Photosensing Properties of Pentacene OFETs Based on a Novel PMMA Copolymer Gate Dielectric

Fausta Loffredo, Immacolata Angelica Grimaldi, Riccardo Miscioscia, Giuseppe Nenna, Fulvia Villani, Carla Minarini, Mario Petrosino, Alfredo Rubino, Hakan Usta, and Antonio Facchetti

Abstract—**In the present work, bottom-gate top-contact organic field effect transistors (OFETs) were fabricated by evaporating a pentacene semiconductor film on top of a new insulating poly(methyl methacrylate) (PMMA) copolymer containing methacrylate units. The PMMA copolymer was synthesized in order to combine the well-known insulating properties of PMMA with the possibility to be efficiently photocured enabling photopatterning-based organic circuitry integration processes. The properties of the pentacene layer deposited on ITO/PMMA copolymer stack were studied through morphological and structural analyses. Device photoresponses and photoexcitated transients were investigated and compared to reference devices based on standard PMMA gate dielectric.**

Index Terms—**Photocurable gate dielectric, PMMA copolymer, pentacene, photoresponse, phototransistor.**

I. INTRODUCTION

IN THE LAST decade, organic field-effect transistors (OFETs) have been extensively investigated for several electronic applications such as all-polymer integrated circuits [1], [2], flat panel displays [3], radio frequency identification tags (RFIDs) [4], and sensors [5].

The great interest for thin film transistors based on organic materials with respect to their inorganic counterpart arises from advantageous characteristics such as mechanical flexibility, light weight, low production costs and facile of fabrication [6], [7]. Moreover, the specific photoresponse properties of many organic semiconductor materials in ultraviolet or visible regions further enlarge the application field of these electronic devices as phototransistors (OPTs), optoelectronic systems capable of integrating light detection and signal amplification in a single device exhibiting high sensitivity and low noise as compared to organic photodiodes [8].

Among several organic materials for high-performance OFET devices, pentacene has been widely investigated because of its high field-effect mobility and commercial availability [9], [10]. Additionally, its good photoresponsivity properties and photocurrent on/off ratio makes it a suitable material for OPT applications [11]–[14].

On the other hand, high OFETs and OPTs performances, strongly depend not only on the organic semiconducting but also on the gate insulator material properties. Therefore, being they equally relevant, several groups have addressed the development of novel dielectrics vis-a-vis monitoring their photoresponse with the organic semiconductor layer.

In the present work, we fabricated bottom-gate/top-contact OFET devices and investigated the photoexcited currents in pentacene layer deposited on top of a novel dielectric layer. The new dielectric material is a poly(methyl methacrylate) (PMMA) copolymer containing methacrylate units which combines the well-known insulating properties of PMMA with the possibility to be efficiently photocured. The fabricated device stack includes Indium Tin Oxide (ITO) as the transparent gate electrode, spin-coated PMMA copolymer as dielectric, evaporated pentacene as organic semiconductor (OSC) material and evaporated gold contacts as source and drain top electrodes. The electrical responses were measured under dark and light conditions. The light excitation wavelength was chosen in the range of the red absorption maxima of pentacene (about 668 nm) [15]. The process of carrier photogeneration by red light exposure (laser wavelength 670 nm) of pentacene films was investigated by analyzing the effect on the output and transfer characteristics.

Electrical parameters such as threshold voltage, and photoresponses were extracted from the experimental data. Moreover, the OFET performances as photosensors were evaluated by exposing the devices to repeated light irradiation cycles and collecting the time-resolved data necessary to model the decay kinetics of the drain current in the saturation operation regime. Finally, the performances of the PMMA-copolymer based devices were compared to those of PMMA-based OFETs fabricated with the same architecture.

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II. EXPERIMENTAL

A. Devices Structures and Materials

OFET devices in bottom-gate/top-contact configuration were fabricated on glass substrates. The OFET stack was: glass/ITO/PMMA copolymer/pentacene/gold.

Commercial ITO-coated glass substrates (Delta Technologies, Loveland, CO, USA), having sheet resistance 4–10 Ω/sq and 120 nm-thick ITO layer, were employed as back gate contacts. They were cleaned by sequential rinsing in detergent and deionized water for 2 h (at 70 °C) in ultrasonic bath, acetone and isopropyl alcohol (each one for 10 min), then dried under nitrogen flow. The patterning process of gate electrode was carried out by conventional photolithography.

The PMMA copolymer $[\mathrm{P}(0.5 : 0.5)]$ was synthesized by Polyera Corporation as described in the next section. Thin films of the gate dielectric were fabricated by spin-coating a 100 mg/ml solution in ethyl lactate. The condition of spin coating rate at 800 rpm for 60 s was utilized to achieve 600 nm thick films. Then, they were photocured at 365 nm with a 300–500 mJ UV dose and post-annealed at 120 °C for 5 min.

