High-photosensitivity *p*-channel organic phototransistors based on a biphenyl end-capped fused bithiophene oligomer

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We report highly photosensitive organic phototransistors (OPTs) based on a 2,5-bis-biphenyl-4-yl-thieno[3,2-b]thiophene (BPTT). The measured maximum sensitivity and the ratio of photocurrent to dark current (I_{ph}/I_{dark}) in BPTT OPTs were 82 A/W and 2.0×10^5 under 380 nm UV light with 1.55 mW/cm^2, respectively. The prepared OPTs show a photocurrent response similar to the absorption spectrum of BPTT. The major mechanisms for photocurrent amplification in this device were verified from experimental results as photovoltaic (turn-on) and photocurrent effect (turn-off) by a fitting to theoretic equations. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1856144]

Conjugated organic oligomers or polymers have attracted a great deal of interest for use in applications of organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic devices. In particular, the fascinating photodetection characteristics of conjugated organic compounds in the UV or visible region could lead to optoelectronic devices such as photovoltaic cells, photodetectors, or photomodulated OLEDs with a photoconducting layer.[1–3] Among these, phototransistors using organic molecules are viable candidates for optical transducers because they combine light detection and signal amplification properties in a single device without the noise increment associated with avalanche photodiodes.[4,5] A few reports on organic phototransistors (OPTs) have appeared in which an organic conjugated polymer or oligomer is used.[6,7] However, the performances such as photosensitivity, the ratio of photocurrent to dark current (I_{ph}/I_{dark}), and charge carrier mobility of those devices were relatively lower than those for their inorganic counterparts and therefore, needed to be further improved for potential applications. [6–9]

This letter reports on an organic field effect phototransistor with excellent sensitivity and I_{ph}/I_{dark} and a high charge carrier mobility based on theuse of a 2,5-bis-biphenyl-4-yl-thieno[3,2-b]thiophene (BPTT). The measured maximum sensitivity and I_{ph}/I_{dark} in BPTT OPTs are 82 A/W and 2.0×10^5. The mechanisms for photocurrent amplification in OPTs are also discussed in this letter.

The chemical structure of BPTT is shown in Fig. 1. BPTT was synthesized using the Suzuki coupling reaction between 2,5-dibromothieno[3,2-b]thiophene[10] and the corresponding pinacolato boronic ester-substituted biphenyl, analogous to previously described reactions.[11] The semiconducting oligomer was purified by vacuum gradient sublimation before evaporation.[2] A BPTT thin film (~50 nm thick) was deposited onto the SiO_2 (300 nm, 10 nF/cm^2) surface of a heavily doped silicon wafer, used as the gate electrode, at a deposition rate of 0.01–0.04 nm/s and a substrate temperature of 150 °C. A more detailed description of the evaporation process can be found in previous reports.[12,13] After evaporation, the OPTs were completed by evaporating gold through a shadow mask to form source and drain electrodes on the semiconducting thin films in the form of a top contact geometry. This device had a channel length and width of 20 μm and 5 mm, respectively. The characteristics of the OPTs were examined with a KEITHLEY 4200 semiconductor characterization system in the dark or under UV irradiation at a wavelength of 380 nm using a Hamamatsu LC5 instrument in air. All measurements were performed at a constant room temperature of 25 °C.

The field effect mobility (μ_{FET}) and threshold voltage (Vth) of BPTT FETs were obtained following the conventional characterization equation for a FET, as proposed by Horowitz *et al.* for saturation regimes.[14] The calculated μ_{FET},

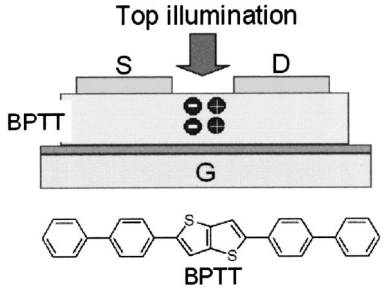

FIG. 1. Cross-sectional view of the OPTs and the molecular structure of BPTT used in this study.

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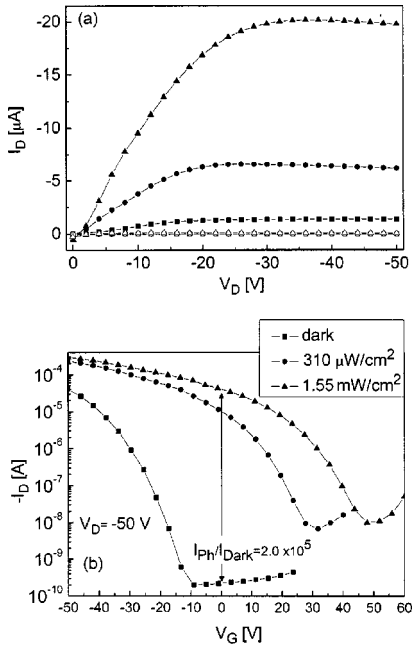

FIG. 2. (a) Output characteristic of OPTs measured in the dark (open symbols) or under UV irradiation (closed symbols) with 1.55 mW/cm^2 at different V_G: closed squares, circles, and triangles were measured at V_G=0, −10, and −20 V under UV light and open squares, circles, and triangles were measured at V_G=0, −10, and −20 V in the dark, respectively. (b) Transfer characteristics of the BPTT OPTs measured in the dark (closed squares) or under UV with 310 μW/cm^2 (closed circles) and 1.55 mW/cm^2 (closed triangles) at V_D=−50 V.

