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著者	畠山 力三
journal or publication title	Applied Physics Letters
volume	92
number	18
page range	183115-1-183115-3
year	2008
URL	http://hdl.handle.net/10097/46372

doi: 10.1063/1.2924300

Photoinduced electron transfer in C_{60} encapsulated single-walled carbon nanotube

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(Received 20 February 2008; accepted 20 April 2008; published online 9 May 2008)

The transport properties of field-effect transistors based on C_{60} fullerene peapods have been investigated and our findings indicate that the transport characteristics of single-walled carbon nanotubes (SWNTs) are highly sensitive to the encapsulated fullerenes due to the charge-transfer effect. Under light illumination, the photoinduced electron transfer characteristics are found in C_{60} peapods, which is different from those observed for empty SWNTs. The response characteristic of peapod devices to light is reflected in a shift of threshold voltage toward negative values, indicating an electron-doping process. After removing light the photoresponse is fully recoverable, indicating complete restoration of transferred electrons. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2924300]

The photoinduced electron transfer (PET) process of donor-acceptor system has long been of interest in chemistry because it is a universal and fundamental phenomenon in nature. Fullerenes such as C_{60} are particularly appealing as electron acceptor[1,2] toward constructing molecule electronic devices, because of their low reduction potential, delocalized π electrons within the spherical carbon framework, small reorganization energy, and adsorption spectra extending over most of the visible region. These unique properties make fullerenes a promising candidate for the investigation of PET process by combining with electron donor compounds.[3–6] On the other hand, single-walled carbon nanotubes (SWNTs) have demonstrated great potential in fabricating nanoscale electronic devices covering from logic circuits to chemical sensors.[7–10] More recently, SWNTs have proven promising candidates for a variety of nanoscale optoelectronic devices ranging from photodiodes to electron-optical modulators.[11–15] In this respect, the presence of fullerenes inside SWNTs, known as peapods, is expected to profoundly affect the electronic structure of SWNTs, which may provide an extremely interesting system for investigating their optical-electronic transport properties. In other words, it would be anticipated that the PET phenomenon takes place between fullerenes and SWNTs. Although some theoretical and experimental studies on the transport characteristics of peapods have been described elsewhere during the past several years,[16–19] the extent of the encapsulated fullerenes' effect on the transport properties of SWNTs is still unclear so far. Furthermore, little is known about how the light initializes the electron transport in nanopeapods. An appreciation of the interactions between the incident light and the transport properties of peapods is important both for their potential applications to such devices and a fundamental understanding of PET process in the fullerene-nanotube system. Here, we have investigated the transport properties of C_{60} nanopeapod both in dark and upon light illumination and our results demonstrate that the PET phenomenon is clearly observed in C_{60} nanopeapod devices.

In this study, the samples of SWNTs with diameter about 1.4 nm are prepared by an arc discharge using Fe/Ni as catalyst.[20] C_{60} fullerene molecules encapsulated SWNTs are synthesized by a vapor reaction method. The purified SWNTs together with C_{60} powders (with high purity of about 99%), are sealed in a glass tube under the vacuum condition $\sim 10^{-5}$ Torr. After that, the sealed glass tube is heated at 420 °C for 48 h to encapsulate fullerene molecules in SWNTs. Raw samples are obtained after the above process, and then purified via a washing process in toluene to remove the excess fullerene attached to the surface of SWNTs. The purified peapods are examined by transmission electron microscopy (TEM) (Hitachi HF-2000) operated at 200 kV and raman spectroscopy (Jovin Yvon T-64000) with an Ar laser at 488 nm in detail (see supporting information). In order to measure their electrical transport properties, C_{60} peapods are fabricated as the channels of FET devices and the device preparation has been described elsewhere in our previous work.[21] The transport measurements are carried out in the temperature range of 10–300 K in vacuum on a semiconductor parameter analyzer (Agilent 4155C). The photoinduced transport experiments are performed under light (390–1100 nm) illumination generated from a 150 W Xe arc lamp (LSX-2501).

