

Relation of Polymer Degradation in Air With the Charge Carrier Concentration in PTB1, PTB7, and PCBM Layers Used in High-Efficiency Solar Cells

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Abstract—This paper presents the analysis of degradation in metal–insulator–semiconductor (MIS) and metal–semiconductor–metal (MSM) structures based on the polymers poly[[4,8-bis (octyloxy) benzo [1,2-b:4,5-b'] dithiophene-2,6-diyl] [2-[(dodecyloxy) carbonyl] thieno[3,4-b]thiophenediyl]] (PTB1), poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl] thieno[3,4-b] thiophenediyl]] (PTB7), and the fullerene [6,6]-phenyl C₆₁-butyric acid methyl ester under air environment (60 ± 5% relative humidity). Capacitance–voltage (C–V) measurement is used to analyze the degradation process during 240 h and its relationship with the carrier concentration to be correlated with its physical mechanisms. The degradation on MIS structures was more stable than that on MSM structures due to the passivation presence by poly(methyl methacrylate) covering the polymer in MIS structures. The analysis on charge carrier concentration permits the identification and evaluation of the intensity of degradation mechanisms over time on devices under air environment, where it is possible to transfer this knowledge to high-efficiency organic solar cells using almost the same materials and structures.

Index Terms—Capacitance–voltage (C–V) method, charge carrier concentration, degradation effects, metal–insulator–semiconductor (MIS) and metal–semiconductor–metal (MSM) structures.

I. INTRODUCTION

IN organic solar cells (OSCs), the use of blends of polymers with fullerenes to fabricate bulk heterojunction (BHJ) active layers has resulted one of the best approaches to improve their characteristics [1]. However, in spite of the advances achieved, the reliability of OSCs is not yet enough for their commercial applications, for which it has been estimated that power conversion efficiency (PCE) above 7% and a minimum of five-year

lifetime are required in solar panels [2]. Important advances in PCE have been achieved using low-bandgap donor materials as poly[[4,8-bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] [2-[(dodecyloxy) carbonyl] thieno [3,4-b] thiophenediyl]] (PTB1) and poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl] thieno[3,4-b] thiophenediyl]] (PTB7) in blend with [6,6]-phenyl C₆₁ butyric acid methyl ester, PCBM, or PC₇₀BM [3]–[5]. Regarding the studies on the lifetime and degradation of OSCs, most of them have been focused on OSCs with P3HT as the polymer [6], [7].

Recently, we have presented a study of the degradation of solar cell electrical parameters observed in high-efficiency OSCs, fabricated with blends of PTB1:PCBM as active layers under different environments [8], where it was determined that the degradation of the efficiency of the solar cells was mainly observed as a reduction of short-circuit current density (J_{SC}) and fill factor, while open-circuit voltage (V_{OC}) was the most stable parameter in all studied conditions.

To further investigate if the degradation of these parameters is related to the variation of the carrier concentration in the components of the active layer, which will vary the conductivity of the layer, in this paper, we use the capacitance–voltage (C–V) method.

BHJ-OSCs consist of interpenetrated p-type and n-type semiconductor regions. The form of the regions, as well as their separation, is determined during the phase segregation but can vary significantly from one to another [9].

The presence of heterojunctions allows the use of the C–V method to determine several properties of the semiconductor and the structure used in the measurements; however, the fact that these heterojunctions are distributed inside the volume of the active layer makes difficult the interpretation of the C–V curves obtained. The C–V curves can be measured in metal–semiconductor–metal (MSM) structures where only one semiconductor layer is studied. However, the C–V curves obtained from metal–insulator–semiconductor (MIS) structures provide easier and more complete information of the semiconductor layer and of other parameters of the MIS structure.

For these reasons, MIS structures containing only one of the active layer constituents were prepared with PTB1 and PTB7 as semiconductor layer, and the Poly (methyl methacrylate) (PMMA) as dielectric. Structure 1 consisted of the layer sequence Au/PTB1/PMMA/Au and structure 2 consisted of Au/PTB7/PMMA/Au. From Table I, showing the energy levels

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TABLE I
ENERGY LEVELS OF EACH POLYMER AND METAL

Material	HOMO [eV]	LUMO [eV]	ϕ [eV]	Ref.
PTB1	-4.90	-3.23	-	10
PTB7	-5.27	-3.64	-	11
PCBM	-6.10	-3.73	-	12
Au	-	-	-5.10	13
ITO	-	-	-4.70	11
PEDOT:PSS	-5.00	-	-	13
Ca	-	-	-2.80	12

