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Photoresponses and memory effects in organic thin film transistors incorporating poly(3-hexylthiophene)/CdSe quantum dots

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This paper describes the optical responses and memory effects of poly(3-hexylthiophene) (P3HT)/CdSe quantum dot (QD) thin-film transistors (TFTs). TFTs incorporating P3HT/CdSe QD blends as the active layer exhibited higher photocurrents than did the corresponding P3HT-only devices because the heterojunction between P3HT and the CdSe QDs enhanced the separation of excitons. Moreover, the CdSe QDs served as trap centers so that the memory effect was maintained for several hours, even when the device was operated without a gating voltage. Here, we demonstrate the potential applicability of such P3HT/CdSe QD TFTs through repeated optical programming and electrical erasing. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2899997]

During the past few years, a tremendous amount of effort has been devoted to studies of polymer-based optoelectronic devices. The use of polymer memory has several advantages, including ease of fabrication and low cost. Many research teams are actively pursuing polymer phototransistors, but few are focusing on memory effects in the polymer devices, especially for polymer devices operated using optical programming and electrical erasing. A simple optically writeable memory device incorporating poly(alkylthiophene) as the active layer has been proposed, with the optically induced charge being trapped at the polymer-dielectric interface.[1] Carbon nanotube networks have also been coated with polymers to form optoelectronic memory devices that are written optically and read and erased electrically, but these blended polymer/carbon nanotube devices lost their memory capability because the carbon nanotubes separated from the substrate and because the nanotube bundles contained metallic nanotubes.[2] In polymer-based memory devices, the dynamic switch phenomenon depends strongly on the gate effect.[3] The "on" state can be returned to the "off" state by removing the gate voltage.[4] Unfortunately, the on states of these devices were not maintained for very long in the absence of an applied gate voltage, which limits their potential use in commercial applications. In this paper, we describe poly(3-hexylthiophene) (P3HT)/CdSe quantum dot (QD) thin-film transistors (TFTs) that exhibit long retention times for their on states even in the absence of a gate voltage. This behavior differs significantly from that reported previously.

Composite films of CdSe QDs and P3HT have been widely used in photovoltaic devices[5] in which exciton dissociation and charge separation occur at the interface between the CdSe QDs and P3HT. Based on this principle, the electrons become trapped in the CdSe QDs when the light is turned off. This behavior enhances the retention time of polymer-based phototransistors. In this paper, we demonstrate that hole-only transport occurs in P3HT/CdSe QD TFTs. The drain-source currents (I_{DS}) of both the P3HT and P3HT/CdSe TFTs increased by up to several orders of magnitude upon irradiation with light when operated in the depletion mode. After turning off the light, the current decayed to a metastable state, where it remained for several hours, when the devices were subjected to a positive or zero gate voltage.

Trioctylphosphine oxide (TOPO)-capped CdSe QDs were synthesized using a modification of a procedure reported previously.[6] A solution of P3HT (Rieke Metals, used as received) in chloroform (5 mg/mL) was blended with a solution of CdSe QDs (diameter of 3.5 ± 0.5 nm). The P3HT and P3HT/CdSe TFT devices were fabricated in a bottom-gate configuration (Fig. 1). An $n+$silicon wafer ($<0.005\ \Omega$ cm) was used as the substrate and gate. 900 Å thermal SiO_2 (capacitance of 38.4 nF/cm^2) was the gate insulator. It was hydrophobically modified using hexamethyldisilazane vapor. The source and drain fingerlike electrodes ($W=3000\ \mu$m and $L=10\ \mu$m) were defined using standard photolithography. A bilayer of Au/Ti (thickness of 1000/100 Å) was thermally evaporated and then lifted off. The P3HT and P3HT/CdSe films (thickness of 100 nm) were deposited through spin coating. The density of CdSe QDs in the thin P3HT film is about 9.93×10^{17} cm^{-3}. The films were subsequently annealed at 150 °C under N_2 for 5 min. The performance of each device was measured under vacuum ($<1 \times 10^{-5}$ torr) in the dark using a Hewlett-Packard 4156C semiconductor parameter analyzer and a cryogenic probe station (VFTTP4, Lakeshore). The devices were illuminated under vacuum using a tungsten halogen lamp.

