Characteristics of light-induced electron transport from P3HT to ZnO-nanowire field-effect transistors

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We fabricated ZnO-nanowire (NW) field-effect transistors (FETs) coated with poly (3-hexylthiophene) (P3HT) and characterized the electron-transfer characteristics from the P3HT to the ZnO NWs. Under irradiation by laser light with a wavelength of 532 nm, photo-induced electrons were created in the P3HT and then transported to the ZnO NWs, constituting a source-drain current in the initially enhancement-mode P3HT-coated ZnO-NW FETs. As the intensity of the light increased, the current increased, and its threshold voltage shifted to the negative gate-bias direction. We estimated the photo-induced electron density and the electron-transfer characteristics, which will be helpful for understanding organic-inorganic hybrid optoelectronic devices. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4833544]

Hybrid organic-inorganic optoelectronic devices, such as polymer solar cells (SCs) and light-emitting diodes (LEDs), have attracted considerable scientific interest in recent years because organic and inorganic nanomaterials aim to integrate the advantages of both classes of materials.[1–6] For example, hybrid organic-inorganic SCs can achieve direct and ordered paths to the collecting electrode for photo-induced charge, corresponding to the improvement of the exciton-diffusion efficiency and the charge-collection efficiency.[7,8] In particular, a one-dimensional nanowire (NW) can serve as a continuous electron-transport pathway in hybrid SCs of NWs and polymers. To demonstrate efficient charge transfer, Olson *et al*. have investigated polymer/nanostructure hybrid devices with poly(3-hexylthiophene) (P3HT) and ZnO NWs.[9,10] Bi and LaPierre have reported GaAS NW hybrid devices with various polymers, including P3HT, chlorobenzene (CB), and ortho-dichlorobenzene (ODCB).[11] The efficient charge transfer from the organic material to the inorganic material is likely to determine the performance of such hybrid devices. Therefore, a detailed understanding of the electron-transfer characteristics is important in such devices.

In this study, we fabricated ZnO-NW field-effect transistors (FETs) that were coated with a P3HT layer and investigated the charge-transfer characteristics from the P3HT to the ZnO NWs. Under irradiation by laser light with a 532-nm wavelength, photo-induced electrons were created in the P3HT and then transported to the ZnO NWs, which resulted in a source-drain current flow at zero gate bias in the originally enhancement-mode P3HT-coated ZnO-NW FETs. As the light intensity increased, the photo-induced electrons increased proportionally, and the threshold voltage shifted in the negative gate-bias direction. We also measured the time-resolved photo-current of the P3HT-coated ZnO-NW FETs and characterized the rise and decay times. Our study will be helpful in estimating the density of transported photo-induced electrons or holes and in understanding the transportation mechanism between organic and inorganic materials.

The ZnO NWs in this study were grown on c-plane sapphire coated with a gold thin film as the catalyst using a carbothermal reduction process. The details of the nanowire growth have been reported elsewhere.[12] A high-resolution transmission electron microscopy (HRTEM) image of a ZnO NW and the chemical structure of the P3HT layer are shown in Fig. 1(a). The ZnO NWs were dispersed in isopropyl alcohol by sonication and dropped onto a silicon wafer to fabricate the ZnO-NW FETs, as schematically shown in Fig. 1(a). A 100-nm-thick, thermally grown SiO_2 layer was used as a gate insulator on a heavily doped p-type silicon substrate. Metal electrodes consisting of Ti/Au (30/50 nm) were deposited on the ZnO NWs with an electron beam evaporator and patterned as source and drain electrodes via a photolithography process. Then, to ensure that the P3HT was coated only on the ZnO-NW surface, the source and drain electrodes were selectively isolated with SiO_2 layers by using the magnetron sputtering process. As the metal electrodes were isolated from the P3HT, the photo-induced electrons from the P3HT layer could only pass into the ZnO NW; they could not be transported to the metal electrodes. A more detailed explanation is provided with schematics of device fabrication process in the supplementary material.[13] The optical and scanning electron microscopy (SEM) images in Fig. 1(b) show the isolated structure of the ZnO-NW FETs.

