Organic phototransistor based on poly(3-hexylthiophene)/TiO_2 nanoparticle composite

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Light sensitive phototransistor based on the composite of poly(3-hexylthiophene) and TiO_2 nanoparticles has been developed. The device shows a quick change in channel current under light exposure, which can be attributed to a positive shift of the threshold voltage, while no change in the field effect mobility and off current can be observed. The shift of the threshold voltage is induced by accumulated electrons trapped by the TiO_2 nanoparticles in the channel. The photosensitivity of the device has been found to be dependent on the concentration of TiO_2 nanoparticles, the incident wavelength and the voltage between the source and drain. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2957981]

The study on organic materials including small molecules and polymers for their applications in the electronics and semiconductor industry has been of great scientific and technological interest for several decades. Although electronic materials research has been dominated by the impressive performance of inorganic materials for many years, the attraction of using organic or plastic devices is driven by many virtues of organic materials, including flexibility, low cost, light weight, solution processibility, biocompatibility, and environmental friendliness.[1–3]

Phototransistors are a type of optical transducer in which light detection and signal amplification are combined in a single device without the noise increment associated with avalanche photodiodes.[4] Organic phototransistors (OPTs) are considered to be one of the feasible application of organic thin film transistor (OTFT) because of their large adsorption properties in ultraviolet (UV) and visible light and the excellent photocurrent generation efficiency of organic semiconductors.[5–15] More importantly, some OPTs can be fabricated by solution process,[13–15] such as printing or spin coating, at room temperature and therefore can be easily integrated in smart clothes, packages, and biological systems as light sensors, biosensors, and multifunctional sensors.

OPTs fabricated by thermal evaporation of some oligomers including pentacene,[5–8] 2,5-bis-biphenyl-4-yl-thieno[3,2-b]thiophene,[9] rubrene,[10] *N*-[7-(*N*,*N*-diphenylamino)-9,9′-spirobifluoren-2-yl]- *N*′-(2,5-di-*tert*-butylphenyl)-3,4:9,10-perylenetetracarboxylicdiimide,[11] and 2,7-bis-(*N*,*N*′-diphenylamino)-2′,7-bis(biphenyl-4-yl)-9,9′-spirobifluorene,[12] have been found to be very photosensitive. Normally, a positive shift of the threshold voltage of a OPT can be observed under illumination, which can be attributed to trapping of electrons generated by photons at the insulator/semiconductor interface of the device. However, as explained by Debucquoy *et al.*,[5] the photosensitivity of pentacene organic TFTs shares the same mechanism of bias stressing effect. Therefore the photosensitive behavior of this type of phototransistor is normally associated with the unstability of the device performance, which will be a shortcoming in its real application.

Solution processible OPTs based on conjugated polymers, such as poly(9,9-dioctylfluorene-co-bithiophene),[12] poly(3-octylthiophene-2,5-diyl),[13] and blends of poly(2-methoxy-5-(3,7-dimethyloctyloxy))-1,4-phenylenevinylene) (MDMO-PPV) and methanof [6,6]-phenyl C_{61}-butyric acid methyl ester[14] (PCBM) have been reported. Light illumination can induce pronounced changes both in threshold voltage and off current of the devices, which can be attributed to trapping of electrons at the semiconductor/insulator interface and light induced photocurrent, respectively. It is worth noting that all of the OPT devices based on conjugated polymer or oligomers that have been reported show relatively long response time (>1 s) to light illumination, which may limit their applications. Although most papers are focusing on the magnitude of current change under illumination, we consider stability and fast response under light illumination is also very important for the application of OPTs.

Semiconducting polymer poly(3-hexylthiophene) (P3HT) (Ref. 1) is solution processible and feasible for roll to roll process. It has a field effect mobility up to $\sim 0.1\ cm^2/V\ s$,[16] which is near the value for amorphous silicon, thus it is a promising material for applications in OTFTs and solar cells. However, OPT devices based on P3HT have rarely been reported. We find that OTFTs based on P3HT/TiO_2 nanoparticle composite film are photosensitive and show promising performance in terms of response time and stability, which will be reported in this paper.