Figure 2 displays the transfer curves (drain-to-source voltage $V_{DS}=-20$ V) of the P3HT-only and P3HT/CdSe QD

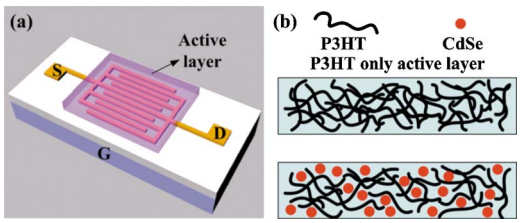

FIG. 1. (Color online) Schemes of devices structure and organic active layers. (a) Schematic representation of the bottom-gate organic TFT configuration with an active polymer layer and interdigitated source and drain (S for source, D for drain; and G for gate). (b) Schematic representations of the P3HT-only and P3HT/CdSe blend films.

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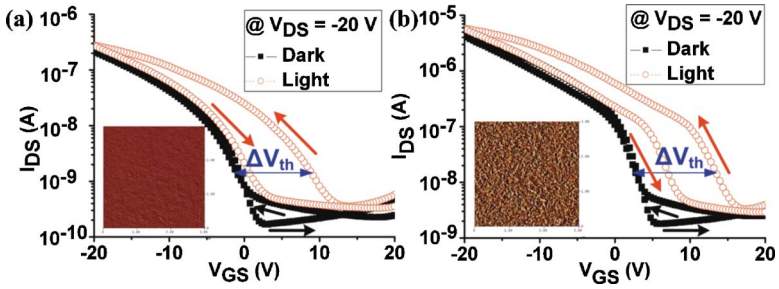

FIG. 2. (Color online) Transfer characteristics obtained for the (a) P3HT-only and (b) P3HT/CdSe blend films (i) initially (in the dark) and (ii) under illumination. Under illumination, all of the devices displayed hysteresis. Transfer characteristics of the devices in the dark and under illumination (0.27 mW/cm^2) were measured at $V_{DS}=-20$ V. Inset: AFM phase images of P3HT films in the (a) absence and (b) presence of CdSe QDs. Image size was 3×3 μm.

blend TFTs in the dark and under a white light of 0.26 mW/cm^2. Both the P3HT and P3HT/CdSe TFTs exhibit the characteristic behavior of *p*-channel field-effect transistors. Ambipolar-type TFTs based on blended donor- and acceptor-type materials have been reported previously.[7] The work function of Au (5.1 eV) matched the highest occupied molecular orbital of P3HT (4.9 eV),[8] forming an Ohmic contact for hole injection. The drain currents measured by sweeping gate voltage at $V_{DS}=20$ V. We observed a weak electron current in the P3HT/CdSe and pure P3HT TFTs. The electron current remains weak even if higher positive gate voltages. Whereas Au strongly suppressed electron injection into CdSe [lowest unoccupied molecular orbital (LUMO): 4.3 eV][9] and P3HT (LUMO: 3.0 eV)[8] because of a large mismatch between its work function and the LUMO band of CdSe and P3HT. In addition, the current in the PH3T/CdSe TFTs is about one order of magnitude larger than for the pure PH3T TFTs in the whole voltage range. Incorporation of CdSe QDs into the P3HT lightly enhances the hole mobility of the devices, it is possible that CdSe reduced the density of traps in the polymer.[10]

The inset of Fig. 2 displays phase images—obtained by AFM (Multimode, DI) in the tapping mode—of both the P3HT and P3HT/CdSe thin films. The P3HT/CdSe composite thin film had a rougher surface morphology (rms roughness of 3.6 nm) in comparison with that of the P3HT-only film (2.0 nm). The surface morphology of the film incorporating the CdSe QDs was rough because of CdSe aggregation. The contrast in the phase image of the film blend indicates phase separation. The transmission electron microscopy image of the blend film (not shown here) revealed that the CdSe QDs had unexpectedly aggregated into clusters. To avoid aggregation of the CdSe QDs, a suitable ligand must be used to passivate the QDs to enhance the performance of the memory devices.

We observed photoconductivity and the photovoltaic effect in the active layer of the transistors upon illumination.[11] We attribute the significant increase in the drain current in the off state, when the device was being illuminated, to the enhancement of the drain current caused by the excitons in the polymer and nanocrystal. When illuminated, the excitons were generated in the CdSe QDs and P3HT. The electrons and holes eventually separated as a result of the electrical field. The drain currents of the P3HT/CdSe devices were larger than those of the P3HT-only devices because of the built-in field present at the P3HT-CdSe interface. The photoexcitation hole density within the thin film also contributed to the drain current and increased the threshold voltage to a large positive value.

