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Photoresponsivity of polymer thin-film transistors based on polyphenyleneethynylene derivative with improved hole injection

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The photoresponse of polymer field-effect transistors (PFETs) based on the 2,5-bis(dibutylaminostyryl)-1,4-phenylene-*b*-alkyne-*b*-1,4-bis(2-ethylhexyl)benzene terpolymer (BAS-PPE) is investigated. BAS-PPE is a photoluminescent conducting polymer with a band gap of 2.25 eV. The BAS-PPE PFETs were fabricated using an open coplanar configuration and light is illuminated onto the top side of the PFETs with no shadowing present. A sweep of V_{DS} demonstrates that I_{DS} saturation is suppressed during illumination, which suggests that pinch-off cannot be reached since the injected photogenerated carriers continue unabated. Also, with incident light, the channel cannot be turned off, even at high positive gate biases, due to the accumulation of photogenerated carriers. A sweep of V_{DS} shows that BAS-PPE can act as a *p*-type polymer and favors hole injection and transport. A sweep of V_{GS} shows an increase in I_{DS} with different light intensities. The I_{light}/I_{dark} ratio reaches as high as about 6000 at an incident light intensity of 4 μW and a photoresponsivity of 5 mA/W is calculated. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1812834]

Conjugated polymers have shown great promise as polymer light emitting diodes (PLEDs) and polymer field-effect transistors (PFETs).[1–7] Shortly after the discovery of polymer light emitting diodes, the light detecting properties of polymer diodes were reported.[8–11] There have not been many reports on light responsive PFETs, but Narayan and Kumar have demonstrated light responsive behavior in PFETs based on regioregular poly(3-octylthiophene-2,5-diyl) (P3OT).[12]

As the dehydrogenated congener of polyphenylenevinylene (PPV), polyphenylene-ethynylene (PPE) did not receive as much attention in the early boost of semiconductor polymer research due to its low highest occupied molecular orbital (HOMO) level.[13,14] However, PPEs show high thermal, oxidative and photostability which makes them attractive for solid state devices. The introduction of cross conjugated PPEs has allowed the manipulation of the parent PPE band gap through the PPV side chain. Thus, the 2,5-bis(dibutylaminostyryl)-1,4-phenylene-*b*-alkyne-*b*-1,4-bis(2–ethylhexyl)benzene terpolymer (BAS-PPE) should demonstrate the combined advantages of both PPV and PPE [Fig. 1(a)].

The maximum and minimum electrochemical band gaps for BAS-PPE are 2.43 and 1.50, ideal for visible light absorption and emission. When BAS-PPE is incorporated into polymer field-effect transistors (PFETs) as the active semiconductor film, it is observed that the BAS-PPE based PFETs are light responsive. The drain-source current I_{DS} is largely increased with incident light. Similar I_{DS} amplification under light illumination has been reported in metal-oxide-semiconductor field-effect transistors, metal-semiconductor field-effect transistors, and other polymer based FETs.[15–19] The working mechanism of light responsive FETs is that light generated electron-hole pairs form either a photocurrent or a photovoltage which in turn enlarges I_{DS}.

For the P3OT light responsive PFETs by Narayan and Kumar, the effect of light illumination from the gate side was attributed to be equivalent to an external gate bias.[12] On the other hand, Narayan and Kumar also remarked that the I_{DS} amplification in light responsive PFETs is analogous to a lateral bipolar action, when light generated holes enter the

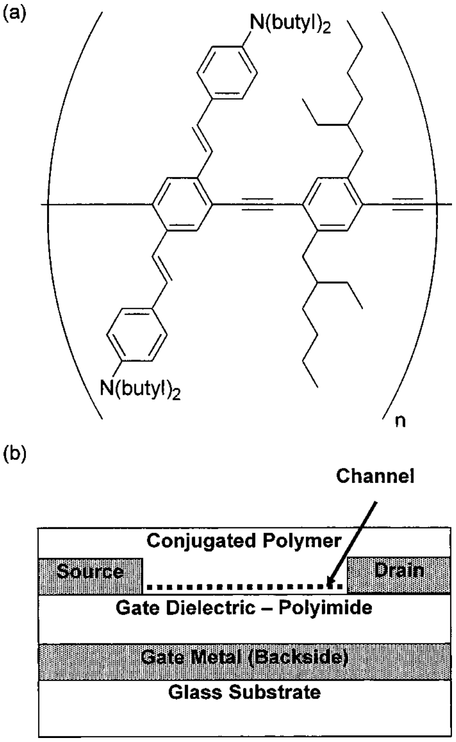

FIG. 1. The (a) chemical structure of BAS-PPE and (b) the schematic of BAS-PPE PFETs.

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channel while electrons stay in the bulk and form a voltage bias against the source.[12] In this letter, we examine the photosensitivity of BAS-PPE PFETs. Light intensity greatly elevates I_{DS}. The ratio of I_{DS} in light and under darkness (I_{light}/I_{dark}) also increases significantly with light intensity. Gate bias also impacts the I_{light}/I_{dark} ratio.

