High-photosensitivity polymer thin-film transistors based on poly(3-hexylthiophene)*

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Polymer thin-film transistors (PTFTs) based on poly(3-hexylthiophene) are fabricated by the spin-coating process, and their photo-sensing characteristics are investigated under steady-state visible-light illumination. The photosensitivity of the device is strongly modulated by gate voltage under various illuminations. When the device is in the subthreshold operating mode, a significant increase in its drain current is observed with a maximum photosensitivity of 1.7×10^3 at an illumination intensity of 1200 lx, and even with a relatively high photosensitivity of 611 at a low illumination intensity of 100 lx. However, when the device is in the on-state operating mode, the photosensitivity is very low: only 1.88 at an illumination intensity of 1200 lx for a gate voltage of −20 V and a drain voltage of −20 V. The results indicate that the devices could be used as photo-detectors or sensors in the range of visible light. The modulation mechanism of the photosensitivity in the PTFT is discussed in detail.

Keywords: semiconducting polymer, thin film transistor, photosensitivity, phototransistor

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1. Introduction

Organic thin film transistors (OTFTs) based on conjugated organic semiconductors, both small molecules and polymers, play a prominent role in organic electronic devices due to their broad range of applications, such as flexible displays, smart cards, radio frequency identification tags, and large area sensor arrays.[1−3] In particular, the fascinating photo-response characteristics of conjugated organic compounds in the UV or visible region are particularly suitable for making optoelectronic devices such as photovoltaic cells, photo-detectors, or photo-modulated organic light-emitting diodes (OLEDs) with a photo-conducting layer.[4−6] Among them, organic phototransistors are promising candidates for optical transducers because they combine light detection and signal amplification in a single device without reducing signal-to-noise ratio since the channel current is not directly related to the area but to the ratio between the channel width and length of the device.[7] More importantly, phototransistors can be easily integrated into flexible electronic products and biological systems as light sensors or biosensors.

There are two types of organic phototransistors that have been developed based on semiconducting oligomers and polymers. One type is based on small molecules such as pentacene[8] and 2,5-bis-biphenyl-4-yl-thienof3,2-bgthiophene (BPTT),[9] which is fabricated by thermal evaporation in a high vacuum environment. The other type of organic phototransistor is based on conjugated polymer materials, which presents a processing advantage due to their mechanical flexibility, light weight, and large-area coverage at low fabrication cost by spin coating, drop casting and inkjet printing. Narayan and Kumar[10] described a phototransistor based on poly(3-octylthiophene) with a photosensitivity of 100 and responsivity of 1 $A\cdot W^{-1}$. Hamilton *et al.*[11] reported on a poly(9,9-dioctylfluorence-co-bithiophene)-based phototransistor with a photosensitivity of 10^3 and responsivity of 0.7 $mA\cdot W^{-1}$ under white-light illumination. In previ-

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ous studies, poly(3-hexylthiophene) (P3HT) showed promising applications in integrated optoelectronic devices due to its relatively high carrier mobility.[12] Recently, Pal *et al.*[13] reported on a high performance phototransistor based on regioregular P3HT with a photosensitivity of 3.8×10^3, with a xenon lamp employed as the illumination source. Yan *et al.*[14] also reported on a highly photosensitive phototransistor based on a composite of P3HT and TiO2 nanoparticles with a photosensitivity of about 1.0×10^3 under light illumination at wavelengths ranging from 370 nm to 590 nm. However, in the reports, all solution preparation, device fabrication, and electrical measurments were performed inside an N_2 filled glovebox.

In the present work, polymer thin-film transistors are fabricated on silicon substrates with SiO_2 serving as the insulator layer and P3HT as the semiconducting active layer to investigate their photo-sensing characteristics under the illumination of visible light. Moreover, the mechanism of photocurrent amplification in the polymer thin-film transistor (PTFT) is also discussed. In the experiments, solution preparation and deposition are completed in a clean room with a relative humidity of 30%, and all device measurements are performed in ambient air for large-area applications.

