Open Journal of Microphysics, **2011, 1, 23-27**
doi:10.4236/ojm.2011.12004 Published Online August 2011 (http://www.SciRP.org/journal/ojm)

Electrical Transport Properties of $C_{59}N$ Azafullerene Encapsulated Double-Walled Carbon Nanotube

Yongfeng Li*, T. Kaneko, R. Hatakeyama
Department of Electronic Engineering, *Tohoku University*, *Sendai*, *Japan*
E-mail: *yfli@plasma.ecei.tohoku.ac.jp
Received May 18, 2011; *revised June* 22, 2011; *accepted July* 18, 2011

Abstract

Electrical transport properties of double-walled carbon nanotubes (DWNTs) are modulated by encapsulating the azafullerene $C_{59}N$ which is synthesized via a plasma ion-irradiation method. The encapsulation of $C_{59}N$ molecules inside DWNTs has been confirmed by both transmission electron microscopy and Raman spectroscopy. The pristine DWNTs with outer diameter 4 - 5 nm are found to exhibit an ambipolar semiconducting behavior due to their small band gap. It is found that C_{60} fullerene encapsulated DWNTs exhibit a unipolar *p*-type semiconducting behavior. By comparison, $C_{59}N$ encapsulated DWNTs display an *n*-type semiconducting behavior. Our findings demonstrate that $C_{59}N$ operates as an electron donor compared with the acceptor behavior of C_{60}, which is further clarified by photoelectron emission spectroscopy.

Keywords: Carbon Nanotubes, FET, Encapsulation, Azafullerene

1. Introduction

Recently, double-walled carbon nanotubes (DWNTs) serving as nanoelectrical materials has received extensive attentions owing to their great potential applications [1,2]. DWNTs represent a good candidate since they possess more stable mechanical properties and thermal stability than single-walled carbon nanotubes (SWNTs) because of their intrinsic coaxial structure. In particular, the large inner diameter of DWNTs makes them especially advantageous as an effective atom/molecule container. Therefore, DWNTs are interesting as material in engineering various kinds of nanoelectronic devices. However, most of previous experiments to date focus on the empty DWNTs which initially show an ambipolar or a *p*-type behavior when fabricated as the channels of field-effect transistor (FET) devices [3-5]. The extensive research using different kinds of nanotubes with controllable electronic properties to construct nanoelectronic devices is extremely important for the progress in this field. Unfortunately, the number of reports on the transport properties of DWNTs is still limited. Moreover, there are few systematic studies concerning the electronic properties of DWNTs modified with electron dopants [6,7].

Here, we have investigated the transport properties of FET devices fabricated based on DWNTs which are modulated with the $C_{59}N$ azafullerene for the first time. The encapsulation of $C_{59}N$ in DWNTs is proven by transmission electron microscopy and Raman spectroscopy. Pristine DWNTs are found to show either metallic or ambipolar semiconducting behavior owing to their narrow bandgap. However, after the $C_{59}N$ encapsulation, DWNTs can exhibit a unipolar *n*-type semiconducting behavior in contrast to the *p*-type behavior of C_{60} encapsulated DWNTs, indicating that the electronic structure of DWNTs is strongly modified upon the insertion of $C_{59}N$ azafullerene in contrast to the case of pristine DWNTs and C_{60} encapsulated DWNTs.

2. Experimental

The azafullerene $C_{59}N$ was synthesized by a nitrogen plasma irradiation method [8]. A plasma was produced by applying an RF power with a frequency of 13.56 MHz, and nitrogen ions in the plasma were generated and accelerated toward a substrate by a sheath electric field in front of the deposited C_{60} fullerene. Detailed experimental conditions are given as follows: plasma density $n_p \sim 10^9$ cm^{-3}, electron temperature $T_e \sim 0.5$ eV, and nitrogen-ion irradiation energy $E_i = 10$ - 40 eV. The fullerene C_{60} after the plasma irradiation was dissolved in toluene and its mixture was separated into a residue and a solution. The mass spectroscopy analysis of the formed $C_{59}N$ azafullerene was performed using a laser-desorption time-

Copyright © 2011 SciRes.

of-flight mass spectrometer (LD-TOF-MS, Shimadzu AXIMA-CFR+).

