



## High Photoresponsivity of Pentacene-Based Organic Thin-Film Transistors with UV-Treated PMMA Dielectrics

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A simple UV-treatment process for poly(methyl methacrylate) (PMMA) dielectric is proposed to enhance photoresponsivity of pentacene-based organic thin-film transistors. The UV treatment creates excess negatively charged sites on the PMMA dielectric, which makes the device exhibit a large photoinduced current and prolongs persistent conductance recovery. In order to describe time-dependent photoinduced current, double-time constant equations are proposed. Based on time-constant fittings, slow-varied responses are found to be influenced by the UV treatment. The rapid-varied response is independent of gate bias and UV treatment. A plausible model for spatial carrier distribution is discussed and proposed to describe this observed phenomenon.  
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Manuscript submitted March 26, 2008; revised manuscript received May 5, 2008. Available electronically June 3, 2008.

Organic thin-film transistors (OTFTs) have received intense attention due to their low cost, light weight, and low-temperature processing compatible with flexible substrates. The integration of OTFTs with other organic devices such as organic light emitting devices and organic solar cells also opens up the field of flexible optoelectronics.<sup>1,2</sup> In this field, OTFTs not only act as field-effect transistors, but their application in phototransistors is also important for light detection and photoswitching. However, only a small number of researchers have published works on organic phototransistors. Researchers have observed reversible photocurrent and light-induced threshold voltage shift.<sup>3-5</sup> Pentacene-based OTFTs with Ta<sub>2</sub>O<sub>5</sub> gate dielectrics were also proposed to obtain high photoresponsivity.<sup>4</sup> In this paper, an approach to enhance photoresponsivity of pentacene-based OTFTs is proposed. By using poly(methyl methacrylate) (PMMA) as the dielectric and applying UV-light treatment, photoresponsivity of OTFTs can be significantly enhanced. By analyzing the response lifetime, the underlying mechanism is investigated carefully. The proposed approach is simple and compatible with the development of all-organic electronics.

### Experimental

First, the Ni/Pd bilayer was deposited on a glass substrate as a gate electrode. The PMMA was dissolved with a 95 wt % in anisole and was spun onto the gate electrodes. The following was the curing process. The glass substrate was heated with PMMA dielectric on a hot plate at 90°C for 30 min at atmosphere. The solvent was removed and the PMMA was solidified to serve as a gate dielectric. The thickness of the PMMA dielectric was about 360–370 nm. Then, some samples were exposed to UV light (Jelight Company, GLS-144 UV Lamp), with a wavelength of 175–285 nm and irradiation of 0.043 mW/cm<sup>2</sup> for 90 s. Both the UV-treated PMMA and the untreated (standard) PMMA dielectrics were transferred into a vacuum chamber for the deposition of 100 nm thick pentacene film and 100 nm thick gold (Au) electrodes. The device channel width (*W*) and length (*L*) were 1000 and 100 μm, respectively. The illumination system was a combination of a probing bench (Cascade microtech, RHM-06) and a halogen lamp (OPTEM, Lamplink 2). The maximum lamp power was 150 W and was filtered by a band-pass filter, which was opened at a wavelength of about 460 nm with a bandwidth of about ±5 nm. The filtered light was guided by an optical fiber and focused on OTFTs using a microscope. The projected light intensity on OTFTs was about 45 μW/cm<sup>2</sup>.

