Control of single-wall-nanotube field-effect transistors via indirect long-range optically induced processes

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We observe significant changes in the response of single-wall-carbon-nanotube-based field-effect transistors upon photoexcitation in the presence of optically active conjugated polymer network. The primary features observed are in the form of an increase in the current in the depletion mode upon photoexcitation. Pulsed measurements indicate that the transistor enters the depleted state prior to the rise in current brought about by the transfer of the photogenerated carriers from the semiconducting polymer to the nanotube under depletion bias. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2209712]

High performance single-wall-carbon-nanotube (SWNT)-based field-effect transistors (FETs) exhibiting high drive currents, excellent transconductance, fast switching response, and large on-off ratios have been demonstrated along with added advantages in responding to changes in its environmental conditions.[1–3] Direct forms of specific chemical sensing have also been demonstrated using a variety of device structures. SWNTFETs are particularly appealing for use as optical detectors. However, methods based on optical excitation of isolated SWNT structures have been rare, possibly because of 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. However, changes in the drain-source current and threshold voltage shift of the SWNTFET upon laser illumination have been reported recently.[4–7] The excitation spectrum of the photocurrent features was correlated to the optical absorption by the third interband gap of the Van Hove singularity of the semiconducting SWNT,[8] and in certain cases was attributed to the Schottky character of the electrode-semiconductor interface.[5] In absolute terms, for a given number of photons per unit area, the photoinduced changes in pristine SWNT-FETs are relatively small compared to semiconducting polymer based FETs which offer a large area of absorption cross section for photocarrier generation and transport.[9,10] In terms of dark-transistor characteristics, polymer based FETs, however, pale in comparison to SWNTFETs. A combination of the characteristics of these two classes of FETs in a single device offers interesting possibilities.

Recent methods to fabricate such structures consisting of optically and electrically active semiconducting polymers on the nanotube have been reported. Upon photoexcitation, FET characteristics display shifts in threshold voltage along with a presence of memory features.[11] The nanotubes have been suggested to act as conduits for hole transport and studies of hybrid photovoltaic devices consisting of these sets of materials exhibit increased efficiency of photoinduced charge separation at the active interface.[12,13] Such hybrid systems offer the combination of efficient transport features of SWNT and the significant optical properties of the conjugated polymers. The percolation behavior in such hybrid systems has also been used to achieve an effective reduction in channel length, thus increasing transconductance. The carriers flowing from source to drain take advantage of the highly conducting rods within the semiconducting matrix, flowing partially within the semiconductor and partially through the rods. Traveling only a fraction of the distance within the semiconductor leads to an effective channel length reduction. The effective channel length reaches vanishing distances as the network of rods approaches three-dimensional (3D) percolation.[14] Optical properties of SWNT have been recently manipulated without their covalent modification by wrapping them with fluorescently labeled polymer.[15]

We present results of studies from conjugated polymer poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV) dispersed SWNTFET structures which reveal interesting features resulting from a combination of molecular process initiated by photoexcitation of the polymer and facilitated by device geometry conditions. The photoexcitation primarily affects the SWNTFET characteristics in the depletion mode. The changes in the current span several orders in magnitude and highlight the utility of the optically active antenna around the nanotube.

A chemical vapor deposition (CVD) based process for the growth of SWNTs that are catalyzed by a thin Al/Ni stack was used for the fabrication of the FETs.[16] Studies were restricted to devices which exhibited semiconducting characteristics (as observed by gate voltage V_g dependence of drain-source current I_{ds}) in ambient conditions. Apart from conventional drain-source electrode structures of channel lengths (interelectrode distances) in the range of $1-4$ μm consisting of isolated SWNT, ring-type electrode structures which can consist of more than one SWNT were also used. The ring-type structure minimizes parasitic effects and leakage currents and also ensures a smooth-radially directed coating of the polymer solution between the electrodes. Structures with an intermediate level of concentration of polymer matrix were used for these studies (i.e., the polymer

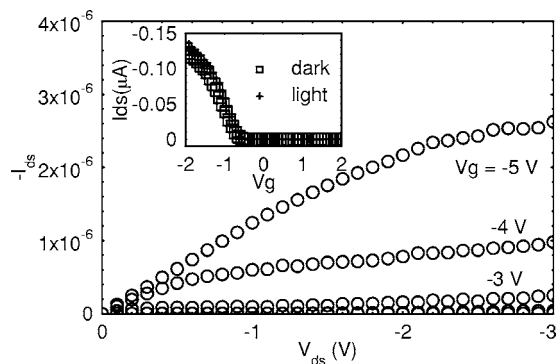[a]Electronic mail: narayan@jneasr.ac.in

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FIG. 1. (Color online) Typical SWNTFET characteristics. Inset is the transconductance response in dark and light (see text for details).