Figure 1(c) shows the energy-level diagram of the individual layers. From this diagram, electron transfer from the P3HT to the ZnO NWs can be expected. The charge-transfer processes occur in three steps: (1) the photo-generation of

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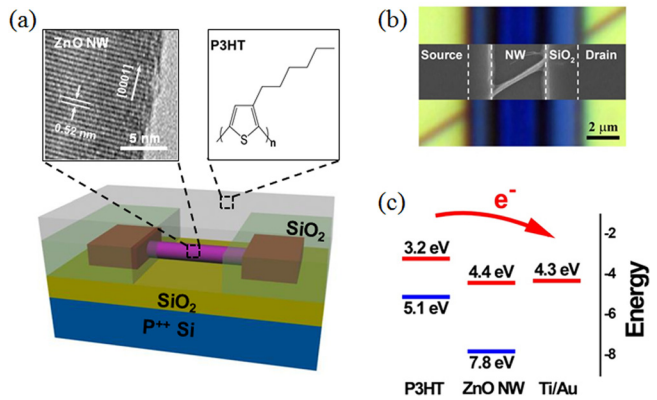

FIG. 1. (a) Schematic diagram of the structure of the P3HT-coated ZnO-NW FETs. The upper left image is a HRTEM image of a ZnO NW, and the upper right image is the chemical structure of P3HT. (b) Optical and SEM images of a P3HT-coated ZnO-NW FET. (c) Energy-level diagram of a P3HT-coated ZnO-NW FET.

electron-hole pairs (i.e., excitons) at the P3HT layer with light irradiation, (2) the migration or diffusion of the electrons that are transported to the ZnO NWs, and (3) the collection of the photo-induced electrons at the drain electrode via the ZnO NWs. Shaw *et al*. have reported that the excitons produced in P3HT have a diffusion length of ~8.5 nm.[14] From the energy-level diagram (Fig. 1(c)), it can be seen that the photo-induced electron-hole pairs can be separated and migrate to opposite electrodes. The photo-induced electrons can be easily transported from the P3HT to the ZnO NWs and eventually to the drain electrode. In contrast, the photo-induced holes are blocked by the ZnO NWs because of the high hole-barrier potential. Finally, the drain current is created by the transport of the photo-induced electrons from the P3HT to the ZnO NWs.

Figure 2(a) displays a series of transfer characteristics (source-drain current versus gate voltage, I_{DS}-V_G) for a P3HT-coated ZnO-NW FET at a fixed drain voltage of 4 V under light illumination with various light intensities (dark, 0.9, 15.0, 43.4, 75.2, and 107.0 mA/cm^2). The wavelength of 532 nm was chosen for the laser light (DPGL-2100 532 nm, PHOTOP Technologies, Inc.) because it excites the P3HT layer but not the ZnO NWs (because of the wide band gap of 3.4 eV).[9] We indeed fabricated and characterized ZnO-NW FET without P3HT layer as a reference device, and we did not observe any noticeable illumination effect (see the results in the supplementary material[13]). To perform a systematic and accurate comparison with various light intensities, we sequentially measured the electrical characteristics on the same P3HT-coated ZnO-NW FET. As the light intensity was increased, the photo-induced electrons also increased, causing the threshold voltage to shift toward the negative gate-bias direction, which corresponds to the enhancement of the electrical conductivity of the ZnO-NW FET. The threshold voltage of the ZnO-NW FET was determined by extrapolating the linear portion of the maximum slope to the zero drain current; here, the point of maximum slope is the point at which the transconductance ($g_m = dI_{DS}/dV_G$) is maximal. The charge density of the P3HT-coated ZnO-NW FET can be calculated from[12]

$$n_e = \frac{Q_{tot}}{e\pi r^2 L}, \tag{1}$$

where Q_{tot} is the total charge in the NWs ($Q_{tot} = C_G|V_G - V_{th}|$), where C_G is the gate capacitance. The gate capacitance C_G can be estimated from the model of a cylinder on an infinite metal plate to be $C_G = 2\pi\varepsilon_0\varepsilon_r L/\cosh^{-1}(1 + h/r)$; here, r is the NW radius (~50 nm), L is the NW channel length (~4 μm), h is the SiO_2 thickness (~100 nm), ε_0 is the permittivity of vacuum, and ε_{SiO2} is the dielectric constant of SiO_2 (~3.9).

