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Citation: Applied Physics Letters **91**, 043510 (2007); doi: 10.1063/1.2763961
View online: http://dx.doi.org/10.1063/1.2763961
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/91/4?ver=pdfcov
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Semiconducting polymer coated single wall nanotube field-effect transistors discriminate holes from electrons

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(Received 9 May 2007; accepted 30 June 2007; published online 25 July 2007)

Single wall carbon nanotube (SWNT) based field effect transistors (FET) coated with semiconducting polymers respond to photoexcitation revealing characteristic features which depend on the electronic structure of the polymer. The authors observe a decrease in the drain source current of the SWNTFET in the accumulation mode in an environment of acceptor type polymer network, and a significant increase in the current in the depletion mode for a donor type polymer network around the nanotube. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2763961]

There has been a tremendous progress in the field of carbon nanotube electronics represented by improved fabrication and performance levels of single wall carbon nanotube (SWNT) based field effect transistor (FET) devices in the past few years.[1,2] The present performances of these devices are approaching the theoretical limits expected from a one-dimensional ideal ballistic nanotube based FETs.[3] These devices have been especially attractive due to the added capability of the nanotube to respond to physical and chemical changes in its environment and have opened up several potential applications related to gas sensors,[4] chemical sensors,[5] and biological sensors.[6] Small but discernible changes in the drain source current (I_{ds}) and threshold voltage (V_t) shift of the SWNTFET upon laser illumination have been reported.[7] However, the use of SWNTFET as optical detectors has been restricted due to physical constraints such as low photon-capture area of the isolated nanotubes, large recombination probability, and other intrinsic reasons leading to low internal photon to current conversion efficiencies. Recent reports have indicated that the optoelectronic properties of SWNTFETs can be significantly enhanced by introducing an optoelectrically active network around nanotube, enabled by a large photon absorption cross section for carrier generation which can be channelized through efficient charge-transfer processes across the SWNT-polymer interface.[8,9] Optoelectronic memory devices based on nanotube FET with photosensitive conjugated polymer have been demonstrated on account of hole transfer from polymer to nanotube.[8] In our previous paper, we demonstrated significant changes in transistor characteristics of the polyhexylthiophene (P3HT) coated SWNTFETs by photoexcitation.[9] The results indicated that in addition to a direct charge (hole) transfer process, an electrostatic induced gating process at nanotube polymer interface plays a major role in the photoexcited properties of such devices. The electrostatic gating process can arise from the negative carrier trap states within the vicinity of the incident photon region and is effective in gating the nanotube. A key ingredient in these studies was the commonality of the "hole-carrier" in the polymer as well as the nanotube. Introduction of an acceptor (A) type (electron transporting) matrix around the p SWNTFET can reveal interesting phenomena such as light induced decrease of current in the device. A comparison of the photoinduced effects in the donor (D) type matrix to an acceptor type matrix can also provide insightful information of relative energy level differences and defect energetics. Cyano derivative of poly (p-phenylene vinylene) (CNPPV), with large electron affinity, has been utilized to act as an acceptor type material in the D-A multilayer devices.[10] We report results of the changes in SWNTFET characteristics upon introduction of the acceptor-type CNPPV network around it and compare with changes introduced by the donor type poly [2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV) network around the nanotube. The SWNTFET structures provide a valuable platform for understanding and comparing different semiconducting polymer systems.

The details of the SWNTFET device fabrication based on Al/Ni catalyzed chemical vapor deposition (CVD) process and characteristics have been previously reported in detail.[11] The SWNTFET used largely consisted of isolated single nanotube of length of 0.8–2 μm bridging Ti/Au electrodes, and average diameter of 1.3 nm. SWNTFET that exhibits p-type semiconducting characteristics, on-off ratio in the range of 10^4-10^6, saturation current (I_{dsat}) of ~5–15 μA, and V_t in the range of −5 to 5 V in ambient conditions was chosen for the present studies. All measurements involving gate voltage (V_{gs}) sweep were carried out from negative to positive V_{gs} with a ramp rate of 0.5 V/s. Pristine SWNTFET characteristics did not show any significant changes with illumination. There was no indication of photoinduced charging of the Si substrate leading to possible gating action of the nanotube device.[12] MEHPPV was synthesized by eliminating the side groups of a dithiocarbamate precursor by thermal elimination method.[13] MEHPPV (3.3 mg/ml) and CNPPV (3.3–5 mg/ml) in chloroform solution was spin coated on SWNTFET, the device was then thermally treated under vacuum at 100 °C for 1–2 h. In the absence of SWNT, the polymer film did not reveal any FET characteristic.