2. Experimental details

The PTFT consisted of the bottom-gate, top-contact field effect transistor configuration. A highly-doped n^+ silicon wafer was used as the substrate material for fabricating the devices. A thin gate-oxide layer was grown by thermal dry oxidation at 1000 °C for 200 min. The oxide film at the back side of the silicon substrate was removed and gold was deposited to form the gate contact of the PTFT device. The solid P3HT polymer was dissolved in chlorobenzene at a concentration of 10 mg/ml and was spin-coated as the semiconducting active layer on the oxide layer at a spin speed of 2000 rpm for 60 s in air, and then the wafer was annealed at 90 °C in air for 10 min. Finally, gold was vacuum evaporated through a shadow mask to form the source and drain electrodes with a comb-shaped structure on the top of the semiconducting polymer film. In order to avoid the influence of H_2O and O_2 in the air on device performance during measurement, a thin solid paraffin was dissolved to form a thin passivation layer at 80 °C.[15] The cross-section of the fabricated PTFT is shown in Fig. 1. The channel length and width were 100 μm and 10 mm, respectively. For better isolation among the devices on the same wafer, a cutter was used to slightly scribe the polymer film into separate islands for reducing the leakage current of the devices under the off-state condition.

The thickness of the silicon oxide was measured to be 150 nm by ellipsometry, while the thickness of the polymer thin film was determined to be 60 nm by surface profilometry. The optical absorption spectrum of the P3HT film was measured by an ultraviolet-visible spectrophotometer, with the film deposited on a glass plate. The electrical characteristics under dark and illuminated conditions were obtained with an Agilent 4156C semiconductor parameter analyzer connected to a probe station at room temperature. An incandescent lamp was employed as the illumination source. The photocurrent ($I_{\rm ph}$) was calculated by subtracting the dark current ($I_{\rm dark}$) from the current under illumination.

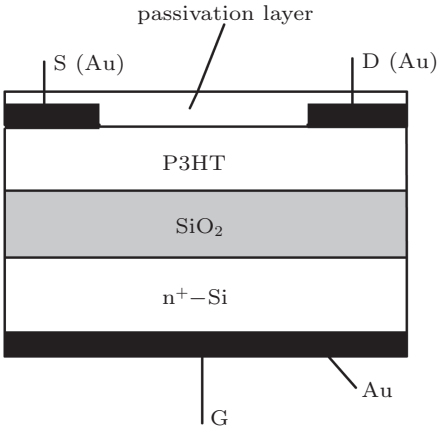


Fig. 1. Cross section of the polymer thin-film transistor.

3. Results and discussion

The ultraviolet-visible absorption spectrum of the P3HT film in Fig. 2 shows that the film has good absorption in the visible range from 390 nm to 650 nm. For the measurement, P3HT films were prepared on a glass substrate by the same processing method as that used for the transistors. The intrinsic absorption peak is at a wavelength of 519 nm and the long-wavelength cut-off is at 609 nm. Hence, the band gap $E_{\rm g}$ calculated from the long-wavelength cut-off λ_0 is 2.04 eV by using the relation $E_{\rm g} = 1.24/\lambda_0$.

Figure 3 shows the light emission spectrum of the incandescent lamp used as the illumination source. The emission peak is at a wavelength of 1100 nm. Moreover, there is also relatively strong emission in a

range from 390 nm to 650 nm, which can make a good match with the absorption spectrum of the P3HT film shown in Fig. 2.

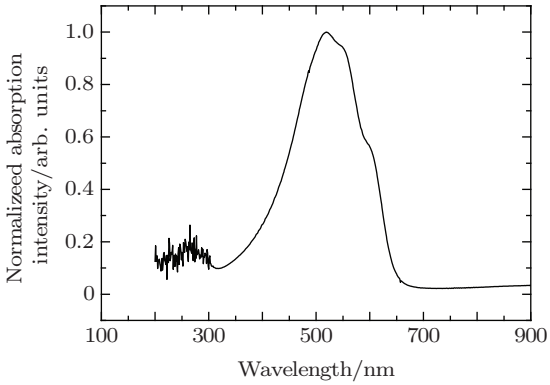


Fig. 2. Normalized absorption spectrum of P3HT film deposited on a glass plate (light-source energy is the same for various wavelengths).