In Fig. 1, we compare the transfer characteristic of SWNTs before and after encapsulating C_{60} fullerenes without interacting with light and remarkable changes are observed in the encapsulated sample. The typical transport properties of pristine SWNTs exhibit the well known *p*-type semiconducting behavior, as shown in Fig. 1(a), where the

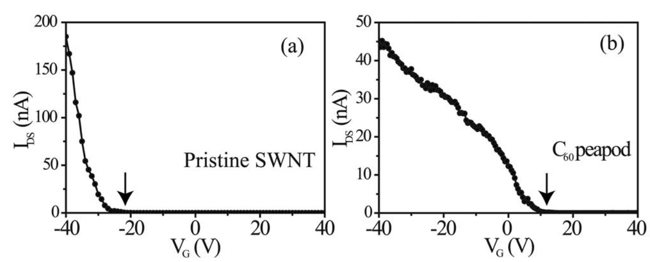

FIG. 1. Source-drain current (I_{DS}) vs gate voltage (V_G) characteristics measured with bias voltage $V_{DS}=1$ V at room temperature for (a) *p*-type pristine SWNT with $V_{th}=-22$ V and (b) *p*-type C_{60} peapod with $V_{th}=12$ V.

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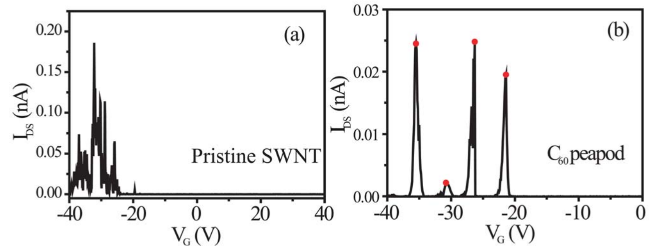

FIG. 2. (Color online) I_{DS}-V_G characteristic for pristine SWNT measured with bias voltage $V_{DS}=10$ mV at 10 K. (b) Coulomb oscillation peaks measured with $V_{DS}=10$ mV at 10 K for C_{60} peapod.

source-drain current (I_{DS}) through the device is measured as a function of gate voltage (V_G) for a fixed source-drain voltage ($V_{DS}=1$ V), indicating that the threshold voltage (V_{th}) for hole conductance is about −22 V. In general, the V_{th} for most of examined pristine SWNTs is less than −20 V, although it has a random distribution. In contrast, after C_{60} encapsulation a striking upshift of V_{th} until 12 V is observed in the I_{DS}-V_G curve for a peapod device, as described in Fig. 1(b). This result has revealed that the hole density along the SWNT is greatly enhanced, which is possibly attributed to the occurrence of electron transfer from the SWNT to C_{60} molecules. Here, it should be noted that the shift of threshold voltage has been observed in many independent C_{60} peapod devices and they have good reproducibility under measurements performed with different source-drain voltages. To get further insight into the transport characteristics of peapods, we have performed the low-temperature measurements, and the results also show a clear difference between pristine and encapsulated samples. For all nanotube devices, the observed current in I_{DS}-V_G characteristics gradually drops when the temperature is lowered from 300 to 10 K. In comparison to the transport characteristics of pristine SWNT [Fig. 2(a)], Coulomb oscillation peaks with fairly regular intervals are strikingly found on a C_{60} peapod device at 10 K, as described in Fig. 2(b), indicating the device is dominated by quantum dots. Since the gate voltage period of oscillation peaks ($\Delta V_G=5.1$ V) is directly related to the size of quantum dots, which can roughly be estimate according to the references.[22,23] In this case, the size of quantum dots in the C_{60} peapod is estimated to be about $L=12$ nm, which is much smaller than the length of nanotube between the drain-source electrodes. The above results suggest that tunneling barriers are possibly formed due to the fullerene-induced modulation of the electronic band of the nanotube.