I_{ds} vs V_{gs} characteristics of the MEHPPV coated SWNTFET (from 3.3 mg/ml solution) in dark show a clear shift in V_t toward positive direction by ~4 V, shown in Fig. 1(a). The positive V_t shift depends on the density of donor polymer chains around the nanotube. This trend can be interpreted in terms of the additional hole transfer from polymer

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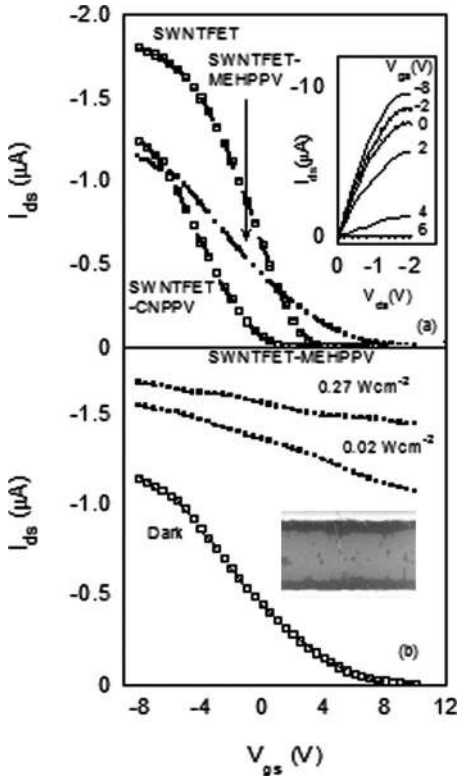

FIG. 1. (a) Transistor characteristics, source drain current (I_{ds}) vs gate bias (V_{gs}), of CVD grown SWNT based FET, MEHPPV (donor-type polymer) coated SWNTFET, and CNPPV (acceptor-type polymer) coated SWNTFET in dark. The inset in (a) shows I_{ds} vs drain bias (V_{ds}) for different V_{gs} of SWNTFET. (b) Transistor characteristics of MEHPPV coated SWNTFET in dark (open squares) and in green light, $\lambda=532$ nm, (solid squares) with two different incident intensity. The inset in (b) shows the FESEM image of polymer coated SWNTFET after a mild rinsing procedure.

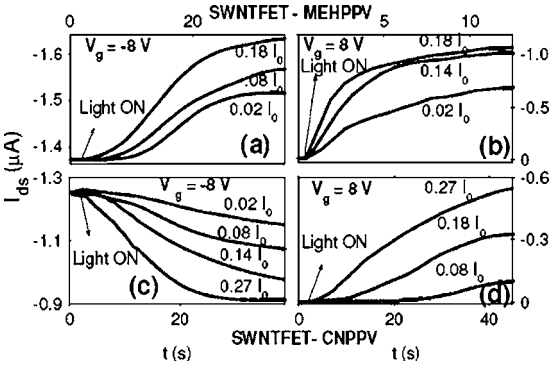

FIG. 2. Light induced transient response $I_{ds}(t)$ of MEHPPV coated SWNTFET [(a) and (b)] and CNPPV coated SWNTFET [(c) and (d)]. Experiments done in ambient conditions, $V_{ds}=-0.5$ V, at different light intensities and different gate biases: (a) and (c) corresponds to accumulation mode and (b) and (d) corresponds to depletion mode.