Pentacene (Sigma-Aldrich) was thermally evaporated in high-vacuum chamber at a base pressure of 10^{-7} mbar. The thickness of semiconductor was about 65 nm.

Gold source–drain electrodes (40 nm) were deposited by vacuum evaporation at a base pressure of 10^{-7} mbar through a shadow mask.

PMMA (Sigma-Aldrich), with an average molecular weight of 120000 a.m.u., was employed as gate dielectric to manufacture the reference devices (OFET stack: glass/ITO/PMMA/pentacene/gold). It was dissolved in propylene glycol mono methyl ether acetate (PGMEA) in concentration 80 mg/mL and was deposited by spin-coating for 60 s at 1200 rpm by means of a Brewer Science Model 100 equipment. Finally, the dielectric films were baked at 80 °C for 2 hours in the oven. The final thickness of the PMMA films, measured by a surface profilometer, was about 900 nm.

B. Synthesis of Copolymers

The schema of PMMA copolymer synthesis is reported in Fig. 1. The details of the synthesis are summarized below.

1) Preparation of P[MMA:HEMA (0.5:0.5)]: A mixture of Methyl Methacrylate (MMA) (10.0 g, 99.88 mmol) and Hydroxyethyl Methacrylate (HEMA) (13.0 g, 99.88 mmol) was dissolved in methanol (60 mL) under nitrogen at room temperature. AlBN (656.1 mg, 3.99 mmol) was then added, and the reaction mixture was stirred at reflux under nitrogen for 24 h. The reaction mixture was cooled at room temperature and then poured into diethyl ether (1 L). The polymer was isolated as a white solid after filtration and drying in vacuum, and it was further purified by additional dissolution-precipitation (100 mL of methanol-1 L of diethyl ether) (19.5 g, 84.7% yield).

2) Preparation of P[MMA:HEMA-methacry (0.5:0.5)]: P[MMA:HEMA (0.5:0.5)] (2.0 g, 8.68 mmol free-OH) was dissolved in dry dichloromethane (25 mL) under nitrogen followed by the addition of Et$_3$N (12.1 mL, 86.8 mmol). After 10 min, methacrylic anhydride (MAAN) (12.93 mL, 86.8 mmol) was added dropwise, and the reaction mixture was stirred at room temperature under nitrogen for 4 h. The reaction mixture was precipitated into diethyl ether (120 mL) yielding a glassy solid, which was then dissolved in dichloromethane (12 mL) and precipitated into hexane (600 mL), which gives the final polymer as a white fibrous solid (2.0 g, 76.9%). For 1H NMR (500 MHz, CDCl$_3$) characterization the polymer was dissolved in CDCl$_3$: δ 6.17 (s, br, 1H, -CH$_2$ =C-), 5.65 (s, br, 1H, -CH$_2$ =C-), 4.37 (s, br, 2H, -OCH$_2$ -), 4.21 (s, br, 2H, -CH$_2$ O-), 3.60 (s, br, 3H, -OCH$_3$).

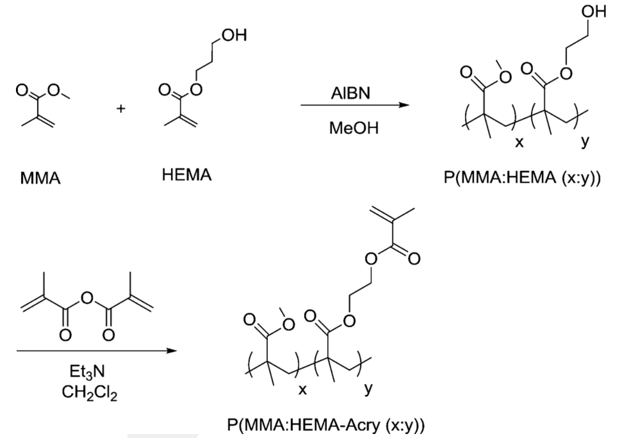

Fig. 1. Synthesis of P[MMA:HEMA-methacry (x:y)] copolymers. Here $x = y = 0.5$.

C. Characterization

The thickness of the films was measured by means of a stylus surface profilometer (KLA Tencor P-10 Surface Profiler). The surface morphology and crystalline structure of the pentacene layer was analyzed by atomic force microscopy (AFM, Veeco, Dimension Digital Instruments Nanoscope IV) in tapping mode and by X-ray diffraction (XRD) using an X'PERT MPD powder diffractometer equipped with Cu cathodic tube, through detector scans at fixed incident angle of 1°.