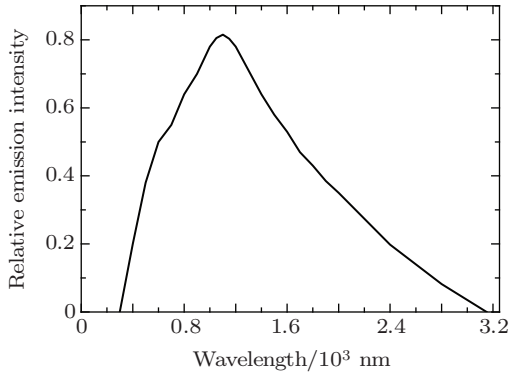


Fig. 3. Light emission spectrum of the incandescent lamp as a function of the photon wavelength.

Figure 4(a) shows the typical output characteristics of the P3HT-based PTFT measured in the dark, where the values of drain current (I_D) each are plotted as a function source-drain voltage (V_{DS}) for different gate voltages (V_{GS}). The V_{GS} varies from 8 V to −4 V with a 4-V interval. The device exhibits well-defined p-type field-effect transistor behaviours and good saturation behaviours in the measurement range. Figure 4(b) exhibits the transfer characteristics of the same device, where I_D is plotted as a function of V_{GS} with a fixed drain voltage of –20 V, both in the dark and under light illumination at 100 lx. Under dark conditions, the device shows excellent gate modulation with a current on/off ratio of more than 10^3. Upon illumination, the off-state current increases significantly, indicating that the photo-generated carrier density is significantly higher than the intrinsic carrier density of the P3HT film. To understand the influence of light illumination on the field-effect carrier mobility and threshold voltage of the P3HT-based PTFT, the square root of drain current versus gate voltage at a drain voltage of –20 V is also plotted in Fig. 4(b) before and after light illumination. It can be seen from Fig. 4(b) that the two curves have the same slopes in the above-threshold region before and after illumination, indicating that the field-effect mobility is unaffected by the incident light. It is noted that there is a deviation from a straight line at high gate voltage ($V_{GS} < -15$ V). This is related to a rapid increase of gate-leakage current when V_{GS} increases up to a critical value. Here, the saturated field-effect mobility (μ_{sat}) can be calculated using the standard saturation equation $I_D = (WC_i/2L)\mu_{sat}(V_{GS} - V_T)^2$, where V_T is the threshold voltage, C_i is the capacitance per unit area of the gate dielectric layer, and W and L are the channel width and length respectively. The mobility calculated from Fig. 4(b) is about 4.5×10^{-4} cm^2·V^{-1}·s^{-1} for both the dark and light illuminations. In addition, it can be found that V_T shifts from 24 V in the dark to a more positive value of 42 V under light illumination. In the literature, the initial threshold voltage was normally negative due to positively-charged trap states in the organic polymer, and the decrease of the threshold voltage under light illumination was observed in these polymer-based phototransistors and was attributed