to nanotube and/or an induced electrostatic gating effect.[13] The interpretation of the V_t shift signature is consistent with the results observed for CNPPV coated SWNTFET where the I_{ds}-V_{gs} characteristics in dark show, as expected, an opposite shift of curve toward the negative voltage. The negative V_t shift depends on the acceptor polymer density, and $\sim$2 V of negative shift is observed for 5.0 mg/ml coated CNPPV solution, shown in Fig. 1(a). Thus for CNPPV the trend can be similarly interpreted in terms of electron transfer from polymer to nanotube and/or an induced electrostatic gating effect by hole traps. Apart from the V_t shift a marginal decrease in saturation drain current I_{dsat} and transconductance (dI_{ds}/dV_{gs}) in dark for both donor and acceptor type polymer coated SWNTFET systems is also observed, which can be attributed to additional scattering processes on the nanotube surface.[14]

Significant optical induced changes in the magnitude and its rate depends on the state of the transistor, D or A nature of polymer, and incident intensity. Upon photoexcitation of MEHPPV coated SWNTFET, I_{dsat} increased from -1.1 μA to the value corresponding to the saturation value of the pristine SWNTFET of ~-1.7 μA, as shown in Fig. 1(b). Photoexcited I_{ds}-V_{gs} characteristics are significantly altered from the quadratic-type response to a practically V_{gs} independent behavior. The V_t shifts to a large positive value under light and is a function of incident intensity. The transient response $I_{ds}(t)$ shows that the increase in depletion mode is more significant by several orders ($\sim10^6$ times) of magnitude [Fig. 2(b)], as compared to the increase in accumulation mode which is by $\sim$20% [Fig. 2(a)]. The rise in drain current cannot be explained solely based on a direct photogenerated hole transfer across the interface, since the estimated carrier generation rate to cause such current changes is $\sim10^{12}-10^{14}$ s^{-1} which is several orders greater than the photoinduced carriers generation rate within the vicinity of the nanotube, which is $\sim10^8-10^9$ s^{-1} (for the given incident laser power). The time scales for the increase in I_{ds} ($\sim$5 s) exceed the carrier diffusion time scale (submilliseconds)[15] required to access the nanotube interface. These results then largely indicate a sizable contribution from an induced gating effect due to the residual localized-trapped electrons in the polymer around the nanotube. The possible modification of the electrode-SWNT junction by the polymer coating is unlikely to be a significant factor for the following reasons. (i) The I_{ds}-V_{ds} curves for $V_{ds}<0$ and $V_{ds}>0$ at different V_{gs} are similar without any assymetry in the responses. (ii) The coating and thermal treatment processes of the polymer on the hydrophobic SiO_2 substrate are more effective than on the metal electrode. (iii) Mild rinsing of polymer coated devices does not substantially alter photo-FET characteristics. (iv) Prelimnary wide field microscopy measurements indicate that light focussed on the regions away from the electrode but around the optically active polymer coated nanotube yields appreciable signals.

In case of CNPPV coated SWNTFET, the interesting feature of light induced *decrease* (by $\sim$35%) in I_{ds} is observed in the accumulation mode [Fig. 2(c)]. This effect clearly arises from the consequence of the larger electron delocalization in the CNPPV chains due to its higher electron affinity, as compared to MEHPPV. The results can be interpreted in terms of the electron transfer to the *p*-SWNTFET causing electron-hole recombination in nanotube and/or the induced gating effect arising from the residual localized-trapped holes in CNPPV around the nanotube. The initial rate of decrease in the current (ranging from 3 to 20 nA/s) upon light exposure and the final magnitude of the light induced I_{ds} are intensity dependent [Fig. 2(c)]. This appearance of a characteristic I_{ds} at large intensity suggests percolation behavior of the charging elements to establish an effective change in I_{ds}. The intensity can then be related to the charging or trap-filling parameter required to set up the induced gate effect that opposes the externally applied V_{gs}. The response profiles upon extrapolation reveal that the threshold intensity needed to establish a charge-active network within

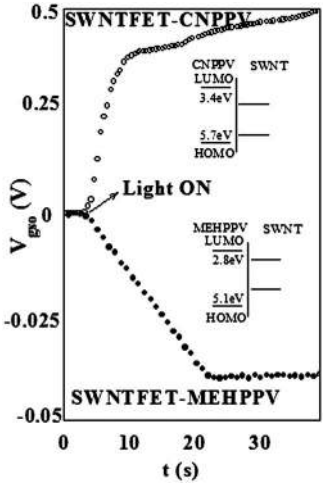

FIG. 3. Light ($\lambda \sim 532$ nm) induced open-circuit voltage response of CNPPV coated SWNTFET (top), and MEHPPV coated SWNTFET as measured between the gate electrode and the shorted drain and source electrodes (band levels are depicted in the inset).