The dielectric constant (k) of the P(0.5:0.5) dielectric films is $\sim$ 3.1. It was measured through 200 μm × 200 μm metal–insulator–metal capacitors in a silicon/dielectric/gold stack configuration.

The electrical characterization of the OFET devices was performed at 20 °C both in dark and light conditions. The measurements were carried out in a Cascade Summit 12000 probe station, connected to a Keithley 4200 semiconductor characterization system. All the measurements were performed in air, at ambient temperature.

The lighting system is a laser diode (Coherent F_67_400 mW_100_FCN, emission wavelength 670 nm, optical incident power up to 6.8 mW) equipped with an optical fiber coupled to a set of optical elements which ensure the collimation of the light (Fig. 2). The calibration of the laser diode output power was performed by using a silicon photodiode (Newport 818 UV).

The laser beam was sent perpendicularly on the top of the device (opposite side of the substrate) using a collimating system that allowed to fully and uniformly illuminate the OFET channel. The measurements in light conditions were performed

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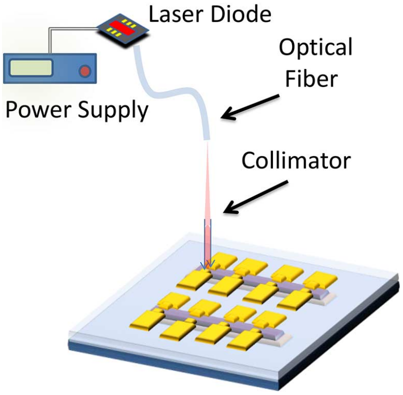

Fig. 2. Schematic view of phototransistors and experiential setup used to spotlight the OFET.

by keeping the optical incident power of the laser diode at 6.8 mW.

III. Results and Discussion

A. Synthesis of New PMMA Copolymers

Insulating polymers containing MMA-HEMA-methacryl units were developed, as shown in Fig. 1. This system was designed considering the good insulating properties of PMMA-like polymers, such as optical transparency, likely solution processability in environmentally acceptable solvents, and possibility to be efficiently photocured. The details of the synthesis are reported in the Experimental section.

The molar ratio between comonomers had to be tuned experimentally to achieve stability of the formulated dielectric solutions and sufficient crosslinking density after UV exposure. The solutions of polymer P(0.5:0.5), obtained with molar ratio 0.5, showed the best stability at room temperature and the corresponding films showed good resistance to solvents. Thus, this copolymer was chosen as dielectric for pentacene-based OFET.

B. Pentacene Film Characterization

In Fig. 3, is reported the AFM images of the pentacene layer deposited on two different dielectric layers: P(0.5:0.5) copolymer and PMMA. In both cases the semiconductor films have dendritic grain structures having mean linear dimensions of about 1.2–1.8 μm and 0.7–0.9 μm for P(0.5:0.5) and PMMA, respectively. Moreover, in the case of P(0.5:0.5), dendrides exhibit more regular and connected fingers and, furthermore, 3D features are visible [16].

Further information about the cristallinity of the pentacene film was extracted by performing X-ray diffraction analysis. In Fig. 4, the X-ray diffraction patterns in the angular range 5°–13° of pentacene layers deposited on the different PMMA like polymers are reported. For both types of pentacene films the X-ray diffractograms show a peak centered at about 5.91° corresponding to the interplanar spacing $d = 1.49$ nm. This peak can be attributed to $00l$ reflection of pentacene bulk crystallographic phase [17], [18] where the pentacene molecules stand with their long molecular axis nearly parallel to the substrate [17], [18]. A closer comparison between the X-ray diffraction patterns suggests that the use of P(0.5:0.5) as underlayer induces the growth of a more crystalline pentacene film with respect to PMMA underlayer. In this last case only the first order reflection is observed with lower intensity respect to pentacene grown on P(0.5:0.5). Additionally, for P(0.5:0.5) also the second order reflection *(002)* is detected.

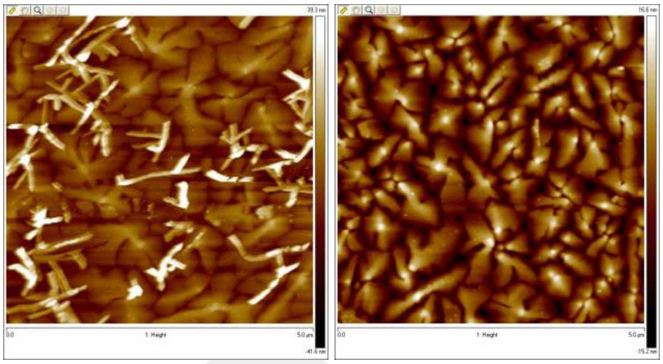

Fig. 3. AFM height images (Tapping mode, scan size 5 μm $\times$5 μm) of pentacene layer deposited on P(0.5:0.5) (left) and PMMA (right) as prepared.