The phototransistor is fabricated on a SiO_2/*n*-type Si substrate. The resistivity of the *n*-type Si is 0.001 Ω cm. The thickness of the SiO_2 is 300 nm. Au source/drain electrodes are deposited through a shadow mask on top of the SiO_2 film by thermal evaporation with channel width/length of 2000/200 μm. Here, the *n*-type Si layer acts as the gate electrode and the SiO_2 layer the gate insulator. Regioregular P3HT with head-to-tail linkages of 98% was purchased from Sigma-Aldrich, and used as received without additional purification. TiO_2 nanopowder with the size of 50–100 nm and a mixture phase of anatase and rutile was purchased also from Sigma-Aldrich. P3HT and TiO_2 powders are dissolved in chloroform and spin coated on the substrate in air. Then the device is annealed at 120 °C for 2 h in a glovebox filled with high purity N_2. All of the devices are measured in the glovebox with a semiconductor parameter analyzer (Agilent 4156 C). Devices with different ratio between P3HT and TiO_2 have been fabricated to find the most photosensitive composition.

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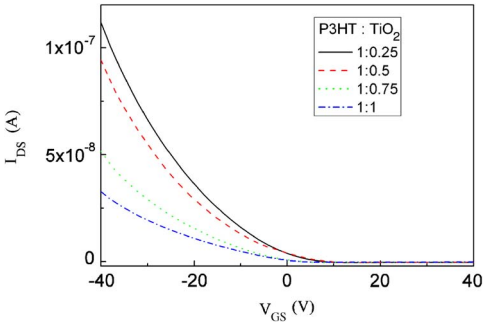

FIG. 1. (Color online) Transfer characteristics of OTFTs based on the composite of P3HT/TiO_2 nanoparticles. V_{DS}=−10 V. From bottom to top, the weight ratio between P3HT and TiO_2 nanoparticles are 1:1, 1:0.75, 1:0. 5, and 1:0.25, respectively.

As shown in Fig. 1, transfer characteristics of OTFTs with different TiO_2 concentration in P3HT have been measured. The effective field effect mobility decreases with the increase in TiO_2 concentration, which can be attributed to the TiO_2 nanoparticles that impede the transport of holes in the channel.

The performance of all of the OTFTs based on P3HT/TiO_2 composite film is photosensitive. As shown in Fig. 2, the channel current of a device (weight ration of P3HT:TiO_2=1:0.75) changes sharply under light illumination. The photosensitive channel currents have been measured at different V_{DS} (10, 5, 2, and 1 V) and the same V_{GS} (0 V). The inset of Fig. 2 shows the transfer characteristics (V_{DS}=−10 V) of the device measured in dark and under white light illumination of 200 μW/cm^2, respectively. The transfer curve exhibits a parallel shift to positive gate voltage under light illumination and no evident change can be found

