Photoresponse of Fullerene and Azafullerene Peapod Field Effect Transistors

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Abstract—**In this work, we have investigated the transport properties of field-effect transistors (FETs) based on various kinds of fullerene (C_{60}, C_{70}, and C_{84}) and azafullerene ($C_{59}N$) peapods without and with interacting with light. The encapsulation of various fullerenes and azafullerene inside single-walled carbon nanotubes (SWNTs) is characterized by TEM. Our results indicate that the electrical transport properties of pristine SWNTs are extremely sensitive to the encapsulation of various kinds of fullerenes or azafullerenes. In addition, the photoinduced transport characteristics of various peapods are systematically investigated, and our findings demonstrate that they exhibit complete different transport behaviors compared with those observed for empty SWNTs. In addition, the conductance of azafullerene peapods shows much higher photoresponse sensitivity than those observed in fullerenes peapods, suggesting a different photoinduced charge transfer mechanism.**

Keywords-carbon nanotubes; fullerene; electronic; transport; light

I. Introduction

Single-walled carbon nanotubes (SWNTs) have demonstrated great promises in constructing a wide range of nanoscale electronic devices covering from logic circuits to biochemical sensors due to their instinct properties, such as high carrier mobility of about 10^6 cm^2 $(Vs)^{-1}$, long phonon scattering mean free path on the order of micron, and near infrared photoluminescence [1]. On the other hand, recent researches have demonstrated that SWNTs also prove promising candidates for optoelectronic devices ranging from photodiodes to photodetectors [2], since light can provide a convenient, precise and simple tool in controlling the conductivity of SWNTs. Therefore, to understand the interaction between instantaneous light and the nanotube transistor is very important for the potential application of such devices. However, in previous works light illumination mainly focus on pristine SWNTs, and little is known about the photoinduced transport properties of foreign materials, such as fullerene, encapsulated SWNTs. Fullerene or azafullerene peapods may provide a more interesting hybrid system than empty SWNTs in investigating the photoinduced transport properties. In this regard, some interesting transport phenomena are expected to take place between fullerens or azafullerene and SWNTs upon light illumination.

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In this work, the photoinduced transport properties of field-effect transistors (FETs) fabricated with various kinds of fullerene and azafullerene $C_{59}N$ peapods have systematically been investigated. Our measurements indicate that the transport characteristics of *p*-type SWNTs are extremely sensitive to the type of encapsulated fullerenes. A series of measurements on the photoinduced transport characteristics of peapods are performed under illumination of light with tunable wavelengths in the range of 390-1100 nm, and our findings indicate that they exhibit completely different transport behaviors compared with those observed for empty SWNTs.

II. Experimental Details

The pristine SWNTs with diameter about 1.4 nm are prepared by an arc discharge using Fe/Ni as catalyst. Before the encapsulation of fullerenes, an air oxidation process is carried out at 450 °C for 30 min to open the ends of SWNTs. The encapsulation of fullerenes (C_{60}, C_{70} and C_{84}) or azafullerene ($C_{59}N$) inside SWNTs is realized by either a vapor diffusion method or a plasma ion-irradiation method [3]. In the former case, the purified SWNTs together with fullerene or azafullerene powders (with high purity of about 99%), are first sealed in a glass tube under the vacuum condition $\sim10^{-3}$ Pa. After that, the sealed glass tube is heated at 420 °C for 48 h to encapsulate each kind of fullerenes or azafullerene in SWNTs. Raw samples are obtained after the above process, and then purified via a washing process in toluene to remove the excess fullerene molecules attached to the surface of SWNTs. The purified peapods are examined in detail by a transmission electron microscope (TEM, Hitachi HF-2000) operated at 200 kV.

In order to measure the electrical transport properties, fullerene peapod samples are ultrasonically dispersed in *N, N*-dimethylformamide solvent firstly and then spincoated on an FET substrate, which consists of 63 pairs of predefined Au electrodes. The Au electrodes with thickness of 150 nm are prepatterned and used as source and drain electrodes. A channel length between the source and drain electrodes is 500 nm. In order to remove excess DMF solution on the FET substrate, a simple baking process at 400 K is finally carried out in atmosphere for 30 min. The transport measurements are carried out both in dark and upon light illumination in vacuum (10^{-5} Pa) using a semiconductor parameter analyzer (Agilent 4155C). The photoinduced transport measurements are performed under illumination of light generated from a 150 W Xe arc lamp (LSX-2501), with wavelengths ranging from 390 to 1100 nm. Light intensities are < 50 mW cm^{-2}.