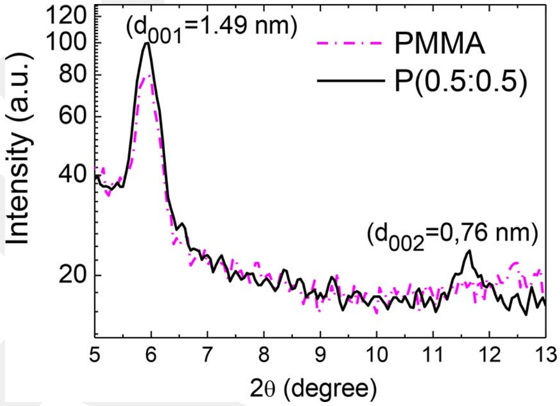

Fig. 4. X-ray diffraction spectra (Cu K α) of pentacene layer deposited on PMMA and P(0.5:0.5).

C. OFET Characterization at Room Temperature

The electrical behavior of OFET devices based on pentacene deposited on different dielectrics—PMMA and P(0.5:0.5)—was investigated by the transfer and output characteristics in ambient atmosphere at room temperature and both in dark and light (at $\lambda = 670$ nm) conditions. As expected these devices showed typical p-type FET operation. Moreover the magnitude of drain current (I_{DS}) increases upon light exposure (Fig. 5). No change in the gate leakages was observed when the devices were illuminated, confirming the presence of free charges only in the OFET channel.

The physical parameters of the devices were estimated from the trans-characteristics obtained in dark and light conditions in saturation mode by using the model [19], [20] described by (1)

$$-I_{\mathrm{DSsat}} = K_0 \cdot (-V_{\mathrm{GS}} + V_T)^m + I_{\mathrm{off}} \tag{1}$$

where I_{DSsat} is the drain current in saturation, K_0 is proportional to the zero-field hole mobility $(\mu_{FET0}), V_T$ is the threshold voltage, m is a temperature-dependent coefficient correlated to the trap distribution and I_{off} is the channel cut-off current. Equation (1) reflects the behavior modeled by Cerdeira

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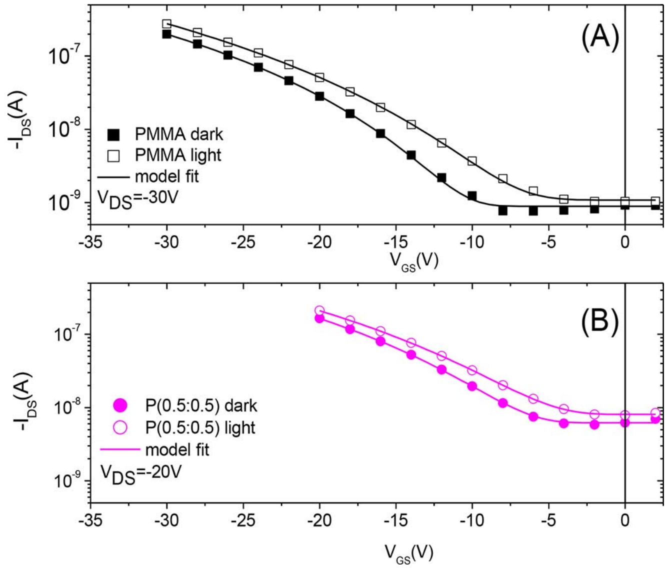

Fig. 5. OFET transfer-characteristics of pentacene transistors based on PMMA. (a) e P(0.5:0.5) (b) dielectrics measured in dark and light conditions. For each device the model fit results are reported as continuous lines.

TABLE I
ELECTRICAL CHARACTERISTIC PARAMETERS ESTIMATED BY TRANS-CHARACTERISTICS MEASURED FOR OFET DEVICES BASED ON DIFFERENT DIELECTRICS AT ROOM TEMPERATURE

Electrical parameter	**PMMA**		**P(0.5:0.5)**	
	Dark	**Light**	**Dark**	**Light**
m	3.53	4.02	2.97	3.02
V_T (V)	-6.66	-1.09	-2.35	-0.19
I_{off} (nA)	0.892	1.09	6.21	8.07
$K_{00}\cdot 10^{-4}$ [cm^2/(V^{m-1} · s)]	6.44	0.806	21.2	16.26

et al. for a-Si TFTs [20] when neglecting the channel length modulation and contact resistance effects. It takes into account trapping mechanisms which are responsible of charge transport activation in disordered materials.