HOMO is the highest occupied molecular orbital. LUMO is the lowest unoccupied molecular orbital. ϕ is the work function.

of the different materials analyzed [10]–[13], it is expected that structure 1 can form an ohmic contact between the Au and the PTB1, while structure 2 is expected to present a non-ohmic contact between the polymer PTB7 and the metal Au. Other MSM structures consisting of the layer sequence indium tin oxide (ITO)/PEDOT:PSS/PCBM/Ca/Ag as structure 3 and ITO/PEDOT:PSS/PTB1/Ca/Ag as structure 4 were also analyzed.

II. EXPERIMENTAL DETAILS

MIS structures 1 and 2 were prepared by depositing an Au layer by sputtering, followed by the deposition by spin coating of the respective polymer, after PMMA was deposited also by spin coating. A second Au layer was deposited by sputtering, on which capacitors with three different areas (540, 440, and 340 μm per side) were patterned by photolithography.

The PTB1 and PTB7 materials were purchased from One-material Company with $M_w \sim 22.90 \text{ kg} \cdot \text{mol}^{-1}$ and $M_w \sim 128.00 \text{ kg} \cdot \text{mol}^{-1}$, respectively. The PTB1 layer was deposited at 1000 r/min for 45 s from a solution of 15 mg/ml in ortho-dichlorobenzene, stirring at 1200 r/min for 24 h at 40 °C. Annealing was done at 120 °C for 20 min. The layer thickness was 14 nm.

The PTB7 layer was deposited by spin coating at 800 r/min for 30 s followed for 3 s at 1500 r/min, from a solution of 10 mg/ml in ortho-dichlorobenzene, which was mixed at 1200 r/min for 24 h at 40 °C. The deposited layer was annealed at 120 °C for 20 min. The layer thickness was 15 nm.

The PMMA layer was deposited at 7000 r/min for 45 s from a 6% solution of PMMA in anisole and annealed at 90 °C for 20 min, obtaining a thickness of 370 nm.

The MSM structures 3 and 4 were fabricated on precleaned ITO-coated glass substrates (15 Ω/square) with 120 nm of thickness, on top of which the PEDOT:PSS FHC from Ossila Ltd. was spin coated at 3500 r/min for 45 s and annealed at 110 °C for 20 min to get a layer thickness of 30 nm. The fullerene material PCBM ($M_w \sim 910.88 \text{ g} \cdot \text{mol}^{-1}$), from Sigma-Aldrich, was dissolved in 15 mg/ml of o-dichlorobenzene (ODCB) solution and left stirring for 24 h at 40 °C, after which, it was deposited on top of the PEDOT:PSS layer by spin coating at 1000 r/min for 30 s, obtaining 45 nm of thickness. Afterward, 25 nm of Ca and 100 nm of Ag were deposited by thermal evaporation. The polymer for the MSM structure with PTB1 was deposited exactly in the same way as was in the MIS structure 1, only that

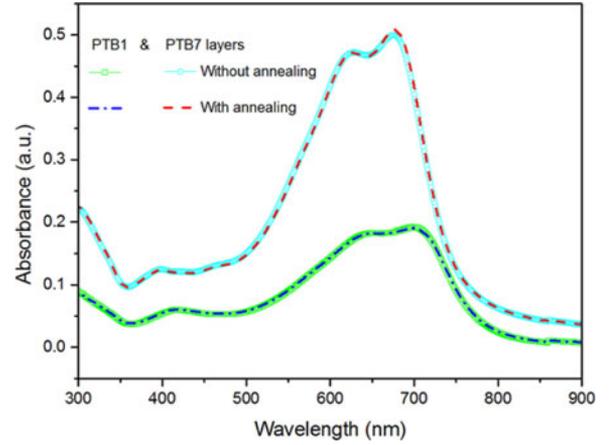


Fig. 1. Absorbance spectrum obtained from PTB1 and PTB7 pristine layers. The annealing for the samples was 120 °C for 20 min. Green square and light blue circles open symbols represent the absorbance spectrum of the layers without annealing for PTB1 and PTB7, respectively. Dark-blue-dashed-dotted and red-dashed lines represent the absorbance spectrum of the layers with annealing for PTB1 and PTB7, respectively.

without the annealing application. The area of the capacitors for MSM structures was 0.09 cm^2 .