The DWNTs used in this work were fabricated by an arc discharge method with Fe as catalyst. $C_{59}N$ aza- fullerene or C_{60} fullerene molecules encapsulated DWNTs were synthesized by a vapor diffusion method. The purified DWNTs together with azafullerene or fullerene powders were first sealed in a glass tube under the vacuum condition ~10^{-5} Torr. After that, the sealed glass tube was heated at 500˚C for 48 h to encapsulate the $C_{59}N$ azafullerene or C_{60} fullerene in DWNTs. The encapsulated samples were obtained after the above process, and examined in detail by field emission transmission electron microscopy (FE-TEM, Hitachi HF-2000) operated at 200 kV and Raman Spectroscopy with a laser wavelength of 633 nm.

The electronic transport properties of various DWNTs are investigated by fabricating them as the channel of FET devices. During the fabrication process, DWNT samples are firstly dispersed by sonication in *N*, *N*-dimethylformamide (DMF) solvent and then spincoated on a substrate, which consists of Au electrodes on a SiO_2 insulator layer. A heavily doped Si substrate is used as a backgate, and the back-gate electrode is prepared by Al evaporation. The fabrication process for nanotube FET devices has been described in detail in our previous studies [9,10]. The transport property measurements are carried out at room temperature in a vacuum using a semiconductor parameter analyzer (Agilent 4155C).

3. Results and Discussions

3.1. TEM and Raman Spectroscopy Characterization

Figure 1(a) shows the mass spectrum of synthesized $C_{59}N$, in which the peak at 722 is the most distinct, corresponding to the $C_{59}N$ azafullerene. While the peak at 720 is well known for the C_{60} fullerene, its peak density is much lower than that of $C_{59}N$, suggesting that $C_{59}N$ is the dominant material in the sample. Such $C_{59}N$ molecules are encapsulated into DWNTs by a vapour diffusion method. **Figures 1(b)** and **(c)** give TEM images of individual pristine DWNT and DWNT filled with the $C_{59}N$ molecules. In **Figure 1(b)**, a pristine DWNT with inner diameter 4 nm and outer diameter 4.8 nm is clearly observed. In contrast, **Figure 1(c)** shows the TEM image of an individual DWNT filled with the $C_{59}N$ molecules. Our results indicate that they have been filled in DWNTs in the amorphous-phase state (indicated by arrows), which is similar to the case of C_{60} encapsulated DWNTs [11], but is different from the chain-like $C_{59}N$ observed in SWNTs [12] because of large diameter of DWNTs. Interestingly, the dimer form of $C_{59}N$, that is $(C_{59}N)_2$, is observed in the DWNT (as indicated by a circle), which is in agreement with the original property of $C_{59}N$ azafullerene which primarily exists in the stable form of dimer, as illustrated in the inset of **Figure 1(c)**. Furthermore, Raman spectra reveal a definate difference between the $C_{59}N$ and C_{60} encapsulated DWNTs, as given in **Figure 2**. After the $C_{59}N$ encapsulation, only the intensity-ratio decrease in the G/D band is found compared with that of pristine DWNTs. In contrast, big changes are recognized on the sample of C_{60}-filled DWNTs. Apart from the decrease in the G/D ratio, two distinct peaks between D-band (1378 cm^{-1}) and G-band (1584 cm^{-1})

