solar cell was fabricated. A poly(3,4- ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) layer was spin-coated onto an ITO/glass substrate. Then, the active layer was fabricated by depositing the bilayer structure onto the PEDOT:PSS layer with 8000 laser pulses for P3HT layer (90 nm) and 4000 for PCBM layer (25 nm). To complete the device structure, LiF (0.6 nm-thick) and Al (ca. 100 nm-thick) were thermally evaporated at low pressure ($< 1 \times 10^{-6}$ Torr). The active area of the devices was 0.03 cm 2 . Current density versus voltage (J-V) characteristics were measured using a Keithley 2400 sourcemeter both in dark and

under AM 1.5-G illumination, filtered irradiation with an incident power of 100 mW/cm 2). All of the measurements were carried out under ambient conditions.

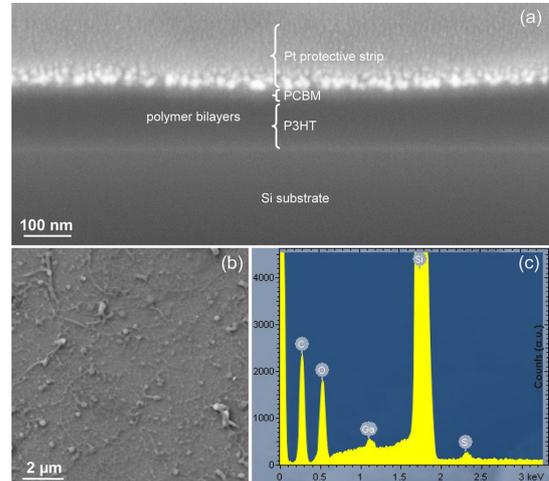


Figure 1. Color online) Cross-section (a), top view (b), and EDS spectrum (c) of the P3HT/PCBM bilayer with a 68 nm thick layer of P3HT and a 25 nm thick layer of PCBM.

Cross-sectional and top view images of the deposited bilayer are reported in Figs. 1(a) and 1(b), respectively. The cross section was prepared in-situ by ion milling: a protective Pt strip was electron-deposited on the surface of the sample, then a rectangular dig was milled and the section carefully polished in order to enhance the visibility of the layers. The polymer bilayer can be observed in the image, with the first layer having a thickness of about 120 nm and the topmost layer with a thickness of about 25 nm. The typical surface morphology of the bilayer is shown in Fig. 1(b). EDS spectra were acquired from the bilayer structure. A typical EDS spectrum is reported in Fig. 1(c); the spectrum was recorded in the spot mode configuration, i.e., by keeping the electron beam in a fixed position inside the polymer bilayer. A series of peaks related to the bilayer composition are visible, i.e., C, S, and O, together with element peaks related to the substrate composition and cross-section preparation, i.e., Si, Ga. The rms roughness values for P3HT and PCBM single layers as well as for P3HT/PCBM bilayer are of about 17 nm, 19 nm, and 50 nm, respectively, as obtained by AFM measurements on a scanned area of 5 micron x 5 micron. As it will be underlined below, these values can be lowered by a suitable choice of the polymer concentration. UV absorption spectra of the single layers of P3HT and PCBM and of the bilayer

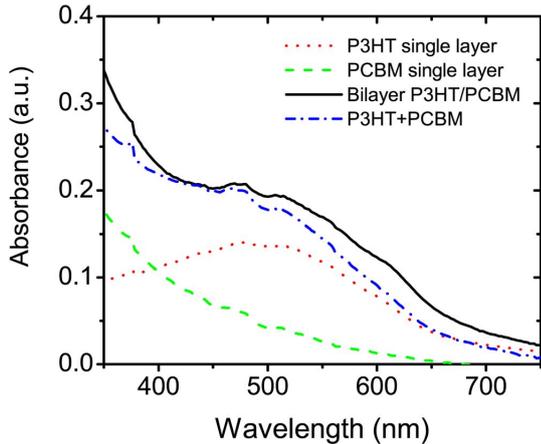


Figure 2. (Color online) UV-visible absorption spectra of the P3HT single layer (dotted line), PCBM single layer (dashed line), and P3HT/PCBM bilayer (full line). The arithmetical sum of the absorption spectra of the two single layer polymers is reported too (dot-dashed line).

P3HT/PCBM, are reported in Fig. 2.