### Results and Discussion

The transfer characteristics of standard PMMA OTFTs and UV-treated OTFTs are compared in Fig. 1a. The latter OTFTs exhibit

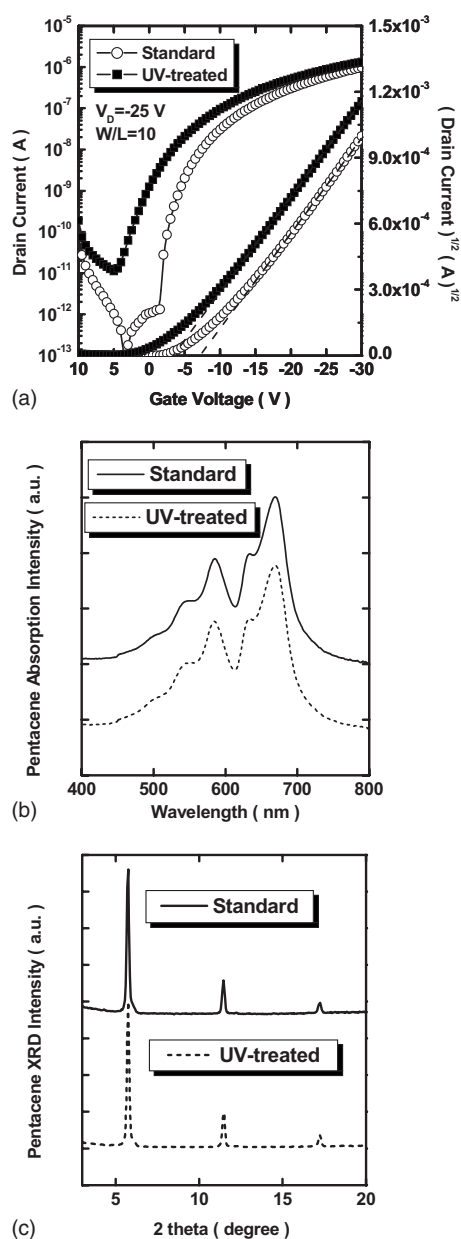
larger subthreshold swing (*S.S.*) and positively shifted threshold voltage (*V*<sub>th</sub>). The results are consistent with other reports, and a plausible explanation is that UV treatment creates excess negatively charged sites on the pentacene/PMMA interface.<sup>6,7</sup> Accordingly, the *S.S.* was enlarged and the *V*<sub>th</sub> positively shifted. However, the linear field-effect mobility (*μ*<sub>FET</sub>) was not affected by UV treatment and was about 0.1 cm<sup>2</sup>/V s for both devices. This indicates that UV treatment does not change pentacene thin-film properties. To verify this assumption, the absorption spectrum and X-ray diffraction spectrum of pentacene films deposited on standard PMMA surfaces and on UV-treated PMMA surfaces are compared in Fig. 1b and c, respectively. No significant difference was found between the standard sample and the UV-treated sample. Thus, it is suggested that UV treatment affects the interface properties significantly but does not influence bulk properties of pentacene.

In Fig. 2a, photoresponsivities (*R*<sub>ph</sub>) of standard devices and of UV-treated devices are plotted as a function of gate bias minus initial threshold voltage (*V*<sub>G</sub> - *V*<sub>th</sub><sup>int</sup>). This measurement was taken after 1000 s illumination at an intensity of about 45 μW/cm<sup>2</sup>. Photoresponsivity (*R*<sub>ph</sub>) is estimated using *R*<sub>ph</sub> = *I*<sub>ph</sub>/(*E*·*W*·*L*), where *I*<sub>ph</sub> is the photoinduced excess drain current and *E* is incident light intensity (W/cm<sup>2</sup>).<sup>8</sup> When the gate bias increases, *R*<sub>ph</sub> is enlarged. This is known as the photofield effect, when electron-hole pairs generated in the band-bending region are swept away by the electric field (from applied gate voltage *V*<sub>G</sub> and drain voltage *V*<sub>D</sub>).<sup>3,9</sup> The larger the gate bias, the easier it is to separate the electron-hole pairs to form the photocurrent. When comparing *R*<sub>ph</sub> of standard and UV-treated devices, the latter devices exhibit larger *R*<sub>ph</sub> than the former. Liang et al.<sup>4</sup> reported that carrier trapping in the insulator or at the insulator/pentacene interface may cause a photoinduced threshold voltage shift (*ΔV*<sub>th</sub>).<sup>3,4,10</sup> In our experiment, it is plausible that the excess negatively charged sites on the pentacene/PMMA interface produced by UV treatment also enhanced the photoinduced *ΔV*<sub>th</sub>.

