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

Yong-Young Noh and Dong-Yu Kim
Center for Frontier Materials, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1 Oryong-Dong, Buk-Gu, Gwangju 500-712, Republic of Korea

Yuji Yoshida and Kiyoshi Yase
Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Byung-Jun Jung, Eunhee Lim, and Hong-Ku Shim
Center for Advanced Functional Polymers, Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

(Received 18 June 2004; accepted 29 November 2004; published online 18 January 2005)

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 (Iph/Idark) 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.

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 photosensitive layer. 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. A few reports on organic phototransistors (OPTs) have appeared in which an organic conjugated polymer or oligomer is used. However, the performances such as photosensitivity, the ratio of photocurrent to dark current (Iphp/Idark), 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.

This letter reports on an organic field effect phototransistor (OPT) with excellent sensitivity and a high charge carrier mobility based on the use of a 2,5-bis-biphenyl-4-yl-thieno[3,2-b]thiophene (BPTT). The measured maximum sensitivity and Iphp/Idark 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 and the corresponding pinacolato boronic ester-substituted biphenyl, analogous to previously described reactions. The semiconductor-photodetecting oligomer was purified by vacuum gradient sublimation before evaporation. A BPTT thin film (~150 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.

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 (μFET) 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. The calculated μFET,

FIG. 1. Cross-sectional view of the OPTs and the molecular structure of BPTT used in this study.
the current ratio of the on and off state \((I_{on}/I_{off})\), and \(I_{th}\) obtained by plotting \(I_D\) and \(I_{D}^{1/2}\) versus \(V_G\) were 0.082 cm² V⁻¹ s⁻¹, \(2.0 \times 10^5\), 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/cm². The OFETs, measured under UV irradiation, showed that the maximum drain current \((I_D)\) increases up to about 20 \(\mu\)A 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.²

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 \(\times 10^5\) and that for all measured devices were typically greater than \(10^4\) under UV light with 1.55 mW/cm². 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/cm². 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 OPTs.⁴⁻⁵
phototransistors. When the device is in the turn-on state \((V_G>V_D)\), the photovoltaic effect is significant because photovoltaic is induced by the large number of accumulated electrons under the source. When the device is in the turn-off state \((V_G<V_D)\), 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

\[
I_{ph,pv} = G_M\Delta V_{th} = \frac{A k T}{q} \ln \left( 1 + \frac{\eta \hbar \lambda P_{opt}}{I_{pd} hc} \right)
\]

where \(\eta\) is the quantum efficiency, \(P_{opt}\) the incident optical power, \(I_{pd}\) the dark current for electrons, \(\hbar\lambda\) the photon energy, \(G_M\) the transconductance, \(\Delta V_{th}\) 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

\[
I_{ph,pc} = (\mu_{pd} P) W D = BP_{opt}
\]

where \(\mu_{pd}\) 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 \((V_G=-50\text{ V}, V_D=-50\text{ V})\) and turn-off state \((V_G=50\text{ V}, V_D=50\text{ V})\). The symbols denote measured data points and the solid lines indicate fitted results using Eqs. (1) and (2).

In conclusion, we fabricated high photosensitive organic phototransistors based on a biphenyl end-capped fused bithiophene (BPTT) oligomer. The device showed excellent photosensitivity and \(I_{ph}/I_{dark}\) of 82 A/W and \(2.0 \times 10^3\). Moreover, the BPTT FETs showed a high UV stability even after 6 h of strong irradiation with an intensity of 50 mW/cm². We expect that the BPTT OPTs could be used in highly sensitive UV detectors or sensors.

The authors wish to thank Dr. K. Hara and Dr. S. Nagamatsu (AIST) for fruitful discussion. This work was financially supported by the Ministry of Education of Korea through BK21 program (GIST) and Center for Advanced Functional Polymers (CAFPoly) through KOSEF (KAIST), respectively. Y.Y.N. was supported by the Korea Science and Engineering Foundation (KOSEF) for visiting research at AIST.