The characteristic absorption features of each polymer, [5] namely, the absorption bands at 450 nm and 500 nm for PCBM and the broad absorption band between 500 nm and 600 nm for P3HT are well reproduced in the experimental spectra. The arithmetical sum of the single layer spectra, labeled as P3HT/PCBM, well reproduces the behavior of the experimental spectrum of the bilayer structure, indicating that both polymeric structures resulted well reproduced and separated in the P3HT/PCBM sample, thus excluding intermixing or damaging phenomena related to the bilayer deposition. As a preliminary application, we tested the ss-MAPLE bilayer production in fabricating a solar cell geometry based on the configuration ITO/PEDOT:PSS/P3HT(90 nm)/PCBM(25 nm)/LiF/Al. The PEDOT:PSS was deposited by spin-coating according to the standard procedure for the preparation of conventional solar cells. The layered structure of the device is sketched in Fig. 3.

After light absorption and exciton formation, charge separation occurs at the interface between the donor, P3HT, and the acceptor, PCBM. Fig. 3 shows the current density-voltage curves (dark and illuminated) of the fabricated bilayer. The open circuit voltage is $V_{oc}=0.32$, the short circuit current is $J_{sc}=0.33$ mA/cm², the fill factor is $FF=28\%$, and $PCE=0.03\%$. Our ss-MAPLE deposition procedure also rules out the contamination consequences related to the MAPLE deposition experiments of organic bilayers, already reported in the literature. In fact, our experimental expedient (double-section target, as discussed

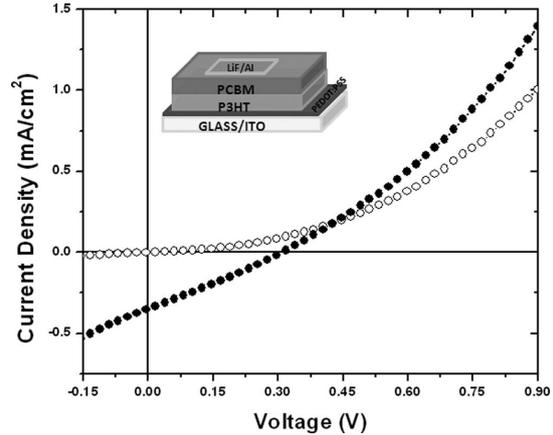


Figure 3. Current-voltage characteristics of the bilayer photovoltaic device in dark (open circles) and under one-sun illumination (AM 1.5 G; filled circles). Inset image: Sketch of the bilayer device structure fabricated by ss-MAPLE technique.

in the experimental details) allows one to deposit a bilayer structure (1) under controllable vacuum condition, (2) avoiding contamination and oxidation problems, (3) in a single step, by switching the laser-beam over the desired frozen solution, and (4) using the same solvent for both polymers. The idea underlying our choice of the ss-MAPLE technique was the fact that a well-designed MAPLE deposition should in principle let overall solvent vaporization. In this respect, the kinematics of solvent evaporation by solute-solvent clusters are currently active area of theoretical studies. At the moment, the MAPLE process is quite questionable and not well understood. Two models are proposed for the interaction of the laser beam with the frozen target. In fact, at the birth of the technique, a fully evaporative process was supposed.¹⁸ Recently, molecular dynamic simulation results have questioned this picture looking at the high roughness values and morphology of the deposited films. These simulations have demonstrated that the laser-matter interaction induces the ejections of solvent-solute droplets (clusters) from the target as a consequence of an overheating process. However, the cluster formation can be efficiently reduced/avoided by decreasing the polymer concentration in the target.[6] A suitable choice of the solvent, background pressure, target-to-substrate distance, and substrate temperature should hamper, or at least decrease the arrival of the solvent on the substrate. As an example, a conservative estimation of the time necessary for a 1 μ m diameter droplet of toluene, the most used solvent in MAPLE deposition and used also in this work, to evaporate is of the order of 0.1 mi-

cron .[7] This value, even being an overestimation because the MAPLE process is performed under vacuum conditions, is lower than the typical time of flight for a droplet to reach the substrate, for both the PLD and MAPLE processes.[8] The value of the toluene droplet diameter has derived from the typical dimension of the structures which characterize the MAPLE deposited films. These observations demonstrate that, in principle, the MAPLE deposition technique is able to effectively minimize/ eliminate the solvent contamination of the polymeric films by a suitable optimization of the process parameters. In conclusion, in this paper, we have demonstrated the potentiality of the ss-MAPLE technique in depositing polymer bilayer structures in a single step under vacuum conditions, using the same solvent for the two considered polymers. The polymers used for the bilayer ss-MAPLE deposition were P3HT and PCBM, since they are technologically interesting as electron-donor and electron-accepting materials, respectively, for the realization of organic solar cells. A prototype of the organic device, the first realized using this deposition technique, was presented. Our approach could represent a general and effective technique for the fabrication of more complex and efficient multilayer polymer device geometries. Optimization of the deposition parameters is in progress to control the film morphology, roughness values, and device performances.

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