PTB1 and PTB7 pristine layers were manufactured and deposited on glass substrates under the same conditions as was described previously for each material. Both polymeric pristine layers were performed with and without annealing in order to determine the absorbance spectrum. The annealing was applied at 120 °C for 20 min.

All process steps for the different structures were done in a glove box under nitrogen atmosphere. Several MIS and MSM structures were prepared on the same substrate to check the reproducibility of the electrical characteristics of devices fabricated at the same time. UV-Vis absorption spectroscopy was done using a Perkin-Elmer Lambda 950 UV/VIS/NIR spectrometer.

The $C-V$ measurements were conducted using an Agilent 4192A impedance analyzer and were recorded at a frequency of 100 kHz and an ac bias of 25 mV. Some measurements were also made at 1 kHz. All measurements were done using the parallel equivalent circuit to obtain the capacitance C_p .

III. RESULTS AND DISCUSSION

Fig. 1 shows the absorbance spectrum from PTB1 and PTB7 of pristine layers with and without annealing. We observed that the properties of the structures did not change.

The value of the polymer carrier concentration in equilibrium was obtained, as usual, from the slope of the $1/C_p^2$ curve, and the modeled $C-V$ curve for p-type materials was calculated using [14]

$$C_p = \left(\frac{1}{C_i} + \frac{1}{C_D} \right)^{-1} \quad (1)$$

where

$$C_i = \frac{\varepsilon_0 \cdot k_i}{X_i} \quad (2)$$

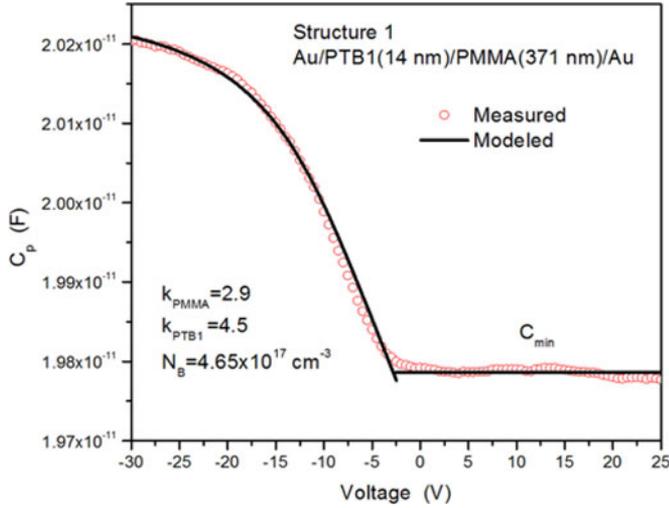


Fig. 2. C - V curves measured and modeled of the MIS structure 1. Obtaining $N_B = 4.65 \times 10^{17} \text{ cm}^{-3}$ for the PTB1. The thickness of PMMA and PTB1 layers was 371 and 14 nm, respectively, measured by ellipsometry.

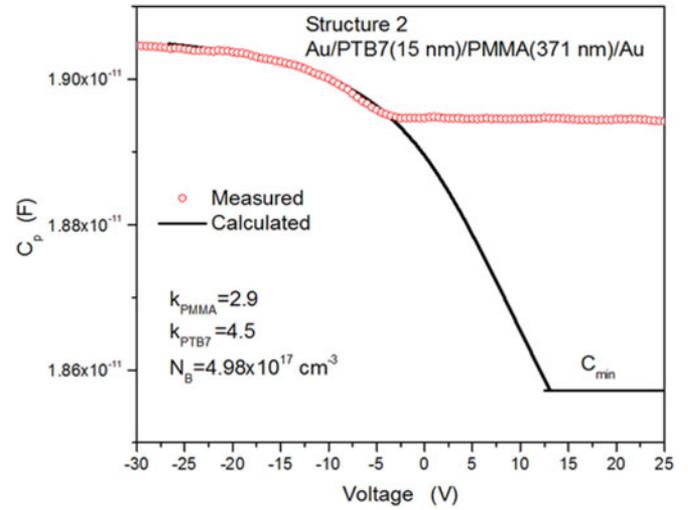


Fig. 3. C - V curves measured and modeled of the structure 2. Obtaining $N_B = 4.98 \times 10^{17} \text{ cm}^{-3}$ for the PTB7. The thickness of PMMA and PTB7 layers was 371 and 15 nm, respectively, measured by ellipsometry.