1 s corresponds to an incident laser of power 2.5 W/cm^2.

In the depletion mode, the increase in the current [Fig. 2(d)] for the CNPPV coated SWNTFET can be partly explained in terms of electron transfer across the interface accompanied by a reduced recombination in the depleted nanotube interface. The rate of increase in the current of CNPPV ($\sim$10 nA s^{-1}) is slower than that of MEHPPV ($\sim$400 nA s^{-1}) in the depletion mode suggesting competing processes. The mechanism of the electrical gating component from the photogenerated carriers in this mode is not clear since the SWNT in its pristine state is unipolar (hole transporting), and for the induced gating process to be effective the barrier for electron injection at the source electrode/SWNT junction would have to be overcome. The I_{ds}-V_{gs} response in most of the light exposed CNPPV devices indicated largely the suppression of the hole current and a small light driven *n*-type current component. The memory features arising from complex trap kinetics under photoexcitation can also mask the observation of intrinsic *n* transport.

Light induced open circuit voltage (V_{gso}) response, as measured between gate and shorted source-drain electrode, shows opposite shift for the donor and acceptor polymer networks on SWNTFET (Fig. 3). Figure 3 shows a positive shift in V_{gso} for the CNPPV coated SWNTFET on illumination, and a negative shift in V_{gso} for the MEHPPV coated SWNTFET system. It must be noted that the final value of light induced V_{gso} largely depends on the history of the sample (exposure to light and air and prior applied gate bias), but the shift is always observed to the positive direction for the acceptor type polymer network on SWNTFET and to the negative directions for the donor-type polymer network on SWNTFET. The time scale of the light induced $V_{gs}(t)$ response is similar to that of the $I_{ds}(t)$ response (Fig. 2). These results indicate that on illumination the channel region is mostly populated with positive carriers in case of donor polymer and with negative carriers in case of acceptor polymer. These observations demonstrate contrasting trends for D and A systems.

A clear picture that emerges is that D-polymer increases I_{ds} and A-polymer networks decreases I_{ds} in the accumulation mode of *p*-SWNTFET. The microscopic process of charge transfer across the interface and the macroscopic process involving a charging process for modifying V_{gs} represent the underlying phenomena. Polymer semiconductors are known to be positional and energetically disordered system, resulting in a broad carrier lifetime distribution. It is reasonable to relate the decay lifetime observed in the transient profiles to represent the long-lived carrier tail distribution. The direct transfer of charge carriers from polymer to nanotube and the electrostatic coupling due to the charge traps can be electrically represented by a passive circuit element model. A correlation of the circuit components and the molecular properties of the polymers and interface should be possible with a set of assumptions. An accurate model constructed by the circuit network components and known profile of the optical beam spot region with respect to the nanotube upon comparison to $I_{ds}(t)$ profiles can yield quantitative information on the charge generation and transport characteristics of the medium around the nanotube. Typical range of capacitance per unit length (C) between the illuminated polymer region and the nanotube can be approximately can be approximated. For a 1.6 nm diameter nanotube and illuminated polymer-nanotube separation of 0.1–50 μm, C is in the range of 10 aF/μm–0.2 pF/μm. For a known model polymer system, $I_{ds}(t)$ responses can also be used to indicate the spatial information (distance from the nanotube) of the photoactive region. These unique characteristics based on the FET response form an alternative concept for imaging the nanotube and its environment.

In conclusion, the studies demonstrate the capability of the nanotube FETs to respond distinctly to donor type and acceptor type environments. The response at different V_{gs} modes highlights the active-optoelectronic processes across the SWNT polymer interface.

The authors thank P. Maniar and the nanotechnology team at Motorola R&D for providing the SWNTFETs. They acknowledge S. Ramakrishnan for providing MEHPPV and help in synthesizing CNPPV.

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