In Fig. 2b, *ΔV*<sub>th</sub> of standard devices and of UV-treated devices are plotted for comparison as a function of time. The devices are illuminated in the initial 1000 s and then recovered in a dark environment. Obviously, the *ΔV*<sub>th</sub> of UV-treated devices is more pronounced than that of standard devices. Because *ΔV*<sub>th</sub> under illumination is due to an increase in carrier density,<sup>3,4,10</sup> it is speculated that UV treatment created negatively charged sites, which enhanced the attraction of photogenerated holes and thus enlarged the threshold voltage shift. When UV-treated devices return to the dark, the negatively charged sites also retard the neutralization of light-induced carriers.

The separation and neutralization of light-induced carriers can also be observed by plotting *I*<sub>ph</sub> as a function of time as in Fig. 2c. UV treatment enlarges the photo excess current under illumination and enhances the persistent photocurrent (PPC) effect during relaxation.<sup>11</sup> The PPC effect has been proposed to be strongly related to interfacial states.<sup>12</sup> PPC can be analyzed using a double-

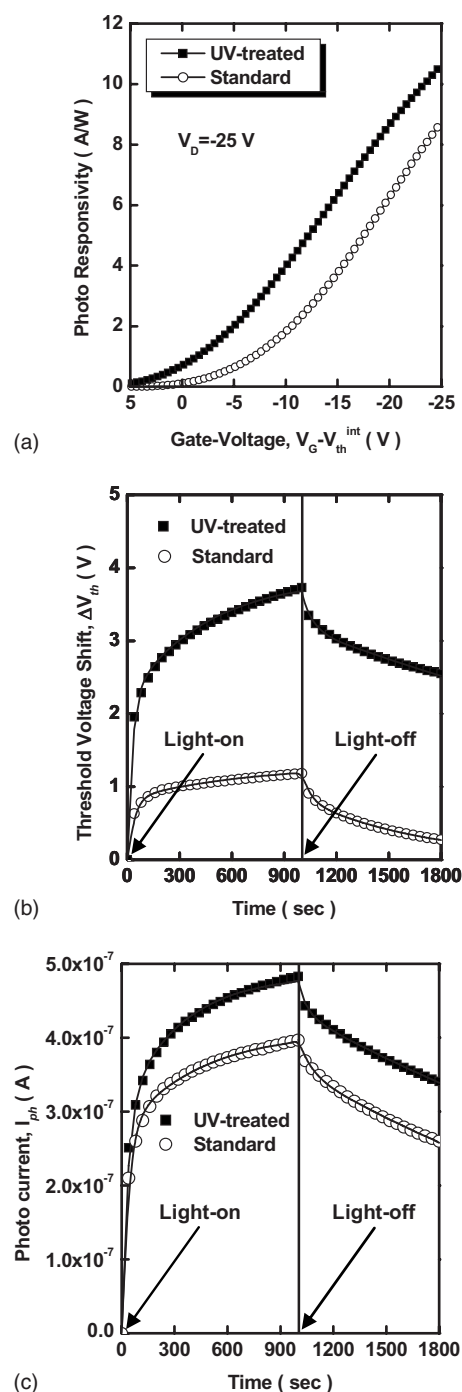
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**Figure 1.** (a) The transfer characteristics of standard PMMA OTFT (opened circle) and UV-treated PMMA OTFT (solid square). (b) The absorption spectra of pentacene films on standard PMMA dielectric and UV-treated PMMA dielectric. (c) The X-ray diffraction spectra of pentacene films on standard PMMA dielectric and UV-treated PMMA dielectric.