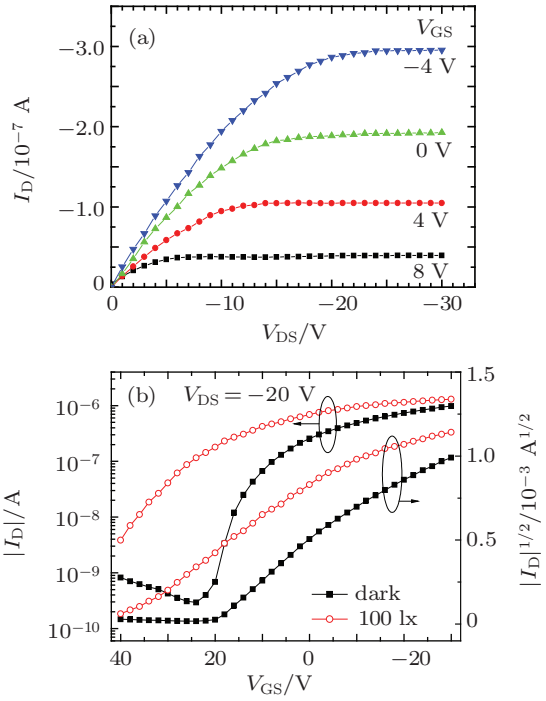


Fig. 4. (colour online) Output characteristics of PTFT in the dark (a) and transfer characteristics of PTFT in the dark and under visible-light illumination of 100 lx at $V_{DS} = -20$ V (b).

to the compensation of positively-charged trap states by photo-generated electrons.[16,17] However, in our devices, the initial threshold voltage is positive due to the effect of air-induced p-type doping on the P3HT polymer during fabrication in air.[15] The threshold voltage moves toward positive voltages as the light intensity becomes higher. This shift is attributed to the enhancement of the hole density in the channel of the device due to photo-generation and dissociation of excitons in the polymer under light illumination, which is similar to the higher intrinsic p-type doping for PTFT devices with a p-type polymer semiconductor resulting in more positive threshold voltage.

Figure 5 shows the transfer characteristics at $V_{DS} = -20$ V for the P3HT PTFTs, measured in the dark and under illumination at various irradiance levels. To study the effect of illumination on the turn-on and turn-off behaviours of these transistors, the drain current is plotted on a logarithmic scale. Two modes of operations can be identified in these curves: one is for the subthreshold region and the other is for the above-threshold region. For the above-threshold mode, the on-state current increases slightly with the increase of illumination intensity and the photosensitivity is only 1.88 at an illumination intensity of 1200 lx and a gate voltage of –20 V, where the photosensitivity is defined as the ratio of photocurrent to dark current (I_{ph}/I_{dark}). However, for the subthreshold mode, the off-state current significantly increases with illumination intensity increasing and the maximum photosensitivity is 1.7×10^3 at the same illumination intensity and a gate voltage of 24 V. The photosensitivity can be further enhanced by using a light source which well matches with the absorption spectrum of the P3HT film. Figure 6 shows the curves of photosensitivity as a function of V_{GS} for various illumination intensities. It is clear from Fig. 6 that the photosensitivity can be tuned by both gate voltage and illumination intensity. For a fixed gate voltage, the photosensitivity increases with illumination intensity increasing. When illumination intensity increases from 100 lx to 1200 lx, the maximum photosensitivity increases from 6.1×10^2 to 1.7×10^3. For a fixed illumination intensity, the change of photosensitivity is about three orders of magnitude from the on-state to the off-state. The results indicate that the device shows a good gate-tuning effect and high photosensitivity even at low illumination intensity, thus it is especially suitable to be used as a photo-detector.

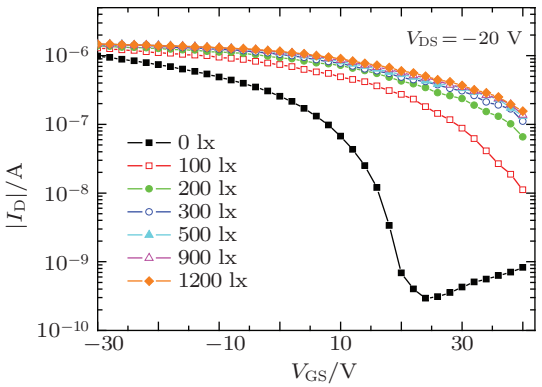


Fig. 5. (colour online) Transfer characteristics of PTFT at $V_{DS} = -20$ V in the dark and under various illumination intensities.