Being

$$K_0 \propto \cdot K_{00} \cdot C_{\mathrm{ins}} \cdot (W/L). \tag{2}$$

where W is the channel width, L the channel length, C_{ins} the surface capacitance of the dielectric, the quantity K_{00} is related to changes in charge transport and hence to the band-mobility μ_{FET0}.

The fit result, obtained for the two types of devices based on PMMA and P(0.5:0.5) are compared in Fig. 5; in Table I the electrical characteristics parameters of the two classes of OFETs are summarized. It is observed that OFETs obtained with P(0.5:0.5) dielectric have an enhanced charge transport and more positive threshold voltage than of the phototransistors obtained with PMMA.

For both types of phototransistors, I_{off} increases when the devices were exposed to light and the V_T shifts to more positive values. In detail the shifts in threshold voltage are lower for P(0.5.0.5)-based OFET respect to PMMA-based devices.

The K_{00} data reported in Table I suggest that the charge transport in P(0.5.0.5)-based OFETs is favored with respect to that in PMMA-based samples in agreement with the higher crystallinity of the pentacene layer as accessed by AFM and X-ray analysis. Modeling of the electrical behaviour indicates a charge transport mechanism related to an exponentially distributed density of states which we considered to be manly influenced by traps located closer to the valence band edge for p-type OFETs [21]. Hence, the obtained data indicate that P(0.5:0.5) has a lower density of shallow traps than the PMMA inducing a higher hole mobility.

For each investigated OFET, the increment of I_{off} under light is due to the dissociation of excitons generated by the absorption of the light in the bulk of the semiconductor which induces an enhancement in the free hole concentration in the channel [21], [22]. The V_T shift towards more positive values is instead associated with the accumulation/entrapping of photogenerated electrons [23]. These results of I_{off} and V_T under light are in agreement with those of other pentacene-based devices reported in literature [21], [22].

Furthermore, by observing the threshold voltages we can assume a lower density of fixed traps in the P(0.5.0.5)-based samples.

In order to investigate the time stability of the manufactured OFETs, photoexcitation transients of the drain currents keeping fix drain and gate voltages were measured (Figs. 6 and 7). The experiments were carried out in saturation regime (the relative outputs are reported as insets in Figs. 6 and 7). The time stability of phototransistors was studied with respect to both light irradiation and electrical stress.

To decouple the effect of bias stress from the photo-activated response, in the first part of the experiments the OFETs were biased in the dark (for 300–500 s) at fixed V_{DS} and V_{GS} evaluating the characteristic times of bias-induced drifts. The time evolution of the dark drain current was modeled to characterize the bias stress effect of the drain current.

After the initial evolution of the bias current in dark condition, the devices were exposed to seven dark/light cycles with equal duration in order to investigate the reversibility of the electrical response to subsequent light stimulus. In detail, the devices were irradiated by laser light alternating dark/light intervals of 40 s (Figs. 6–7).

As observed, for both types of devices, I_{DS} sharply increases in the presence of light, then exhibits a decay. In a similar way, when the laser light is turned off, the I_{DS} undergoes a first sharp drop followed by a slower decay behavior.

A sharp increase in I_{DS} is observed when the process of generation has higher rates than recombination mechanisms. After further time, the system approaches an equilibrium status resulting from the balance of the abovementioned mechanisms. When $V_{\mathrm{GS}} - V_T < 0$ the total increment of I_{DS} (the photocurrent) is a function of two components: the current due to the photogenerated holes (direct photocurrent) and the current associated with the V_T shift (photovoltaic current) towards more positive values. The latter one is specifically due to the accumulation/entrapping of photogenerated electrons [23]. A signif-

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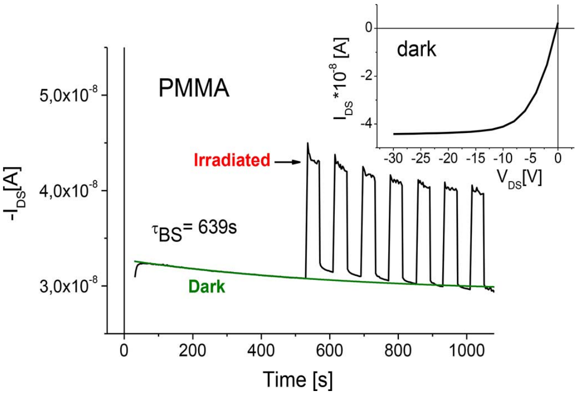

Fig. 6. Source–drain current (black line) measured in air at room temperature at $V_{\rm GS} = -20$ V and $V_{\rm DS} = -20$ V for subsequent dark/light cycles ($t = 40$ s for each step) for pentacene/PMMA-based transistors. The green line is the fit curve corresponding to the decay due to the bias-stress. In the inset is shown the output electrical characteristic measured at room temperature and $V_{\rm GS} = -20$ V in dark.