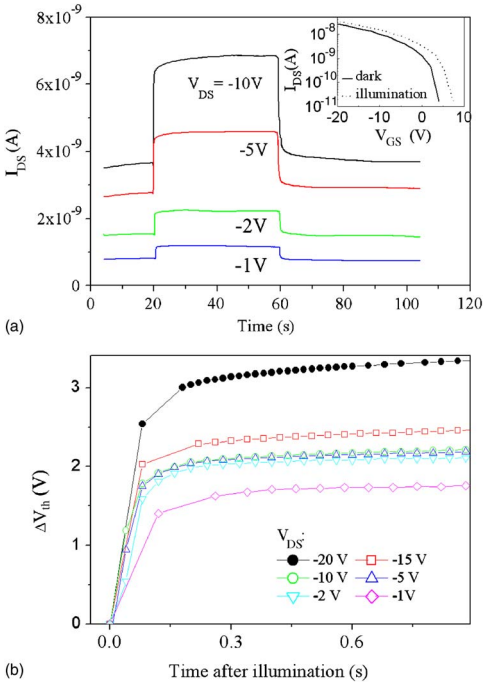

FIG. 2. (Color online) (a) Channel current of an OPT (weight ratio of P3HT:TiO_2 is 1:0.75) measured at different drain voltages V_{DS} and V_{GS} =0 V. The rising and falling edges of current correspond to switching on and off of a white light illumination of 200 μW/cm^2, respectively. Inset: transfer characteristics of the OPT (V_{DS}=−10 V) measured in dark and under light illumination. (b) Shift of the threshold voltage of the OPT calculated from the change of the channel current measured at different V_{DS}.

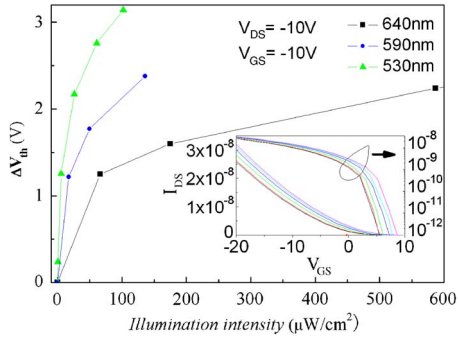

FIG. 3. (Color online) Shift of the threshold voltage of the OPT (weight ratio of P3HT:TiO_2 is 1:0.75) illuminated with different light intensities and different wavelengths. V_{DS}=−10 V. Inset: from left to right, curves for transfer characteristics of the OPT (V_{DS}=−10 V) measured under light illumination (wavelength: 530 nm) with the intensity of 0, 0.43, 5.76, 26.07, 60.82, and 102.09 μW/cm^2, respectively. Linear (log) plot is shown by left (right) axis.

in the field effect mobility, off current, and subthreshold slope. Therefore light illumination only induces a change in the threshold voltage of the OTFT and this change can be directly calculated from the variation of channel current. It can be found that the channel current changes for two orders of magnitude in the subthreshold region due to the light exposure.

P3HT/TiO_2 composite has been used in solar cell. Photons absorbed by P3HT generate excitons in the film and charge separation of the excitons may occur at the TiO_2/P3HT interface since the level of the conduction band (4.3 eV) of TiO_2 is lower than that of the lowest unoccupied molecular orbit (3.2 eV) of P3HT[17] and thus some electrons will be trapped in the TiO_2 nanoparticles. For the application of P3HT/TiO_2 composite in an organic solar cell, high conductivity and continuous paths for electron transport among TiO_2 particles and the anode of the device are critical issues for the device efficiency. We consider that the photosensitive of the OTFT based on P3HT/TiO_2 is also due to the charge separation of excitons at the interface of P3HT and TiO_2. Electrons trapped in TiO_2 nanopartilces will increase the potential of the channel which can be regarded as a floating body effect of the transistor.[18,19] Therefore the more electrons trapped in the channel, the bigger shift of the threshold voltage can be induced.

Charge separation of excitons can be enhanced by applying electric field. We find higher voltage between source and drain (V_{DS}) can induce higher shift of threshold voltage under the same light illumination, which means higher V_{DS} induces higher density of electrons trapped in TiO_2 nanoparticles. So this is a clear evidence for field enhanced charge separation of excitons[20] at the interface of P3HT and TiO_2. On the other hand, our experiments show that the influence of gate voltage on charge separation in the channel is negligible. Normally a gate voltage only can induce electric field in the active layer within several nanometers from the semiconductor/gate insulator interface[21] and thus it has little effect on the charge separation of excitons in the channel.

