Ambipolar field-effect transistor behavior of Gd@C_{82} metallofullerene peapods

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Transport properties of C_{60} fullerene peapods and Gd@C_{82} metallofullerene peapods are investigated by using the field effect in a gated structure. The results show that C_{60} peapods exhibit unipolar *p*-type characteristics, whereas Gd@C_{82} peapods show ambipolar both *p*- and *n*-type characteristics. This difference in transport behavior can be explained in terms of a bandgap narrowing of the peapods. One of the important findings is that tunable electronic properties of peapods are achieved by using the different types of encapsulated fullerene molecules. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1522482]

A type of hybrid carbon nanomaterials of single-walled nanotubes (SWNTs) encapsulating fullerenes (the so-called peapods)[1] has attracted great interest in recent years because of their structural and electronic properties. Upon insertion of fullerenes into SWNTs, the electronic properties such as band gaps of the nanotubes vary significantly without affecting the overall tubular structure. In our previous study, we found that the band gap of semiconducting SWNTs, for example, can be reduced from ~0.5 to ~0.1 eV by doping Gd@C_{82} endohedral metallofullerenes so as to form $(Gd@C_{82})_n$@SWNTs peapods.[2] This is indicative of the fact that metallofullerene peapods can be used as channels for future electronic devices.

One might expect that these peapods can be used as building blocks for molecular devices. The encapsulated fullerene molecules may assemble themselves inside the nanotubes to create tiny circuits tailored for a desirable electronic function. A theoretical study predicts that encapsulated fullerenes severely modify the electronic structure of SWNTs, leading to unusual electric transport properties.[3] Recent discovery of the high-yield synthesis of peapods allows us to prepare various kinds of peapods in large quantity and to investigate systematically their electronic properties.[4–8]

Here we report the transport properties of C_{60} fullerene peapods and Gd@C_{82} metallofullerene peapods by using these as channels of the field-effect transistors (FETs). The results show that the C_{60}-peapods-FETs exhibit *p*-type electronic character, which is similar to the semiconducting SWNTs–FETs.[9] On the other hand, ambipolar *p*- and *n*-type electronic behavior has been observed in Gd@C_{82}-peapods-FETs: Gd@C_{82} peapods can used as both *p* and *n* channels. The origin of the ambipolar character is explained by the band gap narrowing of the SWNTs due to the incorporation of Gd@C_{82} metallofullerenes. The substantial interaction between Gd@C_{82} and SWNTs may highly modify the electric transport properties of the nanotubes.

Details of the synthesis of C_{60} peapods and Gd@C_{82} peapods were described elsewhere.[4] Briefly, the doping materials, C_{60} and Gd@C_{82}, were synthesized by the dc arc-discharge method.[10] The purities of C_{60} and Gd@C_{82} were determined to be >99% by both high-performance liquid chromatography and time of flight-mass spectrometer analyses. SWNT bundles were generated by a pulsed-laser vaporization of Ni–Co (1.2–1.2 at. %) containing graphite target at 1250 °C in 500 Torr under an Ar flow condition (300 sccm). The diameter of the SWNTs produced under these conditions were in the range 1.3–1.6 nm. As-grown SWNTs were first washed with CS_2 to remove the coproduced fullerene molecules and the other soluble impurities. The residual amorphous carbon materials and metal catalyst particles were removed by refluxing such SWNTs with 30% H_2O_2 and washing them in HCl solution. Following these treatments, the SWNTs were heated in dry air at 450 °C for 30 min to open the tube ends.[4] The insertion of fullerenes into inner hollow space of SWNTs was carried out in a sealed glass ampoule at 400–500 °C for 2 days. Prior to the doping, the SWNTs and the fullerenes were degassed at ~185 °C in a vacuum for an hour.

The structures of the so-produced peapods were examined with a transmission electron microscope (TEM) operated at 120 kV (JEOL JEM-2010F).[4] The overall feature obtained by the high-resolution TEM (HRTEM) images of C_{60} peapods and Gd@C_{82} peapods indicated that the doping yields are more than 70% in both cases. A typical HRTEM images of a rope of Gd@C_{82} peapods are shown in Figs. 1(a) and 1(b). Figure 1(b) clearly shows the high doping ratio of Gd@C_{82} metallofullerenes. It shows a crystalline bundle of close-packed nanotubes, all of which contain a one-dimensional array of Gd@C_{82} fullerenes.

The FETs circuits were fabricated on a SiO_2 insulating layer (100 nm) on top of heavily doped silicon substrate.