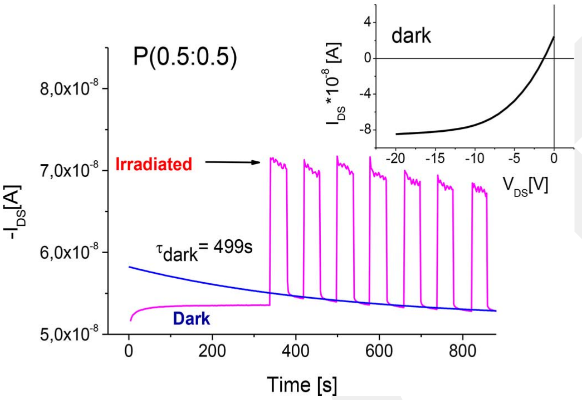

Fig. 7. Source–drain current (magenta line) measured in air at room temperature at $V_{\rm GS} = -15$ V and $V_{\rm DS} = -15$ V for subsequent dark/light cycles ($t = 40$ s for each step) for pentacene/P(0.5:0.5)-based transistors. The blue line is the fit curve corresponding to the dark decay from photoexcited states. In the inset is shown the output electrical characteristic measured at room temperature and $V_{\rm GS} = -15$ V in dark.

icant accumulation of photogenerated carriers at both semiconductor/dielectric and metal/semiconductor interfaces [24] was shown for pentacene-based OFETs.

The illumination effect is almost reversible. When the light is turned off, the $I_{\rm DS}$ decreases following two different kinetics. After a first rapidly decrement of current (faster than the acquisition time of our measurement setup) it follows a second decrease associated to relaxation phenomena which require some hundreds of seconds. The existence of a persistent photocurrent (PPC) visible at the end of each cycle has been associated with a slow relaxation process from the photoexcited status [25]. Literature studies show that the rates of relaxation from the photo-excited state are thermally activated as a result from thermally stimulated currents measurements on single crystals of organic semiconductors. The persistent photocurrent effect is present in addition to fast response mechanisms and it is related to photoexcited electronic states having trapping energy comparable or higher than intrinsic bandgap of the OSC. The time dependent PPC is modeled through a double exponential decay both in OSC conductance experiments [25] and in irradiation studies [26] of OFETs.

TABLE II

CHARACTERISTIC TIMES OF DEVICE DEGRADATION DUE TO THE BIAS STRESS ($\tau_{\rm BS}$) AND DARK DEVICE RECOVERY ($\tau_{\rm DARK}$) FOR OFET OBTAINED WITH BOTH DIELECTRICS

Dielectric	τ_{BS} (s)	τ_{dark} (s)
P(0.5:0.5)	N.A.	499
PMMA	639	866

In our case, PPC is probably associated with the time required to release the trapped electrons. The time needed to free the channel from the whole amount of the photogenerated charges is considered responsible for the slower dark decay.

In order to investigate the effect of different dielectrics on the stability of pentacene-based devices under light and electrical stimulation, the dynamic responses of samples showed in Figs. 6 and 7 were analyzed by fitting the data by a triple exponential decay model (3):

$$\begin{aligned} -I_{\rm DS} = &-I_{DS\infty} + A_{\rm BS}\cdot\exp(-t/\tau_{\rm BS}) \\ &+ A_{\rm dark}\cdot\exp(-t/\tau_{\rm dark}) + A\cdot\exp(-t/\tau_{\rm fast}) \end{aligned} \quad (3)$$

where $I_{\rm DS}$ is the time-dependent drain current, $I_{DS\infty}$ is the steady-state drain current (at $t = \infty$), A_{BS}, $A_{\rm dark}$, and $A_{\rm fast}$ are the magnitude factors for the *bias-stress decay* (due to bias-stress effects), *dark decay* (recovery in dark from photoexcitated states) and *fast decay* ("reversible" photoresponse) mechanisms, respectively, t is the time, $\tau_{\rm BS}$, $\tau_{\rm dark}$ and $\tau_{\rm fast}$ are in the sequence the characteristic times of device degradation due to the bias-stress, dark device recovery from the photoexcited status at long times (considering the entire device history in dark starting from the first cycle to the last one) and fast recovery mechanism related to a single light-dark transition (evaluated on each cycle).

