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Annealing effect on donor-acceptor interface and its impact on the performance of organic photovoltaic devices based on PSiF-DBT copolymer and C₆₀

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In this work, poly[2,7-(9,9-bis(2-ethylhexyl)-dibenzosilole)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PSiF-DBT) was used as active layer in bilayer solar cell with C₆₀ as electron acceptor. As cast devices already show reasonable power conversion efficiency (PCE) that increases to 4% upon annealing at 100 °C. Space charge limited measurements of the hole mobility (μ) in PSiF-DBT give $\mu \sim 1.0 \times 10^{-4} \text{ cm}^2/(\text{V s})$ which does not depend on the temperature of the annealing treatment. Moreover, positron annihilation spectroscopy experiments revealed that PSiF-DBT films are well stacked even without the thermal treatment. The variations in the transport of holes upon annealing are then small. As a consequence, the PCE rise was mainly induced by the increase of the polymer surface roughness that leads to a more effective interface for exciton dissociation at the PSiF-DBT/fullerene heterojunction. © 2015 AIP Publishing LLC.

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Since the first reports on polymer based solar cells,¹ a great number of research have been devoted to understand the conversion of light into electrical current in those devices. In addition, efforts have been made to increase the power conversion efficiency (PCE) and stability of such solar cells. Some milestones in those advances are the discovery of the ultrafast electron transfer between conjugated polymers and fullerene derivatives,² improvement in transport properties by using regioregular poly-3-hexyl-thiophene (P3HT)^{3,4} and post-production thermal annealing that increased the PCE from 2%⁵ to 3.5%.⁶ This PCE improvement was mainly attributed to the increasing of the π - π stacking and crystallinity upon annealing which favored a higher hole mobility.⁷⁻⁹ However, the PCE of P3HT-based devices is limited to 5%⁷ due to the polymer poor absorbance profile of the solar spectrum and its high energy of the highest occupied molecular orbital (HOMO), close to 5.1 eV. The position of the HOMO limits the open circuit voltage (V_{oc}) of P3HT-based devices to values around 0.6 V.

To improve the PCE, donor-acceptor copolymers were synthesized with different functional groups, which decrease the value of the HOMO and the band gap (see Ref. 10 and references therein). The donor-acceptor approach is based on the combination of an electron-rich donor moiety and an electron-deficient acceptor moiety along the chain, giving rise to an internal charge transfer (ICT). ICT leads to a more delocalized electron density, making the conjugated backbone more planar which promotes a better π -stacking. This effect favors the charge transport while the reduction of the band gap improves the absorption of the solar spectrum.¹⁰ Similar to homopolymers, this class of copolymers can also be sensible to thermal annealing due to the possibility of

different chain conformations. For instance, we previously reported an impressive improvement in the hole mobility (from $\sim 3 \times 10^{-11} \text{ cm}^2/(\text{V s})$ to $\sim 2 \times 10^{-5} \text{ cm}^2/(\text{V s})$) of a fluorene-bithiophene based copolymer after thermal annealing at 200 °C.¹¹

Studies about the effect of silole group on molecular orbital shapes, energies, or the interaction between the polymeric chains¹² were reported. Specifically, the poly[2,7-(9,9-bis(2-ethylhexyl)-dibenzosilole)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PSiF-DBT, see Figure 1(b) inset) has been used as active layer in hybrid,^{14,15} inverted, or bulk heterojunction solar cells (BHJ) with fullerene derivatives.^{12,17} The PSiF-DBT copolymer has good thermal stability and high degree of π -electron delocalization, leading to high FET mobility of the charge carriers around $1 \times 10^{-3} \text{ cm}^2/(\text{V s})$.¹³ Wang and coworkers reported the synthesis and BHJ devices of PSiF-DBT;^{13,17} promising values for PCE of 5.40%, short circuit current (J_{sc}) of 9.50 mA/cm², open circuit voltage (V_{oc}) of 0.90 V, and fill factor (FF) of 50.70% were presented. Inverted devices having ZnO as electron extraction layer displayed PCE of 3.80%, J_{sc} of 5.03 mA/cm², V_{oc} of 0.90 V, and FF of 60%.¹⁶

Here, we report the effect of thermal annealing in the performance of photovoltaic devices using PSiF-DBT as active layer and C₆₀ as electron acceptor. Our devices were fabricated as bilayer structures. However, the diffusion of the fullerene into the polymeric film might create an intermixed donor/acceptor region between the PSiF and the C₆₀ layers that mimic a BHJ structure. Those PSiF-DBT/C₆₀ solar cells have shown then a PCE greater than 4.00% after thermal annealing of the polymeric thin film.