The threshold voltage and charge density of the P3HT-coated ZnO-NW FET were determined to be 11.8 V and 2.1×10^{17} cm^{-3}, respectively, in dark conditions (with no light illumination) and 1.5 V and 8.9×10^{17} cm^{-3}, respectively, for light illumination with an intensity of 107.0 mA/cm^2. Note that the charge density was calculated at an arbitrarily chosen gate bias of 15 V, at which the device has a certain current and charge density under all the different light intensities that we applied. The difference in the charge density between dark conditions and light illumination with an intensity of 107.0 mA/cm^2 was 6.8×10^{17} cm^{-3}, which is the concentration of photo-induced electrons. However, considering the electron-transport loss from the P3HT to the ZnO NWs, the true photo-generated-electron density of the P3HT could be larger than this value. The electronic parameters (threshold voltage and charge density) of the P3HT-coated ZnO-NW FET are summarized in Table I.

Figure 2(b) shows a series of output characteristics (source-drain current versus source-drain voltage, I_{DS}-V_{DS}) for the P3HT-coated ZnO-NW FET at a fixed gate voltage of 2 V under light illumination with various light intensities

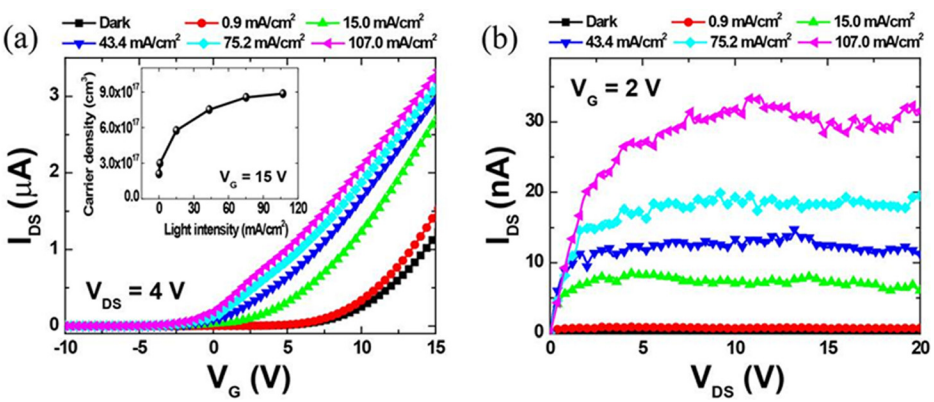

FIG. 2. (a) I_{DS}–V_G curves and (b) I_{DS}-V_{DS} curves for the P3HT-coated ZnO-NW FET under various light intensities (dark, 0.9, 15.0, 43.4, 75.2, and 107.0 mA/cm^2). The inset of (a) shows the photo-induced charge density as a function of the light intensity at $V_G = 15$ V.

TABLE I. Summary of the threshold voltage (V_{th}) and photo-induced charge density of the P3HT-coated ZnO-NW FET under various light intensities.

Light intensity (mA/cm^{-2})	Dark	0.9	15.0	43.4	75.2	107.0
V_{th}(V)	11.8	10.4	6.2	3.5	2.0	1.5
Charge density (cm^{-3} at $V_G = 15$ V)	2.1×10^{17}	3.0×10^{17}	5.8×10^{17}	7.5×10^{17}	8.6×10^{17}	8.9×10^{17}

(dark, 0.9, 15.0, 43.4, 75.2, and 107.0 mA/cm^2). The output characteristics exhibit well-defined linear behavior at low bias and saturation behavior at high bias, indicating the typical characteristics of an n-type semiconductor FET. The electrical conductance increased with increasing light intensity; for example, the drain current measured at $V_{DS} = 10$ V and $V_G = 2$ V increased from 0.4 nA under dark conditions to 31.8 nA under a light intensity of 107.0 mA/cm^2.