Equation (3) was employed to model the time-varying behavior of OFETs described by Figs. 6 and 7 in three different conditions: before the first illumination when the phototransistor is in the dark (bias-stress decay) and only subjected to the bias stress, in the dark after the first illumination (dark decay) referring to the whole long transient and in phase of recovering after each light exposure (fast decay) state. The aim of these experiments was to decouple bias-stress effects ($\tau_{\rm BS}$) from persistent photoresponse ($\tau_{\rm dark}$) drifts and reversible transients ($\tau_{\rm fast}$). The estimated values of $\tau_{\rm BS}$ and $\tau_{\rm dark}$ were summarized in Table II.

From the experimental data of Fig. 7, it was observed that an unexposed P(0.5:0.5)-based device shows a dark bias stress decay with a characteristic time long enough to be not estimable through the fitting on a 300 s-long dataset; on the other hand, PMMA-based OFETs exhibit a $\tau_{\rm BS} = 639$ s.

This result suggests that P(0.5:0.5)-based OFETs have dielectric surfaces less agreeable to electron trapping resulting in a better bias stress stability. Accordingly, P(0.5:0.5)-based transistors are more stable under electrical stress than the PMMA ones.

In Fig. 8, the $\rm I_{DS}$ current of PMMA-based device after the subtraction of the natural decay component is reported being

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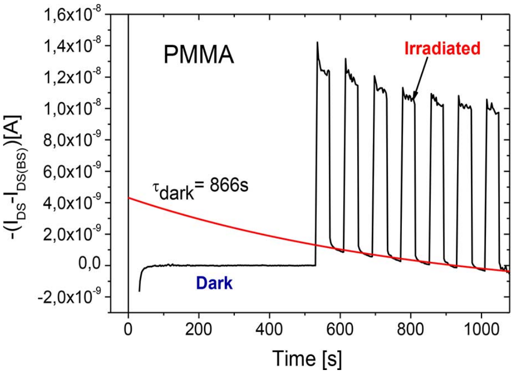

Fig. 8. Source–drain current measured (black line) for pentacene/PMMA-based transistors as shown in Fig. 6 by removing the decay component due to bias-stress $[\mathrm{I}_{\mathrm{DS(BS)}}]$. The red line is the fit curve corresponding to the dark decay from photoexcited states.

$$I_{\mathrm{DS(BS)}} = -A_{\mathrm{BS}} \cdot \exp(-t/\tau_{\mathrm{BS}}). \tag{4}$$

A τ_{dark} value of 866 s was estimated for this kind of devices while a lower value (499 s, Table II, Fig. 7) was observed for pentacene grown on P(0.5:0.5). After the irradiation, the stressed PMMA-based device is slower in recovering the dark current. A larger memory-effect was observed for the phototransistor based on PMMA being the relaxation of persistent photocurrent slower than devices obtained with P(0.5:0.5). Previous works suggested that persistent photocurrent in the dynamic response of p-type phototransistor can be associated with the slower time of release of electron trapped in the OFET [25], [26] in interface states [27]. This hypothesis and the differences observed in our OFETs are in agreement with the presence of a lower number of deep traps in P(0.5:0.5)-based devices.

In order to further analyze the influence of the different investigated dielectrics on the sensing properties of pentacene phototransistors at each exposure cycle as shown in Figs. 6 and 7, the photoresponse, namely the ratio between the I_{DS} current measured under light irradiation and in dark condition, just before the corresponding light stimulation, was calculated and reported in Fig. 9. As it is possible to observe in figure, a more pronounced photosensing effect is visible for the first cycle respect to the successive ones. Indeed, for both the dielectrics the photoresponses slow down after the first cycle and then remain about constant in time. However, the magnitudes of the photoresponses (I_{Dlight}/I_{Ddark}) of OFETs prepared with two different dielectrics are quite unlike. In particular PMMA-based phototransistors present both the higher photoresponse and the higher persistent effect as observed by studying the evolution in the dark.

The difference between devices based on different types of dielectrics could be associated to the different charge trapping properties of the dielectric itself [11].

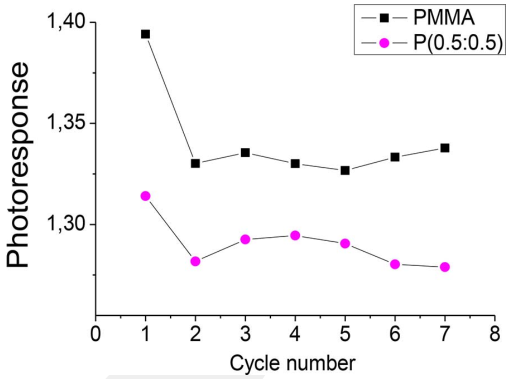

Fig. 9. Photoresponses of pentacene/PMMA like polymers based transistors measured in the successive cycles shown in Figs. 6 and 7.