It is worth noting that the off currents of the phototransitors measured in dark and under light illumination show little difference, as shown in the inset of Figs. 2 and 3. Therefore photocurrent in the channel generated by photon absorption, in other words, a photovoltaic effect,[15] is negligible in the performance of the organic device, which is different

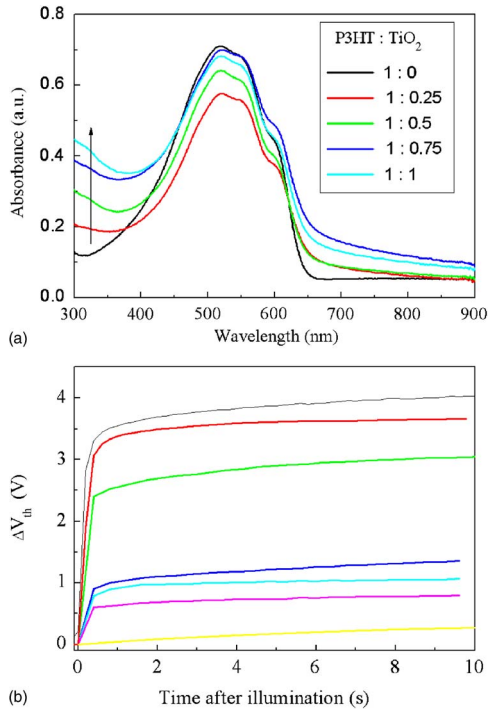

FIG. 4. (Color online) (a) Absorbance of the P3HT/TiO_2 composite films. Along the arrow, from bottom to top, the weight ratio of P3HT:TiO_2 are 1:0, 1:0.25, 1:0.5, 1:0.75, and 1:1, respectively. (b) Shift of the threshold voltage of the OTFTs with different weight ratios of P3HT:TiO_2 measured under the white light illumination of 200 $\mu W/cm^2$ and $V_{DS}=-20$ V. From bottom to top, the weight ratios of P3HT:TiO_2 are 1:0, 1:0.05, 1:0.10, 1:0.25, 1:0.5, 1:0.75, and 1:1, respectively.

from the device based on the composite of MDMO-PPV/PCBM.[15] In our sample, since TiO_2 nanoparticles can not form a continuous conduction path of electrons in the channel, the contribution of electrons to the channel current is very small. In the case of phototransistors based on MDMO-PPV/PCBM, PCBM may form a network for electron conduction in the channel and thus the transfer curve of this type of devices shows pronounced changes in on/off current and the subthreshold slope under light illumination.

The photosensitivity of the OPTs is dependent on light intensity and wavelength. A device with P3HT:TiO_2 =1:0.75 has been measured under three different wave lengths (530, 590, and 640 nm). As shown in Fig. 3(a), the shift of the threshold voltage of the transistor shows a nonlinear relationship with light intensity. This nonlinear behavior can be attributed to the following process. Most of the TiO_2 nanoparticles in the channel are not connected to the source/drain electrodes and the trapped electrons accumulate in the nanoparticles. Therefore the built-in electric field at the interface between TiO_2 and P3HT induced by the accumulated electrons will retard the charge transfer at the interface and induce a lower photosensitivity at higher light intensity. Another possible reason that may induce lower photosensitivity at higher light intensity is the occurrence of exciton-exciton annihilation within the P3HT layer, resulting effectively in a decrease in the exciton lifetime.[17] More detailed theoretical simulation will be carried out for the nonlinear photosensitivity of the device.

The photosensitivity of the device is obviously related to the light absorbance of the composite film. As show in Fig. 4(a), pure P3HT and P3HT/TiO_2 composite thin films both exhibit a maximum light absorbance at 520 nm and a decreasing value with the increasing wavelength. Therefore, the lower photosensitivity for longer wavelength, as shown in Fig. 3, can be explained. In addition, it can be found that TiO_2 nanoparticles increase the light absorbance in the UV region. The UV light sensitivity of the device is under investigation.