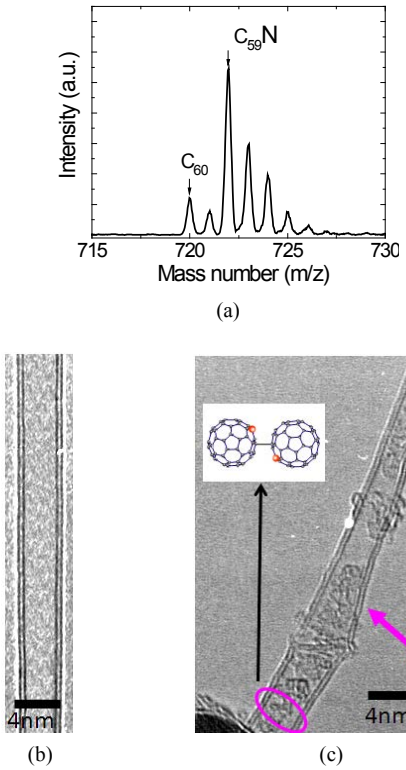

Figure 1. (a) Mass spectrum of synthesized $C_{59}N$, TEM images for a pristine DWNT (b) and a $C_{59}N$ encapsulated DWNT (c).

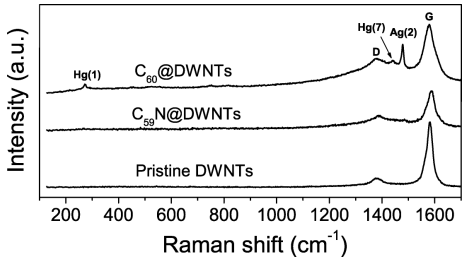

Figure 2. Raman spectra for pristine DWNTs, $C_{59}N$ encapsulated DWNTs ($C_{59}N$@DWNTs) and C_{60} encapsulated DWNTs (C_{60}@DWNTs).

Copyright © 2011 SciRes.

are observed. One strong peak at 1476 cm^{-1} corresponds to the intermolecular Raman active frequency (tangential mode) Ag (2) of C_{60} molecules, and the other weak peak at 1437 cm^{-1} near the D-band can be attributed to the Hg (7) mode of C_{60} molecules. A very weak peak for the Ag (2) mode observed in $C_{59}N$ encapsulated DWNTs compared with that observed for C_{60} encapsulated DWNTs may possibly be explained in terms of their different electronic structure.

3.2. Transport Properties of $C_{59}N$ Encapsulated DWNTs

The electrical transports properties of DWNTs are measured based on an FET configuration, as schematically illustrated in the inset of **Figure 3**. Our measurements demonstrate that the transport properties of pristine semiconducting DWNTs show an ambipolar behavior, as shown in **Figure 3**. The characteristics of source-drain current versus gate voltage (I_{DS}-V_G) curves indicate that the device conducts either electrons or holes depending on the gate bias when different source-drain voltages (V_{DS}) from 0 to 1 V are applied. The region on the left-hand for V_G < –20 V corresponds to the *p*-type conduction and the *n*-type conductance is observed in the right-hand region for V_G > –20 V. The current-voltage characteristics of the device indicate that the source-drain current increases strongly with increasing the negative gate voltage in the *p*-channel and increasing the positive gate voltage in the *n*-channel, respectively. Particularly, the observed saturated conductance in the *p*-channel typically appears to be two or three times larger than that observed in the *n*-channel for pristine DWNT-FETs. In contrast, unipolar *n*-type DWNT-FETs can be obtained by the $C_{59}N$-encapsulation, as shown in **Figure 4(a)**, where the characteristics of I_{DS}-V_G measured at different V_{DS} ranging from 0 to 0.1 V in steps of 0.02 V indicate clearly that the FET device exhibits an excellent *n*-type semiconducting behavior, and no amibipolar behavior is found due to the strong electron-donating property of $C_{59}N$. The threshold voltage (V_{th}) necessary to completely deplete the nanotubes is about –20 V at V_{DS} = 0.1 V, which is similar to the value of V_{th} for the *n*-type region in the pristine ambipolar DWNTs. To further estimate the performance of the *n*-type FET device, the I_{DS}-V_{DS} curves are measured with V_{DS} ranging from –0.1 to 0.1 V by applying different gate voltages from –30 V to 20 V, as shown in **Figure 4(b)**. The conductance of device is significantly suppressed by decreasing the gate voltages from 20 V until the gate voltage reaches about –40 V, which also exhibits a reproducible characteristic for the *n*-type nanotube FETs, being consistent with the result in **Figure 4(a)**. The above result demonstrates