chains which do not form a continuous complete coverage between the electrodes were used for the studies). Regioregular P3HT obtained from Aldrich Inc. was purified using standard procedures (reprecipitation method) and films that were formed use spin coating and casting methods from chloroform solution (1 mg/ml). The devices were then subjected to thermal treatment under vacuum at 60 °C for 24 h. FET measurements of these devices were carried out under ambient conditions on a semiconductor analyzer probe station. The atomic force microscopy (AFM) images revealed the intact nanotubes covered by the polymer network.

SWNTFET characteristics as shown in Fig. 1 were comparable to standard results reported in the literature in terms of saturation current magnitude (1–10 μA), p-type conduction, on-off ratio (100–10000), and low threshold voltage. There were no discernible changes upon photoexciting the device structure. The I_{ds}-V_{ds} characteristics of SWNTFET at different V_g in dark and light-exposed conditions observed in SWNTFET with the polymer coating are shown in Fig. 2. The FET characteristics in the dark do not indicate any appreciable alteration upon addition of the polymer. The saturation current magnitude and I_{ds}-V_{ds} characteristics remain unchanged upon addition of the polymer. However, upon photoexciting the device (white light of 100 μW/cm^2 or λ =532 nm source at ~100 μW/cm^2) the I_{ds}-V_{ds} characteristics are drastically altered and yield a linear response which is nearly independent of V_g [Fig. 2(a)]. The typical semicon-
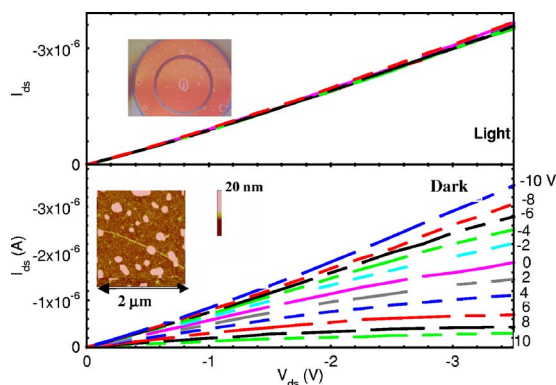

FIG. 2. (Color online) I_{ds} vs V_{ds} characteristics of P3HT coated SWNT device structure in light and dark conditions. Top inset is the image of a typical device structure consisting of concentric regions with the drain and source formed in the outer and inner regions, the intermediate region forms the SWNT, along with the polymer coating on it. Bottom inset is the AFM topography image of a device region showing the SWNT coated with nonuniform polymer patches from a dilute polymer solution.
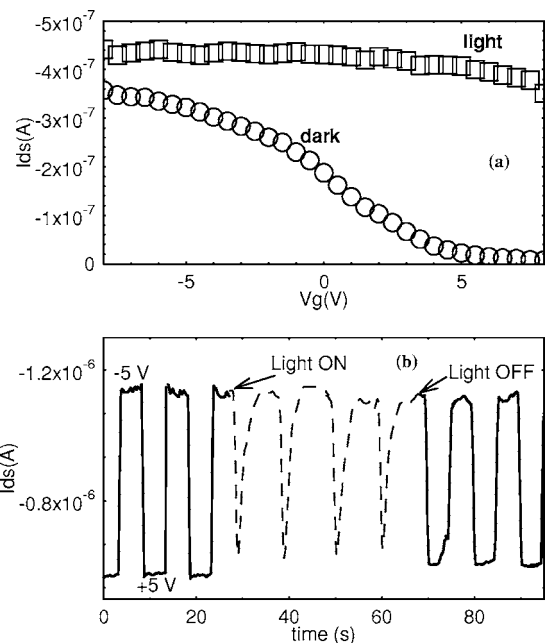

FIG. 3. (Color online) (a) I_{ds} vs V_g in dark and light conditions of the polymer coated SWNT. (b) I_{ds} response to a periodic V_g with an amplitude of 10 V in dark conditions (solid line) and in light conditions (dashed line).

ducting I_{ds}-V_{ds} characteristics can be retrieved from the apparent metallic like behavior only upon switching off the excitation. The response upon switching off the light then evolves over a period (few minutes) to return to the original dark characteristics. The transconductance I_{ds}-V_g characteristic shown in Fig. 3(a) also reflected this change in response upon photoexcitation. The typical quadratic-type dependence with respect to V_g crossed over to a nearly V_g-indepenent behavior [Fig. 3(a)]. Experiments carried out at different intensities revealed the crossover by a corresponding increase in threshold voltage V_t (V_g intercept) from a finite value to large positive value (tending to infinity). The general spectral profile of this response follows the polymer absorbance.