$$C_D = \frac{\varepsilon_0 \cdot k_s \cdot \left[1 - e^{\beta\psi_s} + \left(\frac{n_{po}}{p_{po}} \right) \cdot (e^{\beta\psi_s} - 1) \right]}{\sqrt{\frac{2\varepsilon_0 \cdot k_s}{q \cdot p_{po} \beta}} \cdot F\left(\beta\psi_s, \frac{n_{po}}{p_{po}}\right)} \quad (3)$$

and

$$F\left(\beta\psi_s, \frac{n_{po}}{p_{po}}\right) = \frac{\sqrt{(e^{-\beta\psi_s} + \beta\psi_s - 1) + \frac{n_{po}}{p_{po}} \cdot (e^{-\beta\psi_s} - \beta\psi_s - 1)}}{\frac{n_{po}}{p_{po}} \cdot (e^{-\beta\psi_s} - \beta\psi_s - 1)}. \quad (4)$$

k_s is the relative dielectric constant of the material, ε_0 is the permittivity of air, q is the elementary electron charge, A is the area of the capacitor, N_B is the doping concentration of the material, $\beta = q/kT$, p_{po} and n_{po} are the hole and electron concentration in equilibrium, ψ_s is the surface potential, and X_i is the thickness of the dielectric layer.

The minimum capacitance due to full depletion of the semiconductor layer is calculated as

$$C_{\min} = \left(\frac{1}{C_i} + \frac{1}{C_{\text{DFD}}} \right)^{-1} \quad (5)$$

where C_{DFD} is the semiconductor capacitance in full depletion equal to

$$C_{\text{DFD}} = \frac{\varepsilon_0 \cdot k_s}{X_s} \quad (6)$$

and X_s is the thickness of the semiconductor layer.

The thickness of each layer was measured by ellipsometry. The relative dielectric constant of PMMA at $f = 100$ kHz was considered 2.9 as reported earlier in [15], and the dielectric constant for PTB1 was considered 4.5.

Figs. 2 and 3 show the C - V curve measured at 100 kHz corresponding to structures 1 and 2, respectively, as well as the C - V curve calculated with the above indicated parameter values. The $p_{po} = N_B$ for PTB1 determined from these curves,

in several structures, repeated very well and was in the range $4.45 \times 10^{17} - 5 \times 10^{17} \text{ cm}^{-3}$.

As can be seen in Fig. 3, the measured C - V curve for PTB7 can be well modeled using a carrier concentration similar as in PTB1. The minimum capacitance, however, is bigger than expected, because of the non-ohmic contact formed between the gold and the polymer (see Table I). The interface between PMMA and PTB1 gave interface density of traps in the order of $7 \times 10^{11} \text{ cm}^{-2}$, while for PTB7, it was in the order of $2 \times 10^{11} \text{ cm}^{-2}$.

The MIS structure with PCBM was difficult to analyze due to the even bigger Schottky barrier between gold and the PCBM with LUMO of 3.73 eV (see Table I). For this reason, PCBM layers were analyzed using an MSM defined as structure 3 described above. In this case, the carrier concentration n_{no} was obtained from [16]

$$(1/C_p)^2 = \left(\frac{2 \cdot V}{q \cdot k_s \varepsilon_0 \cdot n_{no}} \right) \cdot A^2. \quad (7)$$

The C - V curve shown in Fig. 4 gave $n_{no} = N_B = 6.6 \times 10^{17} \text{ cm}^{-3}$; however, the measurement voltage range selected from 0 to -1 V, which corresponds to the normal solar cell operating voltage range, allows the capacitance to vary very little, and n_{no} cannot be determined with enough precision, obtaining values between 6×10^{17} and $2 \times 10^{18} \text{ cm}^{-3}$ in the different samples measured.

Since the characterization of the layers was observed and obtained with more precision and repeatability in MIS structures, we used devices with structure 1 to study the possible relation of the degradation of the OSCs with the degradation in the polymer due to changes in its conductivity or other material or structure parameter. These devices were left in ambient conditions under air environment ($60 \pm 5\%$ relative humidity) and measured for more than two weeks in air, which was more than the time in which PTB1:PCBM OSCs left in air stopped working.