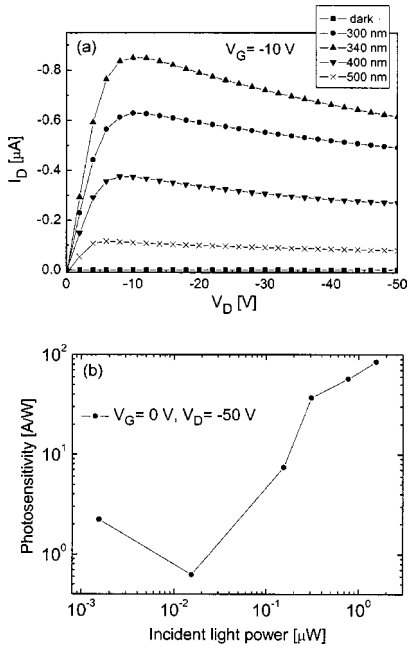

FIG. 3. (a) Output characteristic of BPTT OPTs measured in the dark or under a monochromatic light with different wavelengths at V_G=−10 V. (b) The BPTT OPTs photosensitivity as a function of incident optical power with V_G=0 V and V_D=−50 V.

the current ratio of the on and off state (I_{on}/I_{off}), and V_{th} obtained by plotting I_D and $I_D^{1/2}$ versus V_G were 0.082 cm^2 V^{-1} s^{-1}, 2.0×10^5, and −29 V, respectively. The output and transfer characteristics of the BPTT devices were measured under UV light with top illumination, as shown in Fig. 1.

Figure 2(a) shows the output characteristics of a BPTT device in the dark or under UV irradiation with 1.55 mW/cm^2. The OFETs, measured under UV irradiation, showed that the maximum drain current (I_D) increases up to about 20 μA at V_G=−20 V with well-formed saturation. When measured in the dark, the device showed a maximum I_D in the sub-microampere region because the device was in a turn off state in the V_G. A number of charge carriers are generated when light with a photon energy equal to or higher than the BPTT band-gap energy is absorbed, thus leading to the I_D increase. This indicates that light can play a role as an additional terminal that optically controls device operation with conventional third terminals, source, drain, and gate electrodes.[5]

Figure 2(b) shows the transfer characteristics of BPTT FETs in the dark or under UV irradiation with different powers at V_D=−50 V. The I_{ph}/I_{dark} was obtained at V_G=0 V in order to exclude the effect of electrically induced hole carriers by the gate electrode. The maximum I_{ph}/I_{dark} was 2.0×10^5 and that for all measured devices were typically greater than 10^4 under UV light with 1.55 mW/cm^2. This excellent I_{ph}/I_{dark} is 100 times greater than previous reported values for OPTs, even for amorphous silicon.[6–8] The transfer curves for the BPTT OPTs showed a V_{th} shift with increasing incident optical power. This V_{th} shift can be attributed to the well-known photovoltaic effect by the accumulated electrons in inorganic PTs.[4,5] When absorption occurs in the *p-type* BPTT channel, photogenerated holes easily flow to drain electrode whereas photogenerated electrons accumulate under the Au source electrode. These accumulated electrons effectively lower the potential barrier between the source and the channel. The measured highest occupied molecular orbital level of the BPTT was 5.5 eV, which actually provides an injection barrier for hole carriers from the Au source electrode with a work function of 5.1 eV. The lowered injection barrier induced by light irradiation results in an effective decrease in V_{th} and a significant increase in I_D.[15]

Figure 3(a) demonstrates the output characteristics of BPTT FETs in the dark or under light with a different photon energy, produced by an optical monochromator. The incident light intensity was 0.25 mW/cm^2. The largest I_D was obtained for the case where the device was measured under light with a wavelength of 340 nm because this wavelength corresponds to a maximum absorbance in a BPTT film. Other I_D responses with different photon energies also depended on the intensity of the absorbance, in other words, the extinction coefficient of a BPTT film. When the OPTs were irradiated by light with a photon energy below 520 nm, I_D did not increase compared to the case of the dark device since the photon energy is lower than the band-gap energy (~500 nm) of BPTT. The photosensitivity of BPTT OPTs was calculated as a function of incident light powers as shown in Fig. 3(b). The photosensitivity increased with incident light power. The calculated maximum photosensitivity was 82 A/W. Although this sensitivity is lower than that of amorphous silicon (300 A/W), it is around 100 times higher than those of previously reported organic OPTs with polythiophene derivatives or an organic glass based on a spirocompound using an intermolecular charge transfer mechanism.[6–8]