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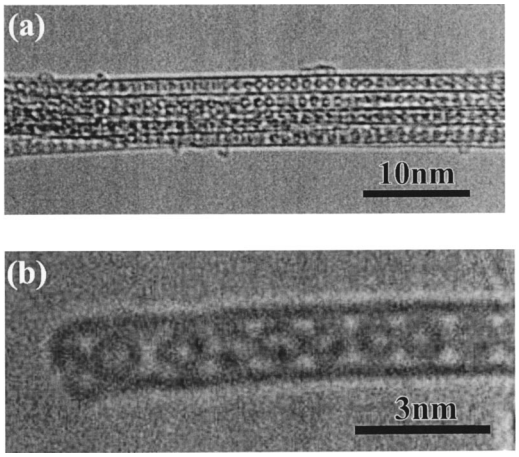

FIG. 1. (a) HRTEM image of a bundle of $Gd@C_{82}$ metallofullerene peapods. (b) HRTEM image of an end cap part of an individual $Gd@C_{82}$ metallofullerene peapod, showing a high doping ratio of $Gd@C_{82}$ metallofullerene molecules in the present study.

Source and drain electrodes were formed by electron beam lithography, metal evaporation (Ti/Au: 3/15 nm) and lift-off processes. The gap between source and drain electrodes was 400 nm. Heavily doped Si substrate was used as a backgate. The backgate electrode was prepared by metal evaporation (Ti/Au: 100/300 nm). The peapods were dispersed in 1,2-dichloroethane solutions and dropped onto the substrate. Scanning electron microscope (JEOL JSM-6340F) and atomic force microscope (AFM) (SEIKO INSTRUMENTS SPI-3700) were used to image the peapods-FETs. In the present study, we used a single rope of the peapods as a FET channel. The heights of the ropes were typically 7–15 nm, which corresponds to ropes consisting of 5–10 of individual peapods. The contact resistance was about 10 MΩ. All transport measurements were carried out at 23 K.

The current–voltage (I_D-V_{DS}) curves at various gate bias (V_{GS}) for a C_{60}-peapods-FET are shown in Fig. 2(a). The curves change from linear to nonlinear dependence around zero bias independent of the gate voltage, suggesting that there are barriers on the peapod/electrode interface. Figure 2(b) shows the current versus gate voltage (I_D-V_{GS}) characteristics of a C_{60}-peapods-FET for different V_{DS}. As is the case for the SWNTs–FETs,[9] the conductance increases as V_{GS} decreases, indicating that C_{60} peapods behave as a *p*-channel FET.

The I_D-V_{GS} characteristics of a $Gd@C_{82}$-peapods-FET are shown in Fig. 3. Starting from a positive gate voltage V_{GS}, the current I_D decreases steeply by three orders of magnitude towards 0 V and then gradually increases. This indicates that $Gd@C_{82}$ peapods exhibit ambipolar FET behavior with both *n* and *p* channels easily accessible by simple electrostatic gates. Similar results were obtained from more than ten independent FET devices composed of a small bundle of $Gd@C_{82}$ peapods. Such ambipolar behavior was not observed in C_{60} peapods.

The origin of the observed ambipolar behavior is closely related to the electronic structure of $Gd@C_{82}$ peapods. It is unlikely that this behavior stems from two independent *p*- and *n*-type $Gd@C_{82}$ peapods coexisting in the small bundle because we have not found any $Gd@C_{82}$-peapods-FET which showed only *p*- or only *n*-type