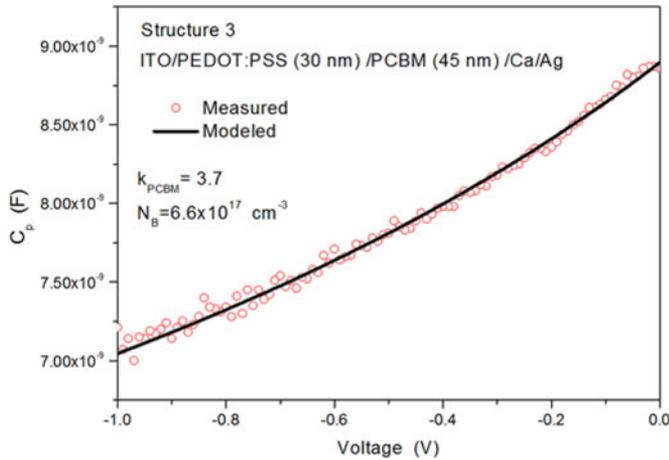


Fig. 4. Measured and modeled C - V curve for the structure 3. Obtaining $N_B = 6.6 \times 10^{17} \text{ cm}^{-3}$ for the PCBM. Voltage was applied to the Ag contact with respect to the ITO.

Fig. 5(a) shows the C - V curves for structure 1 measured as produced and after six and ten days under air environment conditions. Results show practically no variation in the slope of the measured C - V curves in the region of variation of the capacitance, suggesting that p_{po} did not change significantly. Fig. 5(b) shows the C - V curves normalized to C_{p-max} at -30 V. As you can see, the variation of the slope after ten days in air showed a slight increase in the value of C_{min} . The increment of conductivity in polymers left in ambient conditions has been attributed to the oxidation of the polymer molecules in the presence of water or O_2 [17].

Polymeric pristine layers were manufactured to verify the degradation and oxidation of PTB1 and PTB7 materials. The pristine layers were left under air environment for 168 h (seven days). Fig. 6 shows the extent of degradation by the reduction of the absorption peak of PTB1 and PTB7 polymers, and this is indicative of the loss of chromophores resulting from broken conjugation and chain scission reported as degradation mechanisms due to oxidation of the polymers. These results are in good agreement with previous results [18], [19] of similar studies done by other polymeric materials.

The effect seems to be reversible, and several authors have reported the possibility of returning to the initial state after vacuum treatment of the samples [20], [21]. However, in OSCs, reversibility of the degraded samples has not been reported, indicating that other effects are predominant. From another point of view, it has also been reported that PMMA works as an excellent passivation layer when deposited on top of polymers for PTFTs, allowing them to work for long periods of time, usually several months or even years, without any other passivation process [22]. In devices from structure 1, it seems that the presence of the PMMA layer on top of the polymer protected it from significant oxidation during the length of the experiment, and only a small change in p_{po} was observed.

Fig. 7(a) shows the C - V curves for structure 4 fabricated with PTB1 and the configuration MSM. The values of p_{po} obtained for several PTB1 samples fall in the range between 5×10^{17} and

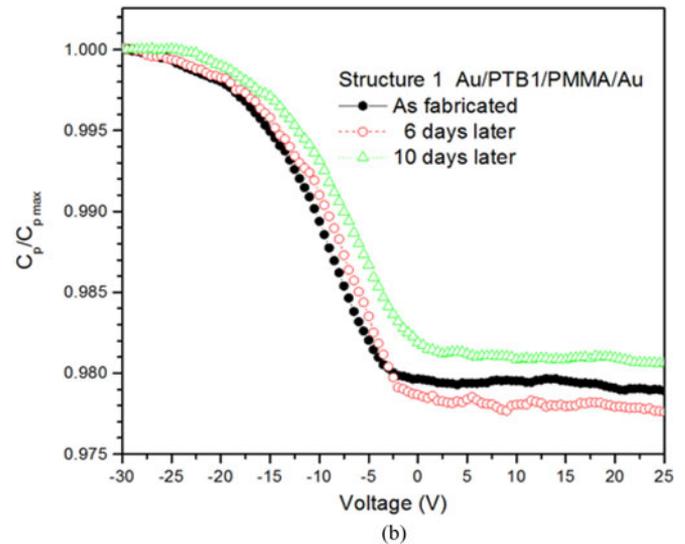
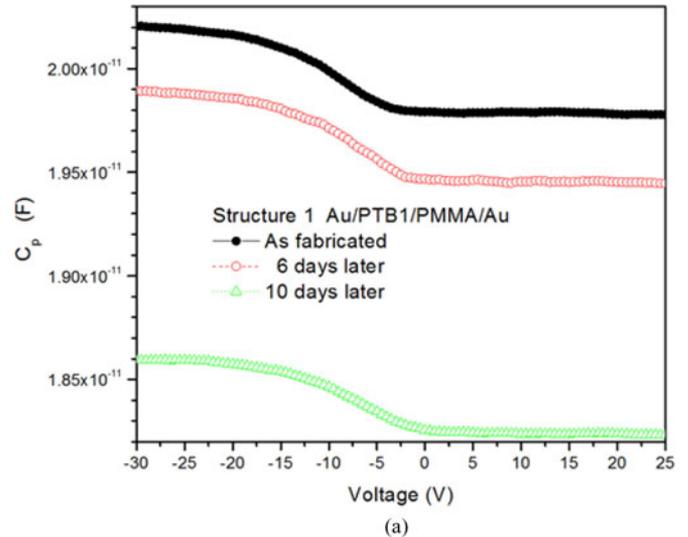