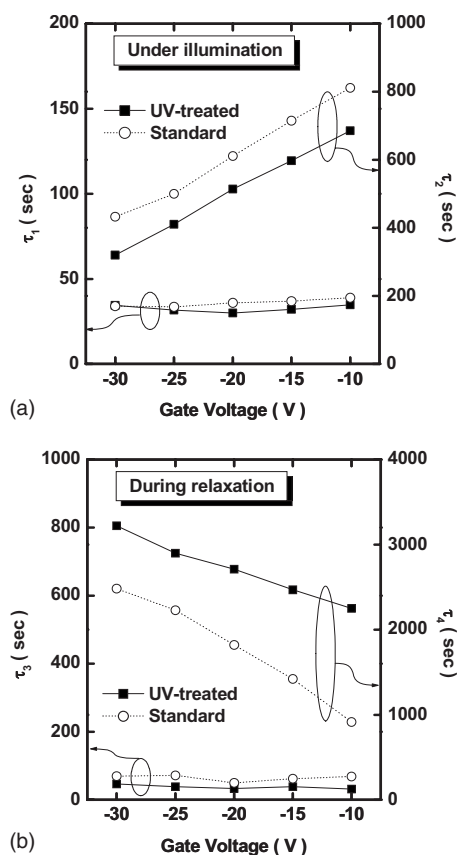
exponential form to fit the photocurrent relaxation.<sup>11</sup> In the following discussion,  $I_{ph}$  under illumination is fitted using  $I_{ph}(t) = I_1[1 - \exp(-t/\tau_1)] + I_2[1 - \exp(-t/\tau_2)]$ , and the excess current during relaxation  $I_{ex}$  is fitted using  $I_{ex}(t) = I_3 \exp(-t/\tau_3) + I_4 \exp(-t/\tau_4)$ , where  $\tau_1$  and  $\tau_3$  are fast time constants and  $\tau_2$  and  $\tau_4$  are slow time constants. The rising time constants ( $\tau_1$  and  $\tau_2$ ) and recovering time constants ( $\tau_3$  and  $\tau_4$ ) obtained under different  $V_G$  are plotted as a function of  $V_G$  in Fig. 3a and b, respectively. It was observed that the fast time constants ( $\tau_1$  and  $\tau_3$ ) are independent of  $V_G$  and are not influenced by the UV treatment. The slow time constants ( $\tau_2$  and  $\tau_4$ ) exhibited a strong dependence on  $V_G$  and were significantly changed by the UV treatment.

Based on previous discussions, the influence of the UV treatment on slow time constants can be easily understood. The UV treatment may modify the PMMA functional end-groups from  $-\text{CH}_3$  to



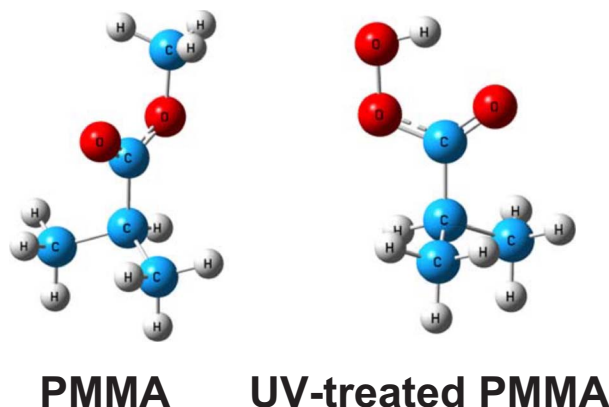
**Figure 2.** (a) The photoresponsivity of standard PMMA OTFT (opened circle) and UV-treated PMMA OTFT (solid square) are plotted as a function of  $V_G - V_{th}^{int}$ . The measurement was made under a drain voltage  $V_D = -25$  V and after 1000 s light illumination. (b) The threshold voltage shift ( $\Delta V_{th}$ ) of standard PMMA OTFT (opened circle) and UV-treated PMMA OTFT (solid square) are plotted as a function of time. (c) The photoinduced drain current ( $I_{ph}$ ) of standard PMMA OTFT (opened circle) and UV-treated PMMA OTFT (solid square) are also plotted as a function of time. Both measurements were made under a  $V_D = -25$  V.