In device structures without the nanotubes, the existing level of polymer content did not exhibit FET characteristics by themselves. I_{ds} magnitudes in the absence of SWNT in the channel regions were quite low (<10 pA). A possible source of explanation for this could be from the nonuniform wetting behavior of the polymer solution on the oxide surface compared to Au sidewalls resulting in a discontinuity for an extended transport network, especially for thin polymer films, and is also indicated in AFM observations. Uniform, continuous, and well-adhered polymer thin films formed in bottom contact devices require specific deposition procedures.[17]

Previous reports by Star *et al.*[11] involved relatively marginal shifts of V_t with the polymer coating under photoexcitation compared to the present case where shifts in the range >10 V (inferred by extrapolating the I_{ds}-V_g), for moderate light intensity ~100 μW/cm^2. It was observed that the photoinduced large I_{ds} persisted upon switching off the photoexcitation and could be annulled only after biasing FET in the enhancement mode ($V_g < 0$).

Since the measurements involving FET characteristics were dc measurements done in a typical routine ($-V_{ds}$ to $+V_{ds}$) at a scanning rate of 0.2 V/s for V_g (-5 to $+5$ V in steps on 0.2 V), a closer examination was carried out using a periodic variation of the gate voltage at a constant V_{ds}. Fig-

ure 3(b) shows the periodic response of I_{ds} to a square-wave-type V_g in dark conditions, and the response indicates the distinct "off" and "on" state of the FET. Upon photoexciting the FET undergoing the periodic V_g cycle, it is observed that the switching off in the depletion mode is followed by a charging current which takes it to the saturation value (similar to $-V_g$ value). The current decrease spike is consistently present in every cycle, prior to the increase in the current. It is also observed that upon switching off the light, the original wave form is recovered partially, and after experiencing the $-V_g$ cycle, the square well type, the original periodic response is completely restored. Measurements were carried out for SWNTFETs of different channel lengths, different polymer concentrations, and optical parameters. These sets of observations were consistently observed for every working SWNTFET device structure.

The possible explanation for these features can be attributed to direct photogenerated charge carrier transfer from the polymer network to the CNT. This process could be effective in the depletion mode where the induced negative charge on the surface of the CNT provides a sink to the photogenerated holes. A direct photoinduced charge transfer (within sub-nanosecond time scale) at the polymer-SWNT interface similar to conventional donor-acceptor system in organic solar cells has been discussed as a source of the increase in the current. However, there is ambiguity in the nature of the type of carrier transfer (hole[11,12] versus electron[13,18]) to explain the increase in the charge carrier efficiency. In the present case the nonreversibility and the magnitude of current indicate magnitude of current conversion efficiency η which is far greater ($\sim 10^4$) than what can be accounted for by mere charge transfer resulting from charge carrier generation in the polymer segments within an accessible distance, (L_{diff} ~ 100 nm) from the nanotube. ($\eta = I_{ph}/eN_{ph}$, where N_{ph} = power per unit area $\times l \times L_{diff} \times \lambda/hc$). Another plausible argument could be charging of the defect sites at SWNT-polymer interface, resulting in a formation of a charged dielectric layer at the interface over a time period and effectively inducing the high I_{ds} in $+V_g$ bias conditions. This picture can then account for the persistence of the current in the depletion mode after it is switched off which is neutralized upon exposing to $-V_g$. This sweeping of the trapped carriers by $-V_g$ can be active even in presence of continuous illumination and can explain the initial drop in I_{ds} upon taking the device back to depletion ($+V_g$) depicted in Fig. 3(b). An equivalent circuit consisting of both resistive and capaci-

tive components along with a current source (photon source) can depict the processes at the interface which can then be used to model the transients.

In summary, polymer dispersed SWNTFETs exhibit appreciable changes of I_{ds} upon photoexcitation. The I_{ds} in dc-mode reveals V_g independent characteristics upon photoexcitation. Upon a closer examination from experiments involving a periodic V_g, it is observed that the FET enters into the off state (for $V_g > 0$) and under these conditions the photogenerated charge carriers induce the large increase in I_{ds} in the nanotube channel. These unusual photoinduced features are obtained upon dispersing semiconducting conjugated polymer solution on SWNTFET structures which are compatible with complementary metal-oxide semiconductor (CMOS) process line.

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