Threshold voltages (V_{th}) were determined from the intercepts of the $\sqrt{I_{DS}}$-V_{GS} plot. In general, the values of V_{th} of the blend P3HT/CdSe devices shifted to more-positive values, indicating the existence of a permanent electric field at the interface. The I_{DS}-V_{GS} curve shifted toward a positive voltage under illumination. As shown in Fig. 2, the value of V_{th} of the P3HT/CdSe device shifted to 10.0 V (illuminated) from 4.2 V (darkness), i.e., $\Delta V_{th}=5.8$ V. In contrast, the value of ΔV_{th} of the P3HT-only device was ~1.9 V. The ΔV_{th} extracted from the backward sweep curve is more pronounced than that extracted from the forward sweep. For the forward sweep, when an initial negative gate voltage is applied, the trapped electrons in the P3HT/SiO2 interface and CdSe QDs would easily detrap and recombine with the hole in P3HT, leading to a reduction in the carrier density. Whereas, the recombination process of electrons and holes in backward sweep took place in the region that is not concerned with the memory functionality.

The increase in the value of the carrier density N^* in the active layer could be estimated using the equation $N^*=C_i\Delta V_{th}/e$, where C_i is the capacitance per unit area of the dielectric layer, ΔV_{th} is the shift of the threshold voltage, and e is the elementary charge. The values of N^* of the P3HT/CdSe device and the P3HT-only device were $\sim1.39\times10^{12}/cm^2$ and $\sim4.53\times10^{11}/cm^2$, respectively, indicating that the P3HT/CdSe devices were more efficient at separating excitons, presumably because of the heterojunction at the P3HT-CdSe interface in the active layer.

Upon sweeping the voltage from positive to negative and then back to positive, we observed obvious hysteresis under illumination, but indistinct hysteresis in the dark (Fig. 2). This behavior was a consequence of the trapped charges present at the polymer-dielectric interface or in the dielectric material. The hysteresis for a P3HT device was typically less than 1.1 V. For the P3HT/CdSe devices, it was ~0.8 V. These similar values indicate a very small difference in their interface trap densities. The manifest hysteresis under illumination has also been observed in P3HT/PCBM phototransistors and organic capacitors.[10,12] Apparent hysteresis occurred upon illumination as a result of an increased number of carriers in the active layer becoming easily trapped, either at the P3HT-SiO_2 interface or in SiO_2 itself. In the P3HT/CdSe devices, some of the carriers were trapped in the CdSe QDs, resulting in the reduced degree of hysteresis.

Hysteresis in the illuminated devices resulted from trapped electrons. When applied a positive gate voltage of 7.5 V (where the hysteresis is most pronounced in the Fig. 2), Fig. 3(a) indicates that the current in the P3HT-only devices reached a metastable state after turning off the pulse light source (30 s). This behavior is consistent with previous observations.[1–3] Trapping of electrons in SiO_2 or at the P3HT-SiO_2 interface screened the back-gate potential, resulting in the metastable state. We attribute the slow current decay to bulk recombination, which is an indication of the slow nonexponential relaxation process inherent to polymer-

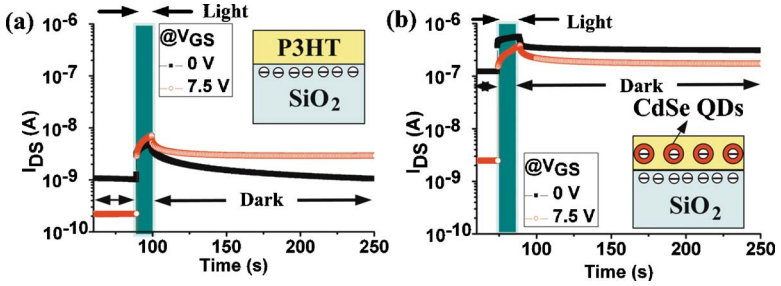

FIG. 3. (Color online) Time responses of the drain current at V_{GS}=7.5 V and V_{GS}=0 V of the (a) P3HT-only and (b) P3HT/CdSe devices to a light pulse (2.75 mW/cm^2, 30 s). Inset: Illustrations of the electron trap mechanisms for the (a) P3HT-only and (b) P3HT/CdSe devices.