We address this result by using electrical measurement and complementary experimental tools in order to relate thermally induced structural variations of the PSiF-DBT layer to the corresponding variations in the photovoltaic response of the devices. In special, we applied positron annihilation spectroscopy (PAS)^{19,20} to probe the amount of free space inside the polymeric thin film. The use of this technique is motivated by the fact that a number of electrical properties of the polymeric film are directly influenced by the presence of defects like open volume structures.¹⁸ PAS can achieve depth-profiles from tens of nanometers up to several mm in thickness so that it can directly detect buried, isolated pores with size of 0.3–50 nm, which are not accessible to conventional probes. The results obtained using different electrical measurements are then compared with PAS experiments of PSiF-DBT films. Using this approach, we found that the increase of the device performance upon annealing is mainly due to improved properties of the donor/acceptor interface after the thermal treatment.

Organic solar cells were investigated using PSiF-DBT (Lumtec[®]) with number average molecular weight (M_n) $>10\,000\text{ g mol}^{-1}$. The devices were fabricated by the deposition of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films (Sigma-Aldrich) and annealed at 100°C for 15 min onto pre-cleaned patterned indium tin oxide (ITO) coated glass substrates. The polymer film was spin coated under a nitrogen atmosphere from 1.5 mg ml^{-1} o-dichlorobenzene solution giving film thickness of $23 \pm 4\text{ nm}$. Three different samples were prepared: as cast, annealed at 100°C and 200°C . Thermal annealing was performed in vacuum by 15 min. Then, 30 nm of C_{60} and 100 nm of aluminum were thermally evaporated under vacuum, at pressure of $5 \times 10^{-6}\text{ mbar}$ through a shadow mask. The final device structure is then ITO/PEDOT:PSS/PSiF-DBT/ C_{60} /Al. All devices received an additional post-annealing treatment for 5 min, in vacuum at 70°C . Hole only (HO) devices were built by using PSiF-DBT solutions with 6 mg ml^{-1} in order to have a thicker film ($32 \pm 2\text{ nm}$) and molybdenum oxide (MoO_3) as electron blocking layer. Thickness measurements were performed with a Dektak 150 profilometer (Veeco Instruments). Film topography was acquired by using an atomic force microscope (AFM, Shimadzu SPM-9700) operating in dynamic mode. Photovoltaic characterization was

performed with a Keithley picoammeter with power supply, model 6487 and a monochromator/spectrometer (1/4 m Oriel). The solar simulation was made using air mass (AM1.5) filter with a power illumination of 100 mW/cm^2 from a 150 W Oriel Xenon lamp. UV-Vis spectrum was collected directly from the film deposited on quartz substrate with a Shimadzu UV-2450 spectrophotometer, using quartz/air as the reference, in the range of 190–800 nm.

The positron experiments were performed employing a variable-energy positron beam where the positron implantation energy can be tuned in the range of 0.5–25 keV. The Doppler broadening of the positron-electron annihilation radiation was measured with a high-purity Ge detector with an energy resolution of 1.4 keV (full width at half maximum) at 511 keV. The Doppler broadened 511 keV annihilation line was analyzed with the help of S and W parameters that represent positron annihilations with low and high momentum electrons, respectively. The integration windows for the parameters were set as $p_L < 0.4\text{ a.u.}$ for the S parameter (p_L is electron momentum along the measurement direction) and $1.6 < p_L < 4.0\text{ a.u.}$ for the W parameter. Generally, an increase in S (and decrease in W) is indicative of increased open volume in the sample. Further details about the technique can be found in Refs. 18, 20, and 21.

Device having as cast PSiF-DBT film as active layer showed a relative high J_{sc} of 5.55 mA/cm^2 , which is close to values previously reported for devices in the same bilayer architecture.^{11,22} After thermal annealing, J_{sc} increased by 90%, reaching a value comparable to those observed in the most efficient devices. Figure 1 shows the J - V photovoltaic characteristics of the device under AM1.5 illumination. For the as cast devices, a J_{sc} of 5.55 mA/cm^2 , a V_{oc} of 0.78 V, and 47% of FF were obtained, resulting in a PCE of 2.03%. After annealing at 100°C , the J_{sc} increases to 10.64 mA/cm^2 , with a small change in V_{oc} (0.79 V) and in FF (47%), which raised the PCE to 4%. Devices with PSiF submitted to annealing at 200°C showed a J_{sc} of 10.83 mA/cm^2 and a R_s of $14.16\ \Omega\text{ cm}^2$, values comparable to those obtained for devices annealed at 100°C . However, R_{sh} decreased to $165.81\ \Omega\text{ cm}^2$, resulting in a lower FF (45%). Along with the V_{oc} loss, this effect reduces the PCE to 3.38%. Table SI²⁵ summarizes the photovoltaic results. The J_{sc} corresponding to the device with PCE of 4% was checked by calculating a value of

FIG. 1. (a) J - V characteristics for ITO/PEDOT:PSS/PSiF-DBT/ C_{60} /Al devices, under AM1.5 illumination (100 mW/cm^2), obtained from as cast devices, and annealed devices at 100°C and 200°C . (b) J - V characteristics in dark for FTO/PEDOT:PSS/PSiF-DBT/ MoO_3 /Al devices, obtained from as cast devices, annealed devices at 100°C and 200°C . The continuous red line shows the fitting of the Mott-Gurney law. The black lines are guides to the eye to estimate the trap-filling voltage (V_{TFL}). The inset highlights the J - V curve in the range where $V \sim V_{oc}$.