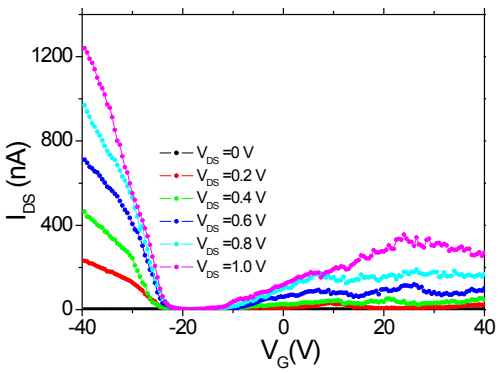

Figure 3. (a) Drain-source current versus gate voltage (I_{DS}-V_G) characteristics for an amibipolar semiconducting DWNT-FET measured with bias voltage (V_{DS}) ranging from 0 to 1 V in steps of 0.2 V. The inset shows the FET configuration.

evidently that there is the strong electron transfer from $C_{59}N$ to the encapsulated DWNT; as a result, the electron density of conduction band of DWNT is strongly modified. In contrast, for the C_{60}-encapsulation, the transport characteristic is completely opposite to that observed for the $C_{59}N$ encapsulated DWNTs, and the unipolar *p*-type semiconducting DWNTs are obtained, as given in **Figures 4(c)** and **(d)**. The I_{DS}-V_G characteristics demonstrate that no *n*-type conductance is found during the measurements performed with V_{DS} in the range of –1 ~ 1 V. The observed V_{th} near –10 V at V_{DS} = 1 V shows a clear upshift compared with that (–20 V) observed for the *p*-type region of pristine DWNTs. In addition, the I_{DS}-V_{DS} curve characteristics in **Figure 4(d)** indicate that the conductance of the FET device is reduced by increasing the gate voltage from –40 to 40 V, which is opposite to that observed in **Figure 4(b)** for the device based on the $C_{59}N$ encapsulated DWNT. The present experiments suggest that the $C_{59}N$ molecules exert a strong electron-donating effect on DWNTs compared with the electron-accepting behavior of C_{60}.

In order to analyze electronic structures of $C_{59}N$ and C_{60}, their work functions are investigated by ultraviolet photoemission spectroscopy (UPS), which can provide a mechanical insight into the charge transfer process between the encapsulated azafullerene and DWNTs. **Figure 5** presents the photoelectron emission spectra of C_{60} and $C_{59}N$, in which the work function of $C_{59}N$ is determined to be about 5.5 eV, much smaller than that (6.1 eV) observed for C_{60}, suggesting evidently that the electronic property of $C_{59}N$ is significantly different from that of C_{60}. Namely, the nitrogen-atom bonding with C atom makes the release of electrons easier in the case of $C_{59}N$ azafullerene. Therefore, by combining the electrical transport properties of FETs and photoelectron emission spectra, the *n*-type semiconducting behavior of DWNTs

Copyright © 2011 SciRes.