$-\text{COOH}$ ,<sup>13</sup> which results in the changing of charged states near the PMMA surface. Based on these assumptions, the standard (with  $-\text{CH}_3$  end groups) PMMA and UV-treated (with  $-\text{COOH}$  end groups) PMMA monomers were estimated using Gaussian 03 with ab initio calculation.<sup>14</sup> The basis sets used in these calculations were 6-311G(d,p), 6-311 + G(2d,p), and 6-311 + G(2df,2p). After



**Figure 3.** (a) The rising time constants ( $\tau_1$  and  $\tau_2$ ) of the fitting curve  $I_{ph}(t) = I_1[1 - \exp(-t/\tau_1)] + I_2[1 - \exp(-t/\tau_2)]$  are plotted as a function of gate voltage. (b) The recovering time constants ( $\tau_3$  and  $\tau_4$ ) of the fitting curve  $I_{ex}(t) = I_3 \exp(-t/\tau_3) + I_4 \exp(-t/\tau_4)$  are plotted as a function of gate voltage.

Hartree–Fock optimization, as shown in Fig. 4, it is found that the UV-treated PMMA monomer shows a larger dipole moment



(2.42–2.5 Debye) than the standard PMMA monomer (1.81–1.9 Debye). A larger dipole moment implies that a larger voltage drop will appear at the PMMA surface, which will create a larger built-in electric field ( $E_{bi}$ ) and enhance hole attraction. Therefore, the generation of  $I_{ph}$  is accelerated and the  $\tau_2$  of UV-treated devices is smaller than that of standard devices. After the removal of light, the recombination of excess electron–hole pairs is retarded due to  $E_{bi}$ . As a result, the  $\tau_4$  of UV-treated devices is larger than that of standard devices.

The underlying mechanism of fast time constants, however, is not well understood. A spatial separation model has been proposed for photocurrent in OTFTs. The photocurrent should be the combination of channel current and bulk current.<sup>15</sup> The channel term has a longer time scale than bulk term and is gate-voltage dependent. However, the bulk term is a signature for fast response and is independent of gate-voltage. In our study, the fast time constants are not affected by UV treatment and are independent of gate voltage. A reasonable explanation of fast time constants should come from photocurrent, which is weakly connected to the channel region.

### Conclusions

UV treatment of PMMA dielectric is proposed to enhance photoresponsivity of pentacene OTFTs. With UV-treated PMMA, a high responsivity of about 10 A/W can be obtained. The enhanced photoresponsivity may be due to negatively charged sites produced by UV treatment on the PMMA surface. As a result, UV-treated devices exhibit increased subthreshold swing, positively shifted threshold voltage, enhanced photoresponsivity, and prolonged PPC during relaxation. By analyzing photocurrent response time, it was found that gate-bias-dependent time constants are significantly influenced by UV treatment. This analysis explains the UV-treatment effect and gives insight into photoexcitation.

### Acknowledgments

This work was supported by AU Optics, Ltd. Partial financial support was also obtained from the National Science Council (NSC-96-2221-E-009-127) and from the Ministry of Economic Affairs (MOEA-96-EC-17-A-07-S1-046).

*National Chiao Tung University assisted in meeting the publication costs of this article.*

Basis set	Dipole moment ( Debye )	
6-311G (d,p)	1.815	2.424
6-311+G (2d,p)	1.894	2.502
6-311+G (2df,2p)	1.912	2.489

**Figure 4.** (Color online) The optimized structures and dipole moments of standard PMMA monomer and UV-treated PMMA monomer are plotted as ball and bond type. The oxygen atom is colored red, the carbon atom is colored blue, and the hydrogen atom is colored gray (calculated by Gaussian 03, Hartree–Fock method).

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