Under light illumination, striking changes in the transfer characteristics of C_{60} peapods are further observed. For the sake of comparison, the response of transport properties of a pristine SWNT to light is shown in Fig. 3(a), where the device is measured before and after exposure to the 390 nm (3.1 eV) UV light. UV irradiation results in a ∼35% decrease in conductance, which is ascribed to photoinduced desorption of oxygen from both the surface of the SWNT and the contact at the metal electrodes.[11,13] However, there is no significant shift in the threshold voltage under light illumination, which is in agreement with previous reports.[13,24] By comparison, in addition to the conductance decrease a distinct change of threshold voltage in the transport characteristics of fullerene peapods is observed when they are measured under light, demonstrating a clear photoswitching effect. Figure 3(b) shows the transfer curves of a C_{60} peapod

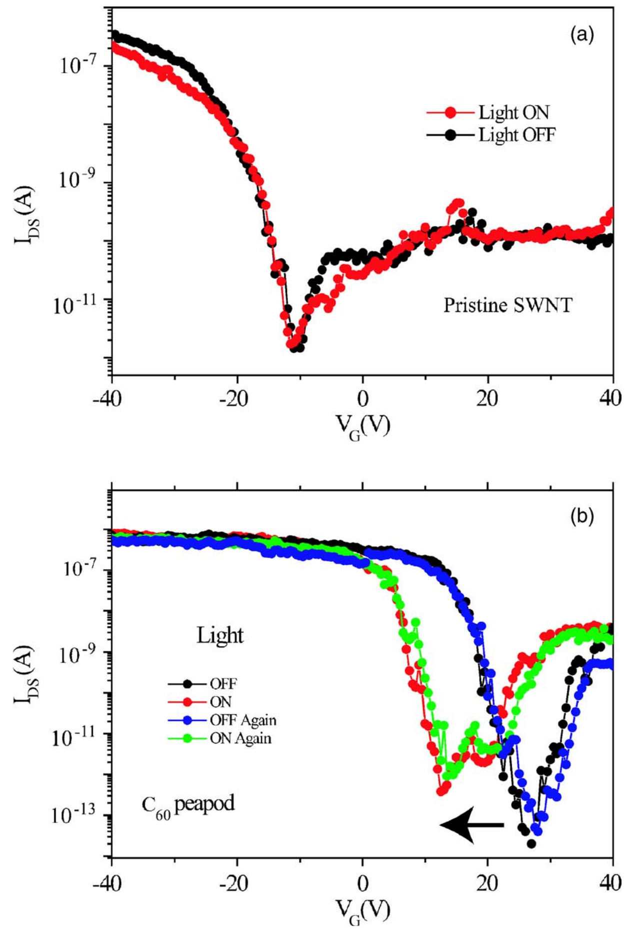

FIG. 3. (Color online) (a) I_{DS}-V_G characteristics of a pristine SWNT-FET device without (black curve) and with light (red curve, 390 nm) illumination for 5 s under an intensity of 5.3 mW/cm^2. (b) I_{DS}-V_G curves of a C_{60} peapod-FET device before (black line) and after 390 nm light (red curve) illumination. The blue line shows the transfer curve after light is again turned off and the green curve indicates the transfer characteristic of device after exposure of light again, showing a good recovery. The red and green curves give about 14 V shift of threshold voltage toward the negative direction, as indicated by an arrow.

FET device, which are recorded in dark (black curve) and upon light illumination (390 nm) (red curve) and again measured in dark (blue curve) and under light illumination (green curve). Obviously, the prominent response of the device to light is the shift of threshold voltage (about 14 V) toward negative voltages, with a little change in transconductance, implying electron doping of SWNTs. Interestingly, such a photoresponse effect is fully recoverable after removal of or exposure to light, demonstrating complete restoration of transferred electrons. The direction of the threshold voltage shift indicates an electron-transfer process from C_{60} to the SWNT, which is quite surprising since C_{60} molecules are normally thought to be an electron acceptor. A reasonable explanation for this phenomenon is the occurrence of PET process in a nanosystem of C_{60} encapsulated SWNTs. Our previous observation in Fig. 1(b) has demonstrated that there is a charge transfer of electrons from SWNTs to the ground state of C_{60}. On the other hand, the PET process may at least partially cause a recovery of these transferred electrons. In other words, upon photoexcitation of the C_{60} molecules, some of the electrons that have been transferred to the C_{60} in the ground state from the SWNT are transferred back to the SWNT when C_{60} is in the excited state. Therefore, the C_{60}