III. RESULTS AND DISCUSSIONS

The encapsulation of C_{60}, C_{70} and C_{84} fullerenes and $C_{59}N$ azafullerene inside SWNTs is confirmed by TEM observations, as shown in Fig. 1, where C_{60}, C_{70}, C_{84} and $C_{59}N$ molecules are clearly observed inside each individual SWNT (fullerene@SWNT). Our studies have indicated that $C_{59}N$@SWNTs show the *n*-type behavior compared with *p*-type C_{60}@SWNTs [4, 5], which is due to the electron donation property of azafullerene with lower ionization potential, as compared with the case of C_{60} fullerene. It is also demonstrated that fullerene or azafullerene molecules inside SWNTs make nanotubes more sensitive to light compared with that of pristine SWNTs.

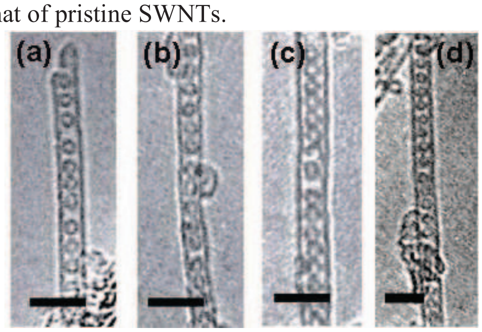

Figure 1. TEM images of various fullerene and azafullerene encapsulated SWNTs: (a) C_{60}@SWNT, (b) C_{70}@SWNT, (c) C_{84}@SWNT, and (d) $C_{59}N$@SWNT, scale bar: 2 nm

A. Photoresponse of fullerene peapods

Under light illumination, striking changes in the transfer characteristics of C_{60} peapods are further observed [6]. For the sake of comparison, the response of transport properties of pristine SWNTs to light is first shown in Fig. 2(a), where the device is measured before and after exposure to the 390 nm (3.1 eV) UV light. UV irradiation leads to ~35% decrease in conductance, which is due to photo-induced desorption of oxygen from the surface of the SWNTs. However, there is no big shift in the threshold voltage under light illumination, which is in agreement with the previous report [7]. 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 2(b) shows the transfer curves of a C_{60} peapod FET device, which are recorded without light (black curve) and upon light illumination (390 nm) (red curve), and again measured without light (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

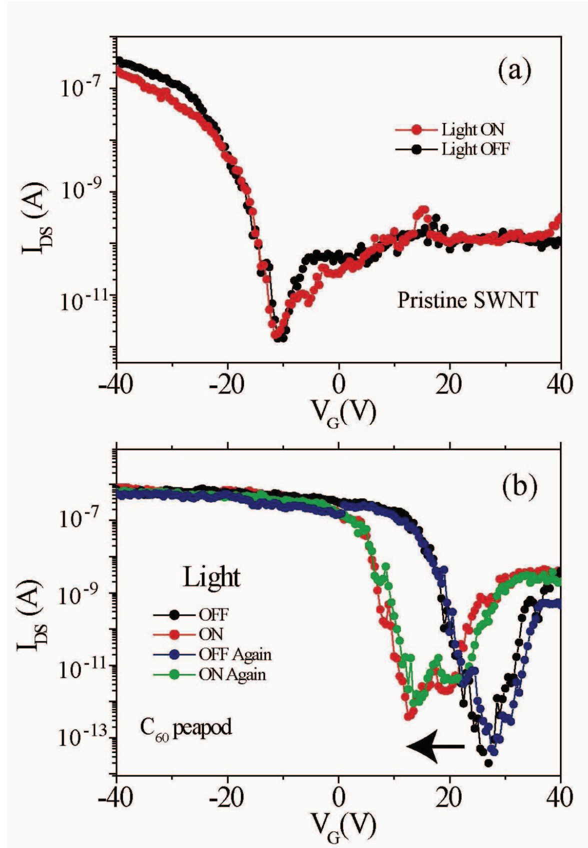

Figure 2. (a) I_{DS}-V_G characteristics of a pristine SWNT-FET device without (black curve) and with light (red curve, 390 nm) illumination for 5 s under an intensity of 5.3 mW/cm^2. (b) I_{DS}-V_G curves of a C_{60} peapod-FET device before (black line) and after 390 nm light (red curve) illumination. 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.

negative voltages, with a little change in transconductance, indicating electron doping of SWNTs. Moreover, such a photoresponse effect is fully recoverable after removal of or exposure to light, showing a 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 photoinduced electron transfer (PET) process in the nanosystem of C_{60} encapsulated SWNTs. Figure 3 shows a schematic illustration of charge transfer cycle in the C_{60} peapod. Electrons are transferred from SWNTs to the ground state of C_{60} in the absence of light, during which the C_{60} behaviors as a good electron acceptor. On the other hand, under light illumination the C_{60} in excited state displays the electron donor behavior, giving back electrons to SWNTs. In other words, the electron withdrawing ability of C_{60} in excited state becomes weaker as compared with that of C_{60} in ground state. As a result, the PET process may at least cause a partial recovery of these transferred electrons, that is, upon excitation 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.