Fig. 5. C - V curves for the device corresponding to structure 1, as fabricated, six days later and ten days later. (a) As measured. (b) Normalized to C_{p-max} (-30 V).

$1.8 \times 10^{18} \text{ cm}^{-3}$. As can be seen, the C - V curve changed completely after three days exposed to air environment. Fig. 7(b) shows the C - V curves normalized to C_{p-max} at 0 V. The maximum capacitance decreases and became practically not dependent on bias. The reduction of the ratio C_{p-max}/C_{min} can be explained by two phenomena: an increment of the carrier concentration in the polymer, resulting in an increment of its conductivity, and the increment of the series resistance of the metallic contact and the contact resistance with the polymer.

In structures 1 and 4 (see Figs. 5 and 7), it was observed that the maximum value of the capacitance decreased with time of exposure in air, while the ratio C_{p-max}/C_{min} slightly decreased in structure 1 and very significantly decreased in structure 4. It was also seen that for structure 4, the reduction of the capacitance with time of exposition to ambient conditions is more severe, reducing after three days, more than for structure 1 after ten days. For both structures, the reduction of capacitance was

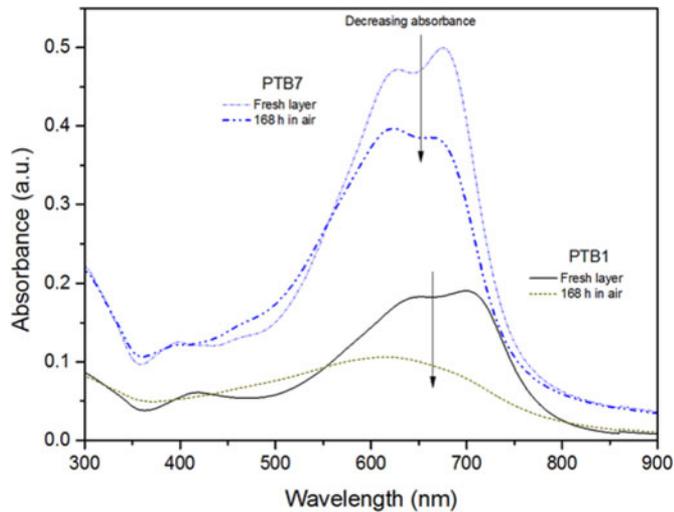


Fig. 6. Absorbance spectrum obtained from PTB1 and PTB7 pristine layers under degradation by air environment during 168 h (seven days).

predominant due to the increment of resistance associated with the contact. This is also consistent with the different behavior observed for structures with contacts of different materials [23]. After 15 days, none of these structures measured anymore, as if the back electrode no longer provided good contact to the polymer.

In addition in a previous work [8], we have observed the same degradation tendency for structure 4 under the same environmental conditions. We have seen that the increment of the polymer conductivity during the first 72 h is more severe and produces the rapid reduction in the shunt resistance, whereas the series resistance at the beginning increases slowly and after of 80 h increases rapidly.