15.49 mA/cm² for the AM1.5G J_{sc} that follows from the integration of the external quantum efficiency (EQE) showed in the inset of Figure 1(a) (for more details see Fig. S12²⁵).

Insights about the underlying reasons behind the variations in photovoltaic parameters are obtained by measuring the hole transport properties of the PSiF-DBT film with and without the thermal treatments. Figure 1(b) shows J - V characteristics in dark for HO devices in the following structure: FTO/PEDOT:PSS/PSiF-DBT/MoO₃/Al following the same protocol used in the previous works^{22,23} that avoids the influence of the series resistance from the substrate.²⁴ FTO is fluorine doped tin oxide. As cast devices show non-linear J - V curves which tends to follow a $J \propto V^2$ dependence at high voltages. This is an indication of space charge limited current (SCLC) behaviour. Those curves also show a sharp variation of J with V at intermediate voltages probably due to a trap-filling (TF) transition.²⁶ The thermal annealing at 100 °C drastically reduces the trap density so that the TF regime is not apparent in the J - V curve of these samples. There is then a direct transition from an ohmic behaviour at low voltages to the SCLC regime at high V . This result agrees with angular dependent Near Edge X-Ray Absorption Fine Structure (NEXAFS) measurements that showed an improvement in film ordering after thermal annealing.²⁷ Using the Mott-Gurney law ($J = 9\epsilon\epsilon_0\mu V^2/8L^3$) to fit the SCLC regime (where ϵ is the permittivity of the polymer, ϵ_0 is the permittivity of vacuum, μ is the effective mobility of holes, V is the applied voltage, and L is the film thickness), we found $\mu \sim 1.0 \times 10^{-4}$ cm²/(V s) for holes in the PSiF-DBT layer. This result does not change significantly when one considers the built-in voltage of the HO devices as showed in Fig. S3.²⁵

It is also clear in Figure 1(b) that the HO device annealed at 200 °C achieves the SCLC regime at slightly higher voltages compared to the HO device annealed at 100 °C. However, both J - V curves coincide at high V (see inset in Figure 1(b)). Since all tested devices have approximately the same thickness, this result indicates that the different temperatures of the annealing treatment did not significantly change the value of μ in the SCLC regime.

We stress that only the polymeric film is submitted to thermal annealing in our bilayer devices. Equally important is the fact that the hole-only devices in Figure 1(b) are around 10 nm thicker than the bilayer devices showed in Figure 1(a). As a consequence, the average magnitude of the electric field in HO devices when $V \sim V_{oc}$ is slightly small to the magnitude of the field in bilayer devices under open circuit conditions. The inset of Figure 1(b) highlights the J - V

curves of the HO devices for applied voltages close to V_{oc} . In this voltage range, the polymeric films treated at 100 °C and 200 °C have the same electrical conductivity (σ). On the other hand, the as cast film has a σ that is only one order of magnitude lower compared to the annealed samples. This result differs from the electrical properties measured in as cast samples of others copolymers,^{11,22} where the density and the energetic depth of the traps produce a trap-limited SCLC regime in the J - V curve at low voltages. For those materials, the trap-filling regime occurs at higher electric fields so that the hole transport of photovoltaic devices under open circuit conditions is trap-limited. In this situation, the decrease of the trap's concentration by the annealing of the polymer induces a dramatic increase of the hole mobility (with a corresponding variation in σ). This effect explains the rise of J_{sc} that results in a seven fold improvement of power conversion efficiency upon annealing.¹¹ Yet, the behavior of PSiF-DBT-based devices is different because V_{oc} (Fig. 1(a)) $\geq V_{TFL}$ (Fig. 1(b)) in those samples, where V_{TFL} is the applied voltage that characterizes the beginning of the trap-filling regime in hole-only devices.²⁶ Hence, a considerable fraction of the traps are already filled in the as cast PSiF-DBT layer under open circuit conditions which reduces the enhancement of μ (σ) after annealing.