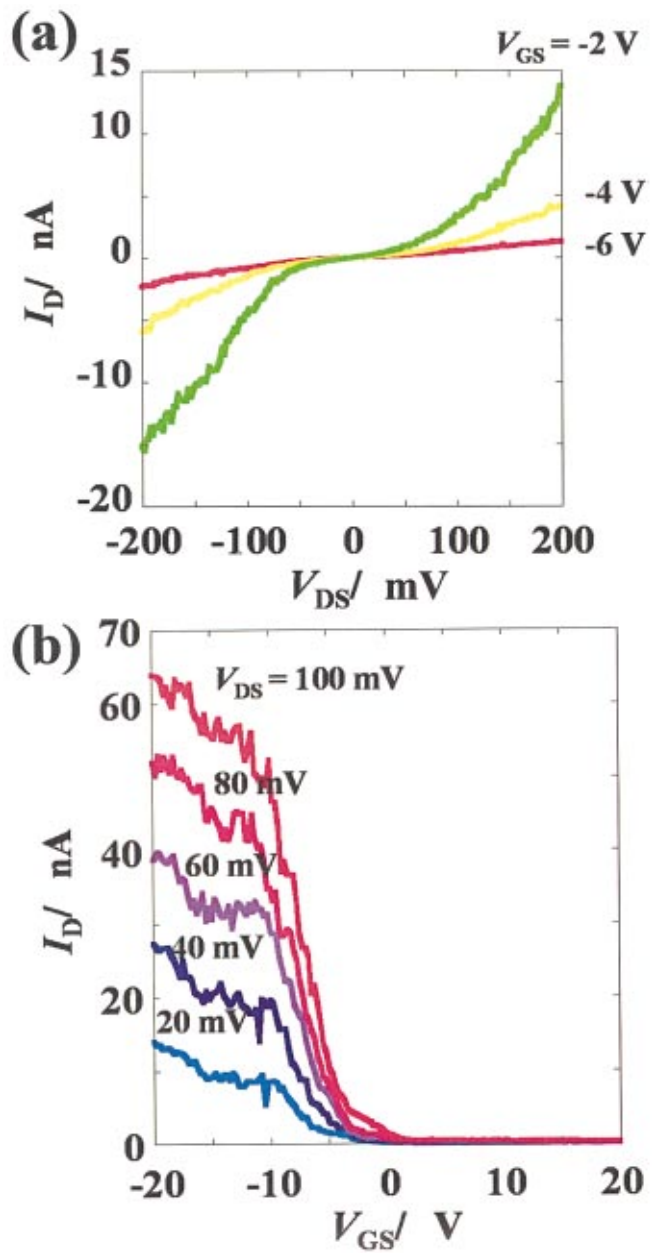

FIG. 2. (Color) Electronic transport properties of C_{60} fullerene peapods: (a) I_D-V_{DS} curve measured at $V_{GS}=-2$, -4, and -6 V; (b) I_D-V_{GS} curves at five different source-drain bias (V_{DS}) as indicated in the figure.

characteristics. Furthermore, it is well known that the coupling between nanotubes in a bundle is weak and thus the current flows only along the individual nanotube.[11,12] The ambipolar FET characteristics are, therefore, due to a direct consequence of the intrinsic electronic properties of $Gd@C_{82}$ peapods.

An empty SWNT with a diameter ~1.4 nm has a band gap of ~0.6 eV,[12,13] which exhibits a *p*-type FET behavior under ambient conditions.[9] This indicates that to show the *n*-type characteristics sufficiently high gate voltages are needed to electrostatically shift down the conduction band of the SWNT by at least 0.6 eV. In contrast, $Gd@C_{82}$ peapods have smaller band gaps.[2] Recent scanning tunneling microscopy and spectroscopy studies[2] revealed that electronic structures of SWNTs are strongly modulated by inserting $Gd@C_{82}$ fullerenes into the SWNTs. For example, a band gap of ~0.5 eV is narrowed down to ~0.1 eV at the sites

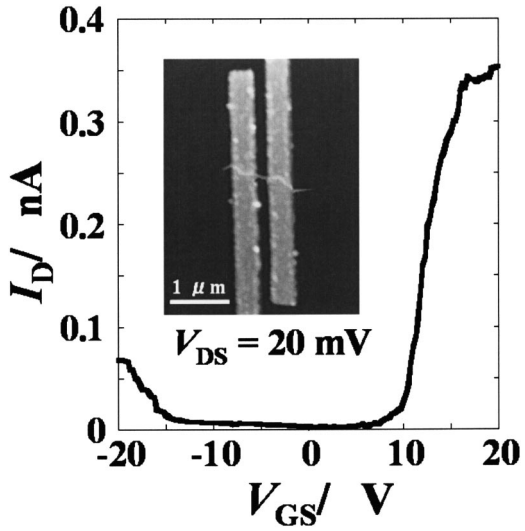

FIG. 3. I_D-V_{GS} curve for Gd@C_{82} metallofullerene peapods ($V_{DS}=20$ mV). The inset is an AFM image of the Gd@C_{82} peapods-FET used in the measurement.

where Gd@C_{82} molecules are inserted. The small band gap can lead to significant carrier transport properties through both the conduction and valence bands. In fact, ambipolar behavior has already been reported previously for large-diameter (3–5 nm) SWNTs that have small band gaps ($\sim$0.2 eV).[14] As compared with the Gd@C_{82} peapods, the doping effect in C_{60} peapods may be much less significant.[15] The C_{60} peapods still have large band gaps and, therefore, the *p*-type characteristics remains unchanged upon C_{60} encapsulation.

A temperature dependent transport behavior of Dy@C_{82} peapod FETs was recently reported by Chiu *et al.*[16] They reported a transition from *p*- to *n*-type conduction when the temperature was decreased from room temperature to 265 K. Further cooling led to a metallic behavior at 215 K. However, in the present study on C_{60}-peapods-FETs and Gd@C_{82}-peapods-FETs, any such transitions have not been observed from room temperature to 23 K. Instead, the conductance of Gd@C_{82}-peapods-FETs was found to decrease monotonically at lower temperatures both for the $V_{GS}<0$ and $V_{GS}>0$ regions. The reasons of the discrepancy between the two experimental results are not clear.

In summary, we have investigated the electronic transport properties of C_{60} fullerene peapods and Gd@C_{82} metallofullerene peapods. Only the *p*-type semiconducting behavior has been observed for C_{60} peapods, whereas Gd@C_{82} peapods show ambipolar behavior with both *p*- and *n*-type characteristics by tuning the gate voltage. These transport properties can be explained by the bandgap narrowing reported earlier.[2] The present results show that inserted metallofullerenes can finely control the electronic structure of SWNTs and that fullerene peapods can be important channels for future nanoelectronics devices.

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