Moreover, we have measured the transport properties of C_{70} peapod under light illumination, and found a similar negative shift of threshold voltage but the value is much smaller than that observed for C_{60} peapods. In contrast, light irradiation gives little effect on the measured I_{DS}-V_G curves of C_{84} peapods, that is, almost no shift or only a negligible change of threshold voltage is found. This result demonstrates that the photoresponse is critically dependent on the type of encapsulated fullerenes.

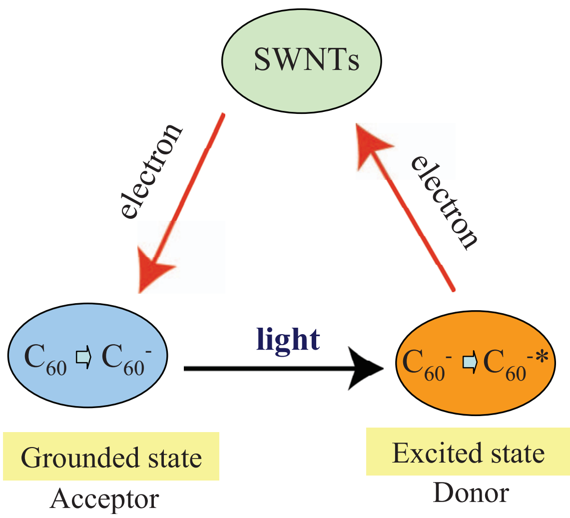

Figure 3. Charge transfer cycle in fullerene peapod with and without light, showing a PET process.

B. Photoresponse of azafullerene peapods

Compared with the case of C_{60} peapod, the photoresponse of azafullerene $C_{59}N$ peapod exhibits a different photosensitive behavior [8]. Figure 4(a) shows the I_{DS}-V_G behavior under instantaneous (400 nm) light exposure for a semiconducting $C_{59}N$ peapod FET device. In contrast to the behavior without light, a drastic decrease of current by over 95% is observed. As the gate voltage is continually swept (with sweeping speed ~1.4 V/s), the current is restored gradually to its initial current during scanning to high positive gate voltages, indicating the recovery can be made by sweeping the gate voltage. Interestingly, we have observed similar photoresponse for a metallic $C_{59}N$ peapod FET device, as seen in Fig. 4 (b), where sharp drop in current is observed two times (as shown by arrow) when the device is instantly illuminated twice. This result demonstrates well that the recovery by the gate is reproducible.

To further investigate the photoswitching characteristics, we have exposed the devices to light during the I_{DS}-V_G measurements. Figure 5 shows the I_{DS}-V_G behavior for a semiconducting FET under 400 nm light exposure in contrast to the behavior without light. It can be seen that *n*-type conductance is greatly reduced. This result is well consistent with that observed in Fig. 4(a). The photoresponse is also found to depend on the wavelength of light. The change of conductance gradually becomes less pronounced with increasing the wavelength of light. This finding demonstrates evidently that the light energy exerts an important effect on the conductance of azafullerene peapod.

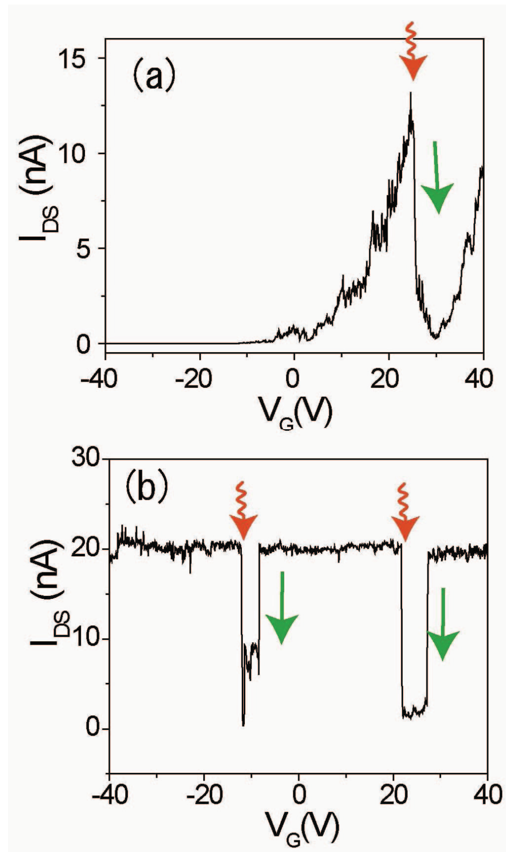

Figure 4. (a) I_{DS}-V_G characteristics for a $C_{59}N$ peapods measured with instantaneous light illumination (400 nm wavelength) for (a) a semiconducting $C_{59}N$ peapod, and (b) a metallic $C_{59}N$ peapod.