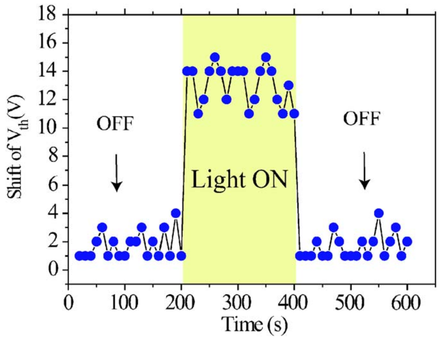

FIG. 4. (Color online) The shift of threshold voltage is measured as a function of time and light is on during time indicated by the shaded area, where V_{th} of about 13 V on average is observed.

fullerene may remain the role of electron acceptor in the excited state.

The time dependence of the change in threshold voltage, namely, the shift of carrier concentration along the SWNT is further analyzed, as indicated in Fig. 4. The cycle is set by turning the light source on and off for a period of 10 min. The observed data have further confirmed that the shift of the threshold voltages arises from the excitation of C_{60} fullerenes. According to the data in Fig. 4, the shift of V_{th} is recognized to be about 13 V on average, from which the number of electrons transferred from C_{60} molecules can be estimated. The carrier (holes or electrons) density P along the SWNT is evaluated according to $P=Q/eL$, where L is the length of nanotube and the total charge Q on the SWNT can be estimated as $Q=CV_{th}$, (C: SWNT capacitance). According to the previous report,[8] the gate capacitance per unit length is $C/L \approx 2\pi\varepsilon\varepsilon_0/\ln(2h/r)$, where $\varepsilon=3.9$ is the average dielectric constant of the device, h, r, and ε_0 are the thickness of oxide silicon layer, radius of SWNT, and the permittivity of free space, respectively. In our case, using $L=500$ nm, $r=0.7$ nm, and $h=500$ nm, the change of electron density along the nanotube is estimated to be 2.42×10^7/cm with $V_{th}=13$ V. This calculation leads to a transfer of about 1.21×10^3 electrons to the SWNT. However, considering the 500 nm thickness oxide backgate of FET device in our case, the efficiency of gate voltage is estimated to be about 10% or less in comparison with the observed values in Fig. 3(b). As a result, the actual number of transferred electrons is possibly less than 120. This value seems to be reasonable when compared with the number of encapsulated fullerenes in actual FET device constructed with a 500 nm length SWNT, which is about 430 according to 0.71 nm diameter of fullerenes and 0.98 nm distance of two adjacent fullerenes.[25] In addition, to understand the observed PET phenomenon the wavelength dependence of transport characteristics for C_{60} peapods is also investigated by monitoring the change of threshold voltage during illuminating light with different wavelength ranging from 390 to 1000 nm. The response of threshold voltage shift is observed to take place for all the wavelengths. As the wavelength of light is larger than 600 nm, however, the photoresponse effect becomes weak, and only a small change of V_{th} about 7 V is sensed, which is plausibly due to the distribution of C_{60} absorption peaks in the low-wavelength region.

In conclusion, our work has demonstrated that C_{60} peapods display an enhanced *p*-type transport characteristic due to the charge-transfer effect. Compared with the case of pristine SWNTs, the PET phenomenon is clearly observed on C_{60} nanopeapod devices. The key signal change of devices responding to light is the shift of threshold voltage toward negative voltages, suggesting that the adsorption of light initiates the transfer of electrons from fullerenes. More importantly, it is found that the photoresponse behavior is fully recoverable without light irradiation and, therefore, the electron transfer and back electron transfer in the nanopeapod system are found to be controllable. The shift degree of threshold voltages depends on the wavelength, reaching a maximum of about 14 V. Such nanopeapod devices with interesting photoinduced properties are expected to have promising applications as a photodetector and photosensitive wire in the near future.

This work was supported by a Research Fellowship of Japan Society for the Promotion of Science (JSPS) and JSPS-CAS Core-University Program on Plasma and Nuclear Fusion.

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