To investigate the photocurrent response, the electronic characteristics of the P3HT-coated ZnO-NW FET were measured at fixed $V_G = 0$ V and $V_{DS} = 4$ V, as shown in Fig. 3(a). Here, $V_G = 0$ V was chosen because in this case, no drain current exists under dark conditions, but it appears under light illumination; in other words, the photo-induced electrons from the P3HT create the drain current under light illumination. From the time-resolved photocurrent-response measurement, we can estimate the rise and decay times of the photo-induced charge. Figure 3(b) shows the result of the photocurrent-response measurement in the case of light illumination (107.0 mA/cm^2). The lifetime of the photo-induced charge (τ) is directly related to the intrinsic properties of the NWs; it can be attributed to the large surface-to-volume ratio and the formation of deep-level surface states on the NWs. The rise-time constant (τ_r) and the decay-time constant (τ_d) of the photocurrent are expressed as simple exponential functions of the following form:[15]

$$I_{ph}(t) = I_{ph}(1 - e^{-t/\tau_r}), \tag{2}$$

$$I_{ph}(t) = I_{ph}e^{-t/\tau_d}, \tag{3}$$

where I_{ph} is the photocurrent after light illumination. As the light intensity was increased, the photocurrent also increased, indicating a large amount of electron generation under light illumination. For metal-oxide NWs, the photocarrier relaxation consists of two decay processes: a fast decay process, which can be explained by the fast carrier thermalization and hole-trapping by the NW surface states, in a time frame on the order of nanoseconds and a slow decay process, which depends on the surrounding gases and the NW surface coating, in a time frame on the order of seconds.[16,17] This slow decay process dominates the final response of NW-based photodetectors. However, as shown in Fig. 3(b), in the P3HT-coated ZnO-NW FET under a light intensity of 107.0 mA/cm^2, the time-resolved drain current did not exhibit exponential decay characteristics. When the light was turned on and off, the drain current was abruptly increased and decreased within a second, i.e., the rise time and the decay time was a second. These second-long rise and decay times for the P3HT-coated ZnO-NW FET are considered to constitute fast photoresponse for a ZnO-NW FET because reported response times in ZnO-NW FETs are typically a few seconds or even greater than hundreds of seconds.[15,17–20] A more detailed explanation will be provided alongside the schematic illustration of the P3HT-coated ZnO-NW FET, as shown in Fig. 4.

Figure 4 illustrates the electron-transport mechanism of the P3HT-coated ZnO-NW FET under light illumination. Our P3HT-coated ZnO-NW FET behaved as an n-channel enhancement-mode (E-mode) FET that had zero drain current at zero gate bias with a positive threshold voltage. The P3HT-coated ZnO-NW FET exhibits a photovoltaic effect by three-step process: (1) laser light illumination with a wavelength of 532 nm that excites only the P3HT layer, (2) creation and migration of electron-hole pairs (i.e., excitons) that are photo-induced in the P3HT layer at the P3HT-ZnO NW interface, and (3) charge separation at the interface and transportation of the photo-induced electrons from the P3HT to the ZnO NWs. From the energy-level diagram in Fig. 1(c), it can be seen that the photo-induced holes in the P3HT cannot be easily transported from the P3HT to the ZnO NWs because of the high energy-barrier potential in the valence band between the P3HT and the ZnO NWs. In contrast, the photo-induced electrons can be easily transported from the P3HT to the ZnO NWs because of the low energy-barrier potential in the conduction band between the P3HT and the ZnO NWs. As a result, the enhancement in the drain current arises from the additional large number of photo-induced