The lower value of V_{TFL} compared to measurement performed using similar copolymers indicates that the PSiF-DBT films are reasonably well stacked when deposited without annealing. This result is further confirmed when we probe the morphology of these films by PAS. PAS provides important information about the material packing.^{28–30} Changes in the S and W parameters were monitored for the as cast film and the annealed films. Figure 2 shows the evolution of both S and W parameters. These parameters did not change when the films are submitted to temperatures lower or equal to 200 °C, which indicates that the film molecular packing did not change significantly after the thermal treatment.

Returning to the photovoltaic parameters, the as cast device already has J_{sc} and PCE quite comparable with values reported for other bilayer and BHJ devices.^{23,31} Yet, there is a significant increase of J_{sc} and PCE in the devices submitted to the thermal treatment. As discussed above, the better performance of these solar cells cannot be attributed to an improvement in the transport of holes along the polymeric film. This result suggests that thermally induced morphological changes in the surface of these films might be the reason behind the improved performance of the annealed samples.

FIG. 2. Positron annihilation S and W parameters as a function of positron implantation energy for the as cast and the annealed at 100 °C and 200 °C thin films.

FIG. 3. AFM topography images from (a) as cast, (b) 100 °C, and (c) 200 °C PSiF-DBT films and their respective profiles.

AFM measurements were then applied to investigate these variations. Figure 3 shows the topography of PSiF-DBT as cast and annealed films deposited onto ITO/PEDOT:PSS substrates. It is possible to verify that the surface roughness increases after thermal treatments (from 22.34 nm for devices without annealing to 27.90 nm and 29.1 nm for devices annealed at 100 °C and 200 °C, respectively). Thus, higher contact area between donor and acceptor layers is provided after thermal annealing and more excitons can be dissociated at the interface. As result, there is then a corresponding increase of J_{sc} in the devices submitted to the thermal treatment (see Table S1²⁵). The series resistance in these devices also decreases due to the higher σ of the annealed polymeric films.

Despite showing similar hole transport properties in HO devices, the photovoltaic performances of samples annealed at 100 °C and 200 °C are different. Moreover, we found that higher degrees of roughness of the polymeric film induced by those annealing temperatures do not correspond to improved power conversion efficiencies. From the AFM measurements in Figure 3, we found that the roughness of the layer annealed at 200 °C is higher compared to roughness of the sample annealed at 100 °C, but the PCE of the respective solar cell is lower. This happens because there is a V_{oc} loss for the sample annealed at 200 °C. Moreover, the annealing at 200 °C reduces the shunt resistance of the device relative to the value when the thermal treatment is at 100 °C. These two factors contributed to a lower the FF and PCE of the photovoltaic heated at 200 °C.

Probably the higher roughness of the polymer film surface after the annealing at 200 °C induces a more intimate contact between donor and acceptor at the polymer/ C_{60} interface. Although this effect raises the number of excitons that are able to reach the donor/acceptor interface, it may also open new recombination channels across the heterojunction that results in lower values of V_{oc} and R_{sh} . Similar behavior was reported for bilayer devices using a block copolymer as active layer.³¹ Further evidences to support this hypothesis are found in the dark J - V curves of the photovoltaic devices (see supplementary material for dark J - V curves²⁵). These curves show that the dark saturation current (J_0) is lower for

the devices annealed at 100 °C compared to the device annealed at 200 °C. From the principle of detailed balance, lower values of J_0 correspond to higher values of V_{oc} .^{32–34} In addition, smaller dark saturation currents are also related to lower recombination rates across the heterojunction which tends to enhance R_{sh} when the device is under illumination.

In conclusion, we report PCE of 4% for organic photovoltaic devices using PSiF-DBT copolymer as active layer submitted to thermal annealing at 100 °C. Yet, we found that even PSiF-DBT-based devices without annealing already exhibit a PCE of 2%. This is due to the fact that the as cast PSiF-DBT film had a well stacked morphology after deposition which decreases the concentration of defects that can behave as charge carrier traps. As a consequence, thermal annealing at 100 °C and 200 °C did not significantly improve in the hole transport of PSiF-DBT films. On the other hand, annealing is very effective to increase the roughness of the polymeric film which enhances the donor/acceptor effective contact area for exciton dissociation. As the C_{60} can diffuse during the sublimation process, the increased roughness also enhances the polymer/fullerene intermixing layer. This effect is responsible for increasing the J_{sc} (and consequently of PCE) after annealing at 100 °C. Nevertheless, the even higher roughness of the polymeric film annealed at 200 °C did not improve the device's performance. This happened because the small increase of J_{sc} observed in those devices was associated to a considerable drop of V_{oc} . The closer proximity between the hole in the acceptor and the electron in the C_{60} tends to increase the probability of the electron-hole recombination at the heterojunction producing a loss of open circuit voltage. This phenomenon is related to higher dark saturation currents measured in photovoltaic devices annealed at 200 °C.

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