As shown in Fig. 4(b), the photosensitivity of the OTFT based on P3HT/TiO_2 is dependent on the concentration of TiO_2 nanoparticles in the composite film. The shift of the threshold voltage increases with the increase of TiO_2 weight ratio under the same intensity of white light illumination, which can be explained in terms of higher density of electrons trapped in the channel by higher density of TiO_2 nanoparticles. Since light absorbance of TiO_2 nanoparticles to white light is negligible, the photosensitive behavior of the device can be attributed to light absorption of P3HT part, which generates excitons in the composite film. Charge separation of excitons occurs at the interface of P3HT/TiO_2. For higher density of TiO_2 nanoparticles, bigger interface area exists in the composite film and thus more electrons can be trapped in the TiO_2 nanoparticles and induce higher photosensitivity of the device.

In conclusion, photosensitive OTFTs based on the composite film of P3HT and TiO_2 nanoparticles have been fabricated and show a stable performance and relatively fast response time under light illumination. Since the device can be fabrication by solution process, it can be easily integrated in organic circuits and multifunctional sensor chips, which implies a broad potential application in the future.

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[1] H. Sirringhaus, Adv. Mater. (Weinheim, Ger.) **17**, 2411 (2005).
[2] Y. Hong, F. Yan, P. Migliorato, S. H. Han, and J. Jang, Thin Solid Films **515**, 4032 (2007).
[3] F. Yan, Y. Hong, and P. Migliorato, J. Appl. Phys. **101**, 064501 (2007).
[4] M. A. Romeo, M. A. G. Martinez, and P. R. Herczfeld, IEEE Trans. Microwave Theory Tech. **44**, 2279 (1996).
[5] M. Debucquoy, S. Verlaak, S. Steudel, K. Myny, J. Genoe, and P. Heremans, Appl. Phys. Lett. **91**, 103508 (2007).
[6] Y. T. Noh and D. Y. Kim, Solid-State Electron. **51**, 1052 (2007).
[7] B. Park, P. Paoprasert, I. In, J. Zwickey, P. E. Colavita, R. J. Hamers, P. Gopalan, and P. Evans, Adv. Mater. (Weinheim, Ger.) **19**, 43553 (2007).
[8] Y. Hu, G. Dong, C. Liu, L. Wang, and Y. Qiu, Appl. Phys. Lett. **89**, 072108 (2006).
[9] Y. Y. Noh, D. Y. Kim, Y. Yoshida, K. Yase, B. J. Jung, and E. Lim, Appl. Phys. Lett. **86**, 043501 (2005).
[10] V. Podzorov and M. E. Gershenson, Phys. Rev. Lett. **95**, 016602 (2005).
[11] T. P. I. Saragi, K. Onken, I. Suske, T. Fuhemann-Lieker, and J. Salbeck, Opt. Mater. (Amsterdam, Neth.) **29**, 1332 (2007).
[12] T. P. I. Saragi, R. Pudzich, T. Fuhrmann, and J. Salbeck, Appl. Phys. Lett. **84**, 2334 (2004).
[13] M. C. Hamilton, S. Martin, and J. Kanicki, IEEE Trans. Electron Devices **51**, 877 (2004).
[14] K. S. Narayan and N. Kumar, Appl. Phys. Lett. **79**, 1891 (2001).
[15] N. Marjanovic, T. B. Singh, G. Dennler, S. Gunes, H. Neugebauer, N. S. Sariciftci, R. Schwodiauer, and S. Bauer, Org. Electron. **7**, 188 (2007).
[16] H. Sirringhaus, N. Tessler, and R. H. Friend, Science **280**, 1741 (1998).
[17] J. E. Kroeze, T. J. Savenije, M. J. W. Vermeulen, and J. M. Warman, J. Phys. Chem. B **107**, 7696 (2003).
[18] H. C. Shin, I. S. Lim, M. Racanelli, W. L. M. Huang, J. Foerster, and B. Y. Hwang, IEEE Trans. Electron Devices **43**, 318 (1996).
[19] F. Yan, P. Migliorato, and R. Ishihara, Appl. Phys. Lett. **88**, 153507 (2006).
[20] P. Peumans and S. R. Forrest, Chem. Phys. Lett. **398**, 27 (2004).
[21] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).