It is known that two different effects i.e., *photoconductive and photovoltaic effects*, occur in an active semiconductor layer as the result of photoirradiation for inorganic

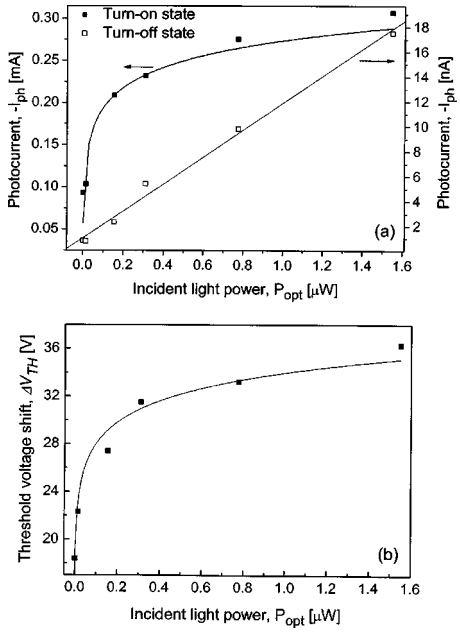

FIG. 4. (a) Photocurrent as a function of incident light power under turn-on ($V_G=-50$ V, closed squares) and turn-off (minimum I_D, open squares) states at $V_D=-50$ V. (b) The threshold voltage shift as a function of incident light power of the BPTT OPTs. Symbols denote measured data points and the solid lines indicate fitted results using Eqs. (1) and (2).

phototransistors.[4,5] When the device is in the turn-on state ($V_G > V_{\text{th}}$), the photovoltaic effect is significant because photovoltage is induced by the large number of accumulated electrons under the source. When the device is in the turn-off state ($V_G < V_{\text{th}}$), the I_D shows a relatively small increase with optical power due to a photoconductive effect. The photocurrent caused by photovoltaic effect can be expressed as[16]

$$I_{\text{ph,pv}} = G_M \Delta V_{\text{th}} = \frac{AkT}{q} \ln\left(1 + \frac{\eta q \lambda P_{\text{opt}}}{I_{\text{pd}} hc}\right) \tag{1}$$

where η is the quantum efficiency, P_{opt} the incident optical power, I_{pd} the dark current for electrons, hc/λ the photon energy, G_M the transconductance, ΔV_{th} the threshold voltage shift, and A the fitting parameter. The photocurrent induced by a photoconductive effect in device turn-off state can be describe as[17]

$$I_{\text{ph,pc}} = (q\mu_p pE)WD = BP_{\text{opt}}, \tag{2}$$

where μ_p is the hole mobility, p the hole concentration, E the electrical field in the channel, W the gate width, D the depth of absorption region, and B the fitting parameter. In Fig. 4(a), I_{ph} are plotted as a function of incident optical powers at the device turn-on state ($V_G=-50$ V, $V_D=-50$ V) and turn-off state (V_G was selected at the minimum I_D, $V_D=-50$ V). The symbols denote measured data points and the solid lines indicate fitted results using Eqs. (1) and (2). The well-fitted line indicates that OPTs based on the conjugated oligomer also follow the photovoltaic effect in the turn-on state and the photoconductive effect in the turn-off state the same as for inorganic counterparts. Moreover, Fig. 4(b) shows the measured threshold voltage shift as a function of incident optical power on the same device and the fitted one using Eq. (1). The well-fitted curve also indicates that the device follows the photovoltaic effect in the device turn-on state.

Finally, we measured OPTs with copper phthalocyanine (CuPC) as a *p*-type organic semiconductor to confirm the high performance of BPTT OPTs. CuPC molecules were evaporated at a substrate temperature of 150 °C and the measured μ_{FET} and V_{th} was 0.021 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ and −15.3 V, respectively. The device, under the same UV lamp irradiation, showed a maximum sensitivity and $I_{\text{ph}}/I_{\text{dark}}$ of 2 A/W and 2.8×10^3, respectively. This indicates that the high performance of BPTT OPTs might be obtained from their intrinsic material properties such as excellent photoinduced charge generation properties of that material and a nice performance of BPTT FETs. Two requirements should be simultaneously fulfilled, for high performance OPTs to be produced. First, the performance of OFETs must be good in the absence of irradiation of light. In previous studies, the performances of OFETs for OPTs were reported to be relatively worse than pentacene or thiophene devices.[6,7] The next requirement is that an organic semiconductor having good photocurrent conversion efficiency must be used. We selected the BPTT molecule based on these requirements. A more detailed report on structure–property relationships with more extended conjugated organic semiconductors will appear in our next publication.

In conclusion, we fabricated high photosensitive organic phototransistors based on a biphenyl end-capped fused bithiophene (BPTT) oligomer. The device showed excellent photosensitivity and $I_{\text{ph}}/I_{\text{dark}}$ of 82 A/W and 2.0×10^5. Moreover, the BPTT FETs showed a high UV stability even after 6 h of strong irradiation with an intensity of 50 mW/cm^2. We expect that the BPTT OPTs could be used in highly sensitive UV detectors or sensors.

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