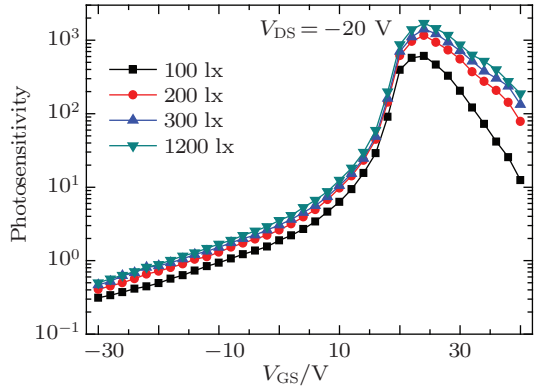


Fig. 6. (colour online) Curves of photosensitivity of PTFT as a function of gate voltage with $V_{DS} = -20$ V for various illumination intensities.

For a PTFT under operation, the drain current is composed of the channel current (I_{CH}) and the bulk current (I_B) as shown in Fig. 7. For the p-type polymer P3HT, when a negative bias ($V_{GS} > V_{th}$) is applied to the gate electrode, the channel is in the accumulation mode; when a positive bias is applied to the gate electrode, the channel is in the depletion or inversion mode. In Fig. 7, R_B and R_{CH} are the bulk and channel resistance. R_S and R_D include the contact resistance plus the parasitic series resistance. The contact resistances originate from the work-function differences between the metal and the polymer semiconductor, respectively, in the source and drain terminals. Since there is negligible nonlinearity near the drain voltage of 0 V for different gate voltages (as shown in Fig. 3(a)), the contact resistance can be neglected for the Au/P3HT contact. However, the parasitic series resistances coming from the narrow depleted or low-mobility region in the vicinity of the source/drain contacts depend on the gate voltage

and drain voltage, and thus cannot be neglected.[18] Therefore, $I_{\rm B}$ and $I_{\rm CH}$ depend on both bias voltages. When the device is in the above-threshold operating mode, the majority carriers in the channel region are gate-induced holes and are confined to a thickness of 1 nm∼2 nm within the semiconductor near the gate-dielectric/polymer interface.[19,20] When light absorption occurs in the p-type P3HT layer, the generation of charge carriers by absorption of photons is based on exciton formation and subsequent dissociation into free electrons and holes.[21] Once generated, these free charge carriers move under the applied electric fields (due to the applied $V_{\rm DS}$ and $V_{\rm GS}$) and in opposite directions through the channel of the PTFT. The photo-generated holes can easily flow to the drain electrode and contribute to the photocurrent, while the photo-generated electrons accumulate under the source electrode to effectively lower the potential barrier between the source and channel, thus causing a reduction in $R_{\rm S}$ and then an $I_{\rm CH}$ increase. On the other hand, photo-generated carriers outside the channel reduce the bulk resistance, giving rise to an increase in $I_{\rm B}$. For the above-threshold region, the bulk current is negligible compared with the channel current, and the number of photo-generated carriers inside the channel under limited illumination intensity are normally less than that of the holes induced under a large gate voltage. So, the relative change of the photocurrent with illumination intensity increasing is small. On the other hand, for the subthreshold region, the channel layer is in depletion mode, and with the increase of positive gate voltage, the depletion layer expands to cover the whole polymer film of 60 nm, resulting in a minimum drain current. When the gate voltage increases, electrons become the majority carriers. At low-level illuminations, the photo-generated holes do not contribute to the drain current because most of the holes recombine with electrons in the channel induced by the gate bias, thus causing a reduction of the depletion layer depth. In this case, the change of photocurrent is dominantly due to the change of intrinsic bulk resistance with the reduction of the depletion layer depth. With illumination intensity increasing, the depletion layer disappears, and the polymer thin film can be regarded as a thin-film resistor. The photo-generated holes contribute to the drain current, resulting in a strong increase in drain current. However, the photocurrent is less than that of the above-threshold region because the photo-generated holes can recombine with the gate-induced electrons in the subthreshold region. Therefore, the high photosensitivity of the PTFT originates from a small off-state current in the dark.