In this work, BAS-PPE PFETs were constructed using a coplanar configuration, as shown in Fig. 1(b). Fabrication commenced by depositing gold as the gate metal on a glass substrate. A commercially available polyimide (HD MicroSystems) was used as the gate dielectric. The polyimide was spin coated on top of the gold gate from solution and then cured by soft baking at 200 °C for 30 min and hard baking at 350 °C for 1 h. The thickness of the gate dielectric was determined to be 1 μm by Dektak profilometry. A thick gate dielectric ensures that no electrical breakdown occurs even at high gate voltages. Interdigitated source and drain electrodes were defined by standard liftoff photolithography. BAS-PPE PFETs with a range of sizes were built with the dimensions of the PFETs denoted by $W \times (L \times n)$. The gate length, L, ranged from 1 to 7 μm, and the gate width, W, varied from 10 to 75 μm. The number of channels n was chosen so that the overall shape of the interdigitated area was approximately a square. After the source and drain contact metal was defined by light-off, the BAS-PPE is applied in solution from (about 2% w/w in the solvent toluene) by spin coating at 5000 rpm for 30 s. The thickness of the resulting BAS-PPE film is determined to be about 40 nm. The BAS-PPE PFETs were characterized with an Agilent HP 4156 semiconductor parameter analyzer using a Cascade probe station. White light illumination is provided by an incandescent light bulb. The incident light is normal to the top side of the sample. Overall light intensities were controllably varied by filtering the light source with a neutral density filter set without modification of the spectral output. Spectral analysis of the white light showed a broad output from approximately 400 to 800 nm and a peak wavelength of 600 nm, which was assumed for photoresponsivity calculation.

Figure 2 shows the $I-V$ characteristics of a BAS-PPE PFET with a 75 μm $\times$ (3 μm $\times$ 12) channel dimension. It is demonstrated that the terpolymer BAS-PPE works successfully as the semiconductor channel in PFETs. A sweep of V_{DS} shows that BAS-PPE can work as a *p*-type semiconductor. The barrier for hole injection is largely reduced by cross conjugation with the electron donating dibutylaminostyryl substituents: the HOMO level varies between 5.1 and 5.5 eV in the BAS-PPE samples studied to date.[13]

The electrical measurements under illumination also clearly indicate a strong dependence on overall incident light intensity for the BAS-PPE PFETs. A much higher value of I_{DS} is obtained under strong light illumination than under darkness. With incident light, the gate voltage still has a slight modulation on the conductance of BAS-PPE PFETs, but saturation of I_{DS} is suppressed during strong illumination. The lack of saturation region suggests that pinch-off cannot be reached due to persistent photogeneration in the channel. However, in previously reported P3OT PFETs, saturation was observed under illumination.[12] The difference in the saturation region could be caused by the disparate device configuration of the PFETs. The P3OT PFETs utilize a staggered configuration, or top contact configuration, while the BAS-PPE PFETs studied here used a coplanar, or bottom contact, configuration. It can be assumed that in a staggered configuration, photoillumination can be shadowed by source/drain electrodes so that only the channel area is illuminated. On the other hand, PFETs in a coplanar configuration will not shadow the illuminated region and light is concurrently incident on the channel and the source/drain contacts. Therefore, the semiconductor polymer has a much larger effective collection region.

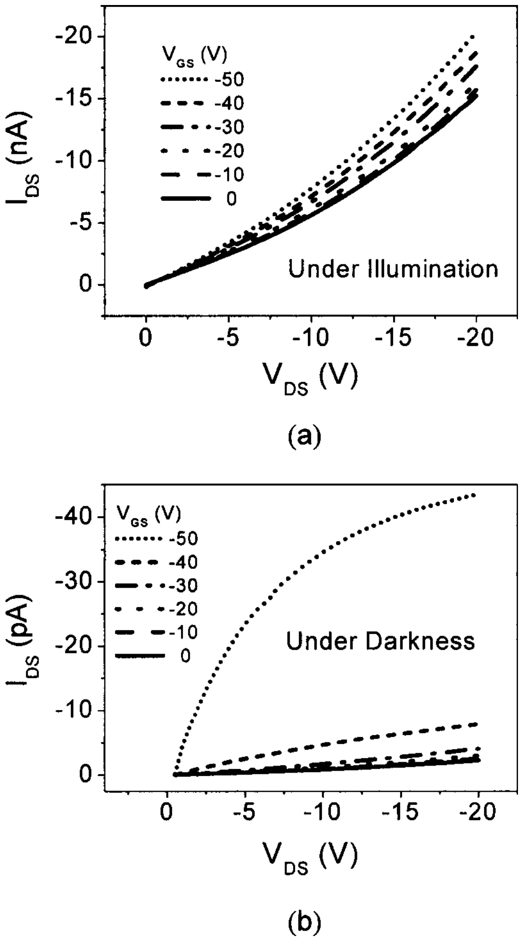

FIG. 2. $I_{DS}-V_{DS}$ of BAS-PPE PFETs with $75 \times (3 \times 12)$ gate lengths under (a) illumination, and (b) darkness.