based devices. After turning off the light source, the drain current decayed rapidly when the gate voltage was equal to zero. The current moved back to the initial state in the P3HT devices after turning off the light (100 s). In the absence of a gate voltage, there was no external electrical field to induce the electrons; thus, the trapped electrons escaped from the trap centers (i.e., from the SiO_2 or the P3HT-SiO_2 interface) into the active layer, resulting in decay of the drain current in the P3HT devices.

Relative to the P3HT-only devices, the P3HT/CdSe devices displayed entirely different behavior, as shown in Fig. 3(b). Under illumination, the electrons were trapped not only in SiO_2 and at the P3HT-SiO_2 interface but also in the CdSe QDs. After photoexcitation, the trapped electrons escaped from the trapping centers (SiO_2 or P3HT-SiO_2) after a few minutes. In contrast, the highly localized electrons inside the CdSe QDs had difficulty jumping back into the polymer. Also, the presence of TOPO on the surface of the CdSe QDs enhanced the trapping of electrons. This metastable state was maintained for several hours, even in the absence of a gate bias. The P3HT/CdSe devices exhibited higher I_{ON}/I_{OFF} ratios (>100) than did the P3HT-only devices (10). A large on/off ratio can also be achieved for the P3HT/CdSe and P3HT-only devices providing an appropriate gate voltage is applied. Our observations show that the on/off ratio of P3HT/CdSe TFTs is at least one order of magnitude larger than that the pure P3HT TFTs near the threshold voltage. Moreover, there is a much long retention time for the P3HT/CdSe devices than the P3HT-only devices in absence of a gate voltage. Although the P3HT/CdSe devices exhibited a memory effect in the absence of a gate voltage, their I_{ON}/I_{OFF} ratios were too low to meet the required memory window.

Upon illumination with white light (2.75 mW/cm^2), the drain current of the P3HT/CdSe device rose from 1.5 to 415 nA (Fig. 4). After turning off the white light, the drain current dropped slowly and eventually settled at a metastable state of 260 nA. Moreover, this metastable state could be erased efficiently using a single pulse of a gate voltage for a short duration (−15 V, 100 ms). When this negative pulse gate bias was applied, trapped electrons quickly recombined with the majority carriers from the trap centers. After applying the negative electrical field, the Fermi level of CdSe also modulated up toward the conduction band, reducing the built-in field and, hence, enhancing recombination. Based on this mode of operation, we could repeatedly program the P3HT/CdSe device optically and electrically erase it.

In summary, we have investigated the electrical and optical properties of polymer memory TFTs incorporating P3HT and P3HT/CdSe as active layers. Upon illumination, the P3HT/CdSe TFTs exhibited stronger carrier induction in the channel and greater electron trapping ability than did the P3HT-only devices. This phenomenon resulted in a relatively high I_{ON}/I_{OFF} ratio. After introducing the CdSe QDs as electron trap centers, the retention time of the metastable memory state of the P3HT/CdSe TFT improved in the absence of a gate voltage. We are currently optimizing the working point of V_{th} at values of V_{GS} near 0 V to maximize the photoresponse so that the memory window can be widened further. We are also investigating replacing the TOPO molecules with long alkyl chains to enhance the retention time.

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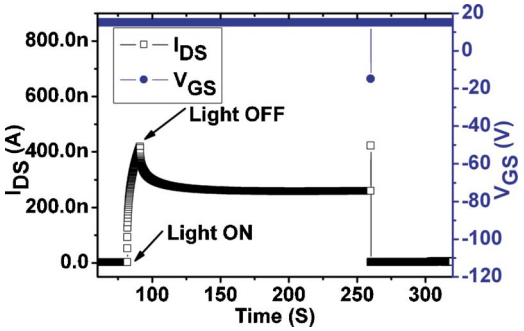

FIG. 4. (Color online) Dynamic responses of the optical programming and electrical erasing of a typical P3HT/CdSe device. Light was turned on at t=80 s and turned off at t=90 s. A short (100 ms) negative gate voltage pulse was applied at t=260 s to erase the memory.