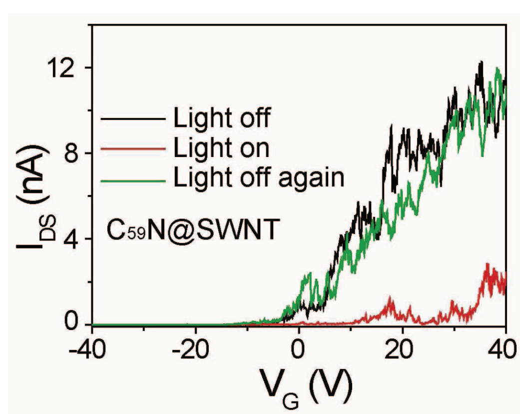

Figure 5. I_{DS}-V_G characteristics for a $C_{59}N$ peapod with and without light illumination (400 nm wavelength).

Obviously, the photoresopnse of $C_{59}N$ peapod is significantly different from those observed for C_{60} peapod which shows the photoinduced charge transfer due to the excited C_{60}. The observed current is found to show an extreme decrease for $C_{59}N$ peapod under light illumination. Figure 6 gives the characteristics of I_{DS} as a function of time at $V_G = 40$ V and $V_{DS} = 1$ V for a $C_{59}N$ peapod (a) and a C_{60} peapod (b) FET device measured under instantaneous light (1 s) illumination. As a comparison, a sharp decrease in current is immediately observed at 130 s upon the UV light pulse on $C_{59}N$ peapod, and the change is much bigger than that observed for C_{60} peapod. A different photoinduced charge transfer mechanism is considered to exist between fullerene and azafullerene peapods. The specific sensitivity of electronic structure of $C_{59}N$ to light seems to be responsible for the observed photoswitching characteristic. It is well known that $C_{59}N$ radical is very active, and can easily lose or gain an electron by binding to other atoms or molecules [9, 10]. Therefore, the *n*-type behavior is possibly due to the charge transfer from encapsulated $C_{59}N$ to SWNT by formation of chemical bond. Under light illumination such bond will break by high photo energy.

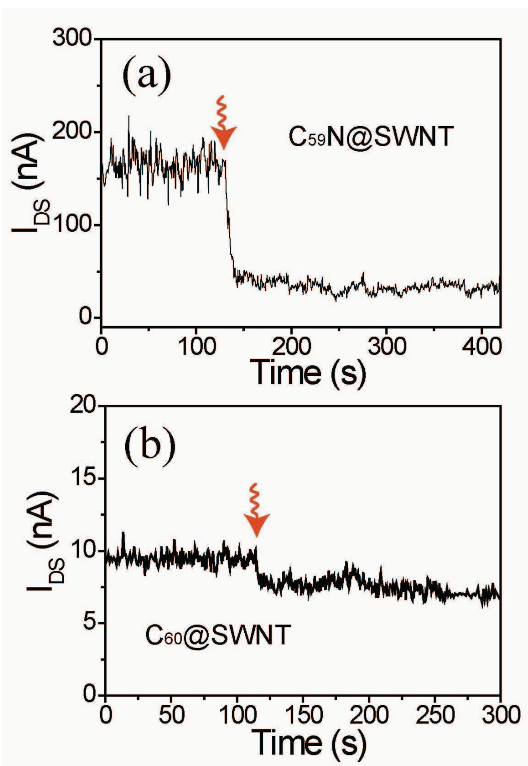

Figure 6. I_{DS} characteristic measured as a function of time with instantaneous light (400 nm wavelength) for (a) a $C_{59}N$ peapod device and (b) a C_{60} peapod device.

IV. SUMMARY

Our studies demonstrate that SWNTs become sensitive to light after encapsulating various forms of fullerenes or azafullerene. The photoinduced electron transfer phenomena are observed for fullerene peapods. The response characteristic of peapods to light is reflected in a shift of threshold voltage toward negative values, indicating an electron back-transfer process. In the case of azafullerene peapod, it is found that the conductance can repeatedly be switched by exposure to UV light when the azafullerene molecules are inside SWNTs. The photoswtiching characteristic is found to be dependent on the wavelengths, opening opportunities for SWNT-based photo-switches which are wavelength-selective. The specific sensitivity of electronic structure of $C_{59}N$ to light appears to be the main contribution to the observed photoresponse of $C_{59}N$@SWNTs.

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