For the BAS-PPE PFETs studied with incident light, the channel cannot be turned off, even at high positive gate biases. The number of thermally generated carriers should be small compared to the photogenerated carriers when the light is incident, so that the current at zero gate bias is mostly attributed to light generation in and near the channel region. Figure 3(b) illustrates that BAS-PPE has a relatively low current carrying capability under darkness, and that the saturation region is clearly present without the influence of light.

A sweep of V_{GS} demonstrates an increase in I_{DS} with different light intensities [Fig. 3(a)]. It is observed that the dependence of I_{DS} on gate bias becomes weaker as the light intensity increases, coincident with P3OT PFETs. This phenomenon indicates that light generated carriers are less restricted by gate bias. Light generated carriers can reach the drain electrode from the channel, but they can still be collected at the drain without going through the channel because they are created throughout the bulk semiconductor polymer. As the population of light generated carriers surpasses the number of source injected carriers, the gate bias gradually loses its ability to modulate the channel conductivity.

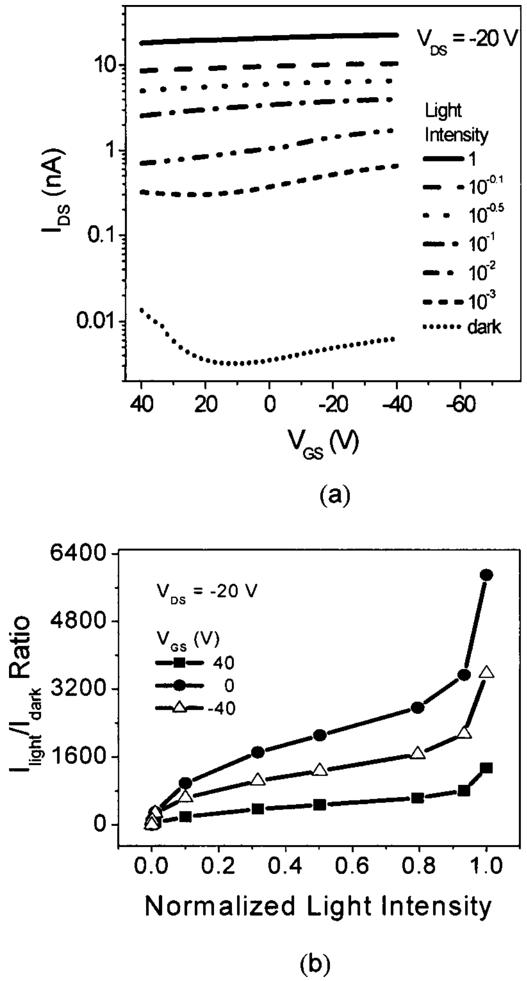

FIG. 3. The effect of light intensity on BAS-PPE PFETs (a) $I_{DS}-V_{GS}$ of BAS-PPE PFETs at varying light intensities and (b) I_{light}/I_{dark} ratio vs light intensity.

The intensity of the incandescent light source peaks at 600 nm, so the intensities of the incident light are measured with a calibrated Si photodetector assuming this wavelength. The peak light intensity used in this experiment is set to correspond to the light intensity of 16 mW. The lower filtered intensities are normalized to the highest intensity. The approximate size of the incident light spot is about 5 mm in diameter. The samples tested have an active area of 75 $\times 75$ μm^2, which equates to an approximate incident optical power of 4 μW. The photoresponsivity in the BAS-PPE PFETs is calculated to be about 5 mA/W. Figure 3(b) shows I_{light}/I_{dark} ratio increases with higher lift intensities. At zero gate bias, the highest I_{light}/I_{dark} ratio reaches as high as about 6000 at an incident light intensity of 4 μW.

The cross-conjugated polymer BAS-PPE enables successful engineering of HOMO level to favor hole injection, which ensures its performance as a *p*-type PFETs. In addition, BAS-PPE PFETs are greatly light sensitive whereby a much larger I_{DS} is measured under light illumination than under darkness. Gate bias still modulates I_{DS} in the presence of incident light, but the dependence of I_{DS} on gate bias is weakened with the increase of light intensity. The weaker effect of V_{GS} at higher light intensity can be explained by the large amount of photogenerated carriers outside the channel. It is observed that not only I_{DS}, but also the ratio of I_{light}/I_{dark}, increase with light intensity. Comparing the data at V_{GS} of −40, 0, and 40 V, it is found that the highest I_{light}/I_{dark} ratio occurs at zero gate bias, probably due to the lowest dark current at this point among the three gate bias.

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