IV. CONCLUSION

The charge carrier density in equilibrium for donor layers of polymers (PTB1 and PTB7) and fullerene PCBM was determined from MIS and MSM structures using the C - V method, obtaining values in the order of 4.4×10^{17} - $5 \times 10^{17} \text{ cm}^{-3}$ and $6.6 \times 10^{17} \text{ cm}^{-3}$, respectively. The measured C - V curve in MIS structures with PTB1 can be well modeled using the obtained value of carrier density and measured values of film thickness and capacitor area. In the case of the PTB7 layers, the presence of a non-ohmic contact at the Au-polymer interface increases the value of the minimum capacitance expected for structures with this material. MIS and MSM structures were also used to analyze variations in the C - V curves with time of exposure to ambient conditions, concluding that both the $C_{p-\max}$ and the ratio $C_{p-\max}/C_{\min}$ are reduced with time of exposure for MIS and MSM structures, but more intensity was in MSM regarding the MIS structure. The reason was the passivation presence of PMMA layer covering the polymer in the MIS structures. In the presence of PMMA, the variation of the conductivity in the polymer is relatively small, and the increase in the ratio of $C_{p-\max}/C_{\min}$ can be attributed to an increase of series resistance, which, since there is little change in the conductivity of

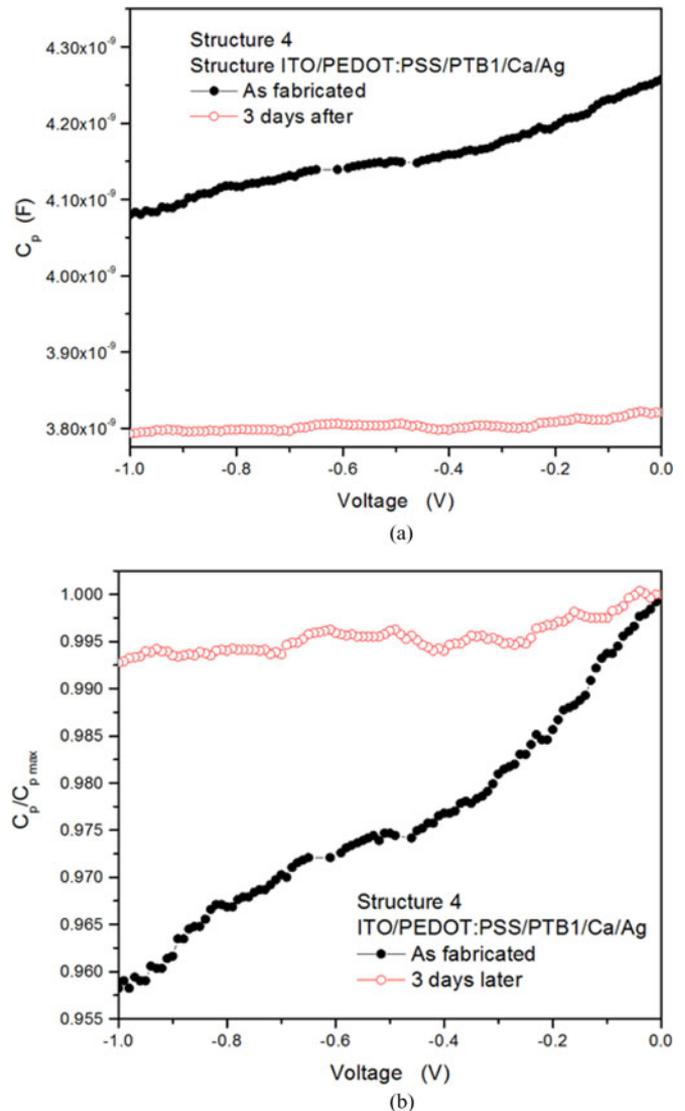


Fig. 7. C - V curves for the device corresponding to structure 4, as fabricated and three days layer; (a) as measured; (b) normalized to $C_{p-\max}$ (0 V).

the material and always in the sense of increasing the conductivity, has to be due to an increase or modification of the contact resistance.

Moreover, in structures without PMMA, the increase of conductivity of the polymer during the first three days of exposure to ambient conditions is more severe and could produce the rapid reduction in the shunt resistance. The rapid increase in the series resistance is consistent, as reported for OSCs at ambient conditions, and is due to contact effects, possibly with the creation of an isolation layer between the polymer layer and the metallic contact. The observed reduction of capacitance for both MIS and MSM structures is consistent with the presence of contacts effects and varies as different materials are used for the electrode.

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