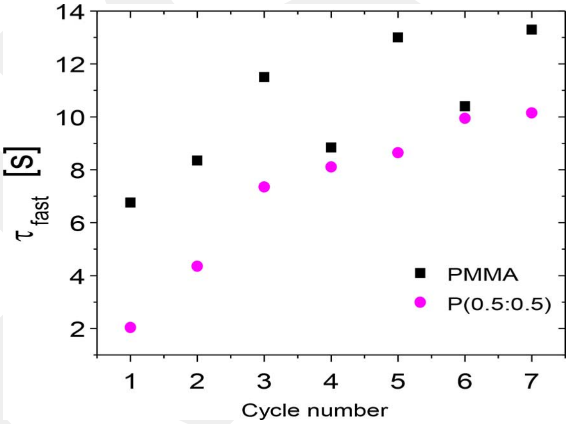

Fig. 10. Fast decay times of the drain current estimated when the pentacene-based phototransistors obtained with different PMMA like dielectrics are exposed to subsequent light-dark transitions.

In Fig. 10, the characteristic times of the fast evolution (τ_{fast}) of observed light-dark transitions for OFETs based on PMMA and the new copolymer are reported as a function of the cycle number. For both the typologies of devices the τ_{fast} increases with the number of light solicitations. Furthermore, the recovery of the device based on P(0.5:0.5) is faster than that one obtained with PMMA in each stage. The result of this ageing process of the device is to slow down the fast dark recoveries. Hence, the devices based on the new copolymer are more stable and show smaller τ_{fast} denoting a more prompt response recovery of the phototransistor. Fig. 10 also evidences scattering for the PMMA-based devices, which could be attributed to a more disordered system that reflects into a more random response to light pulses.

The above-mentioned results are coherent with literature findings which compare the light irradiation effects on the electrical characteristics of OFETs with the memory effect on the photoconductivity observed in many organic materials [28] and model the time-resolved evolution of the drain current through double exponential decays [25], [26]. In addition, the bias-stress effect is decoupled from PPC effects resulting in a three exponential current decay model. By employing such decoupling procedure, we could state that the P(0.5:0.5)-based device having a reduced bias-stress effect was also the one which recovers more readily from persistent photoexcited states because of its lower concentration of deep traps. These results are in agreement with the studies performed on PMMA-pentacene OFETs having suitably modified dielectric/semiconductor interfaces [26], [27] where it was demonstrated that the bias-stress effect is higher in the devices

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that in dark conditions recover more slowly after photoexcitation. This behavior is attributed to higher concentration of deep traps at the dielectric-semiconductor interface. Additionally, in the same literature references it was also proved that trap states responsible of PPC behaviors do not influence directly the charge mobility and exhibit decay times at the first order not dependent on the gate bias [26]. Therefore, in agreement with the literature [29] our results comparing the phototransistors based on new copolymer and PMMA suggest that the dielectric surface based on P(0.5:0.5) exhibits a lower concentration of deep electron traps resulting in a reduced bias-stress effect and faster recoveries from long-living photoexcited states connected to persistent photocurrents.

IV. CONCLUSION

A novel PMMA copolymer was synthesized and used as dielectric in pentacene-based OFETs. The morphology of the pentacene films showed the formation of large grains grown on P(0.5:0.5) layer which represents a suitable condition for electronic applications. Moreover, pentacene/P(0.5:0.5)-based OFETs show lower threshold voltages and higher mobilities than pentacene/PMMA-based devices used as reference. These properties suggest that the interface between semiconductor and the new copolymer is characterized by a lower concentration of traps. In order to verify this hypothesis for both types of devices the stability to bias electrical stress and to consecutive light stimulations was investigated. In particular, the process of carrier photogeneration under red light exposure ($\lambda = 670$ nm) was investigated showing a positive shift of V_T when the device was measured in presence of light. The transient electrical response of phototransistors at repeated short light stimulations was studied and the time-resolved evolution of I_{DS} was investigated revealing two different photo-induced mechanisms: a slow (long-time) relaxation process and a quick (fast-times) recovery process. The new copolymer based-OFETs showed a more stable behaviour than PMMA ones under the effect of bias stress. Moreover, by analyzing the persistent photocurrent, $\tau_{\text{dark copolymer}} < \tau_{\text{dark PMMA}}$ indicates reduced persistent photoexcitation effects for the copolymer. Finally, $\tau_{\text{fast copolymer}} < \tau_{\text{fast PMMA}}$ suggests a quicker recovery of the new copolymer electrical response at each cycle with respect to the case of PMMA-based devices. Thus, due to reported performances, the presented dielectric could be used in future for the fabrication of more complex and stable circuits also taking advantage from its photopatternability.

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