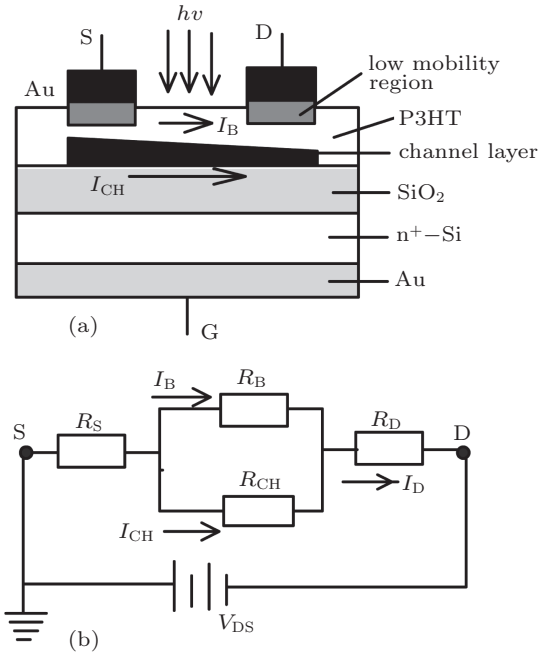


Fig. 7. Proposed operational model of the PTFT: (a) working principle of the device; (b) equivalent circuit.

Figure 8 presents the transfer characteristics of the PTFT after turning off a light illumination of 1200 lx. The drain current decreases rapidly at the beginning and then slowly with time, especially in the subthreshold region. Moreover, the transfer characteristics cannot recover back to its initial state before light illumination even after a time of 13 min, indicating that the detrapping of the trapped charges is a very slow process. It can be explained as follows: there are some defects in the bulk and at the interface of the polymer such as P3HT. The distribution of

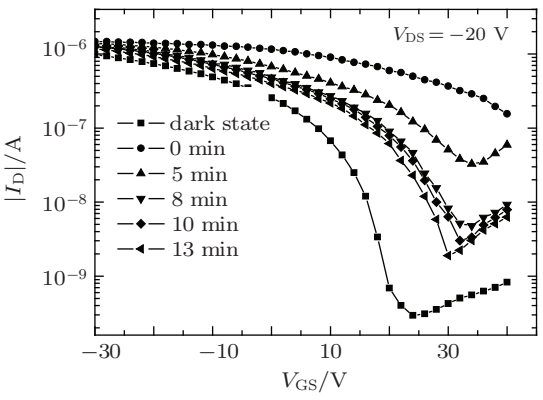


Fig. 8. Transfer characteristics of PTFT at $V_{\rm DS} = -20$ V for various delay times after turning off light illumination of 1200 lx.

trapped photo-carriers depends on the distribution of defects. Photo-generated holes are easily trapped by the lower-energy defects near the interface, but photo-generated electrons are trapped in the deeper-energy states in the polymer bulk,[22] and thus more difficult to detrap.

4. Conclusions

Photo-sensing characteristics of polymer transistors based on a P3HT semiconductor are investigated in the visible-light region. The optical absorption spectrum indicates that the P3HT thin film has superior sensitivity to visible light at room temperature. Upon illumination, a significant increase in drain current of the PTFT is observed in the subthreshold operating mode, with a maximum photosensitivity of 1.7×10^3 at an illumination intensity of 1200 lx. On the other hand, only a slight increase in the drain current appears in the above-threshold operating mode with a low photosensitivity less than 2 at the same illumination intensity. Moreover, the photosensitivity could be tuned by the gate voltage. It is also found that under low illumination intensity, the threshold voltage shifts towards the positive direction, but the field-effect mobility is almost unaffected by the illumination. The drain current decreases gradually with time going by after switching off the light, which is associated with the trapping and detrapping of photo-generated carriers. The results imply that the devices could be used as highly sensitive detectors or sensors in the range of visible light.

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