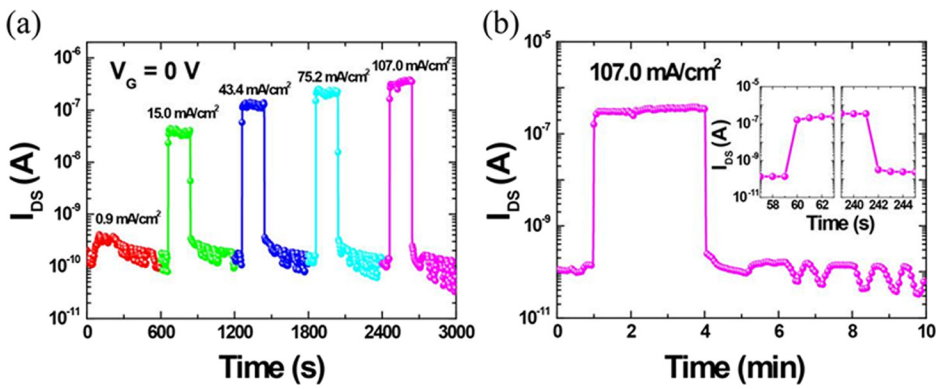

FIG. 3. (a) Photoconductivity responses of the P3HT-coated ZnO-NW FET under various light intensities (0.9, 15.0, 43.4, 75.2, and 107.0 mA/cm^2) at $V_G = 0$ V. (b) Photoconductivity characteristics for the investigation of the decay times.

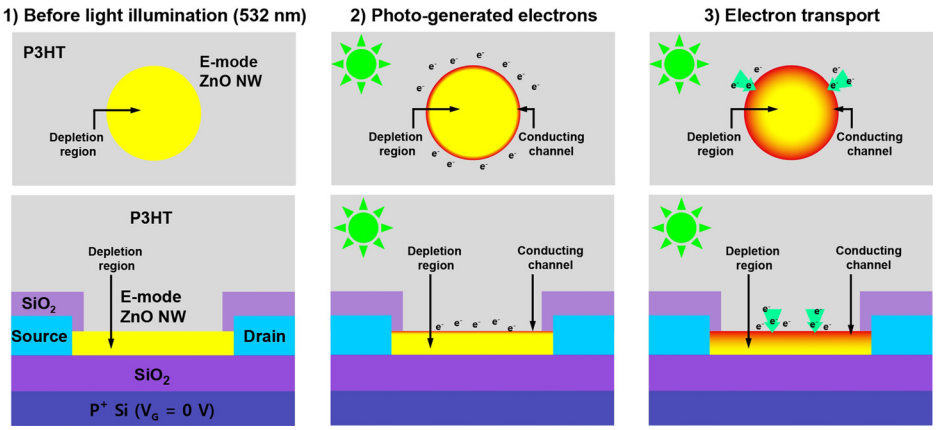

FIG. 4. (a) Schematic diagram illustrating the effect of light-induced-electron transportation. The upper and lower panels show cross-sectional schematics near the ZnO NWs and FET device, respectively. The light-induced electrons are transported from the P3HT to the ZnO NWs, so the initial enhancement-mode (E-mode) operation of the ZnO-NW FET exhibits a current flow at zero gate voltage.

electrons in the drain electrode. Therefore, from the difference of the drain current in the P3HT-coated ZnO-NW FET, we can estimate the total number of electrons that were generated in the P3HT and then transported to the ZnO NWs under light illumination. The photo-induced-electron density in different light-intensity cases are summarized in Table I.

In conclusion, we investigated the photo-generated electrons and the transport characteristics in P3HT-coated ZnO-NW FETs under laser light illumination with a wavelength of 532 nm at various light intensities. As the light intensity increased, the drain current of the P3HT-coated ZnO-NW FET was proportionally increased, and the threshold voltage was shifted toward the negative gate-bias direction. This indicates that photo-induced electrons are generated in the P3HT and transported to the ZnO-NW FET. In addition, from the photocurrent-response measurements, we estimated that the rise and decay times of our P3HT-coated ZnO-NW FET were each less than 1 s, which is considered to be a fast photoresponse. This study provides useful insights into the electron concentration and electron-transportation mechanism in organic-inorganic hybrid optoelectronic devices.

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