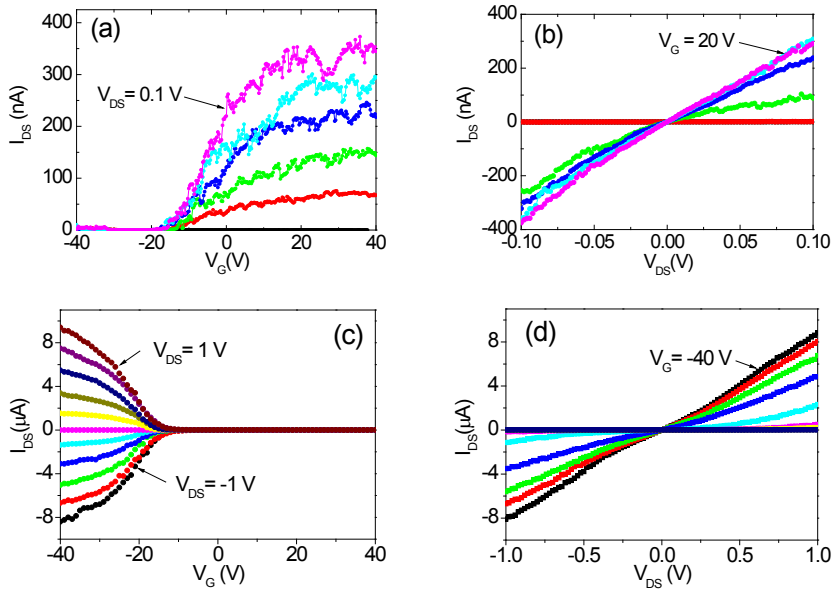

Figure 4. (a) I_{DS}-V_G characteristics for an *n*-type $C_{59}N$ encapsulated DWNT with V_{DS} ranging from 0 to 0.1 V in steps of 0.02 V. (b) I_{DS}-V_{DS} curves for an *n*-type $C_{59}N$ encapsulated DWNT with V_G ranging from 20 to –30 V. (c) I_{DS}-V_G characteristics for a *p*-type C_{60} encapsulated DWNT with V_{DS} ranging from –1 to 1 V in steps of 0.2 V. (c) I_{DS}-V_{DS} output characteristics for a *p*-type C_{60} encapsulated DWNT measured with V_G ranging from –40 to 40 V.

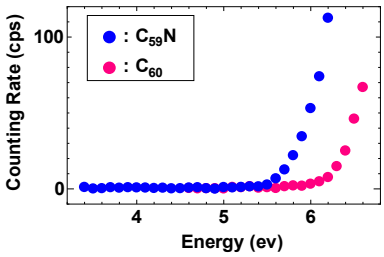

Figure 5. Photoelectron emission spectra of $C_{59}N$ and C_{60}.

can be understood by the charge transfer from $C_{59}N$ to DWNTs, which shifts the Fermi level towards the conduction band. In other words, the Fermi level of DWNTs is strongly modified by the interaction between DWNTs and $C_{59}N$ azafullerene.

4. Summary

TEM observations and Raman spectra have confirmed that the $C_{59}N$ azafullerene has successfully been filled inside DWNTs. Electrical transport measurements indicate that pristine DWNTs can exhibit the amibipolar semiconducting behavior. On the other hand, unipolar *n*-type semiconducting DWNTs are significantly observed after the $C_{59}N$ encapsulation, proving the electronic structure of DWNTs is strongly modified. Compared with C_{60} with the electron accepting behavior, the $C_{59}N$ azafulle- rene shows the interesting electron-donating behavior, which is confirmed by photoelectron emission spectra. The DWNTs are a promising candidate for creating FET devices showing various properties including *p*-type, *n*-type and ambipolar behaviors.

5. Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and JSPS-CAS Core-University Program on Plasma and Nuclear Fusion. We are grateful to Professor K. Tohji and Mr. K. Motomiya for their help in TEM observation.

6. References

[1] A. A. Green and M. C. Hersam, "Properties and Application of Double-Walled Carbon Nanotubes Sorted by Outer-Walled Electronic Type," *ACS Nano*, Vol. 5, No. 2, 2011, pp. 1459-1467.

[2] D. A. Tsyboulski, Y. Hou, N. Fakhri, S. Ghosh, R. Zhang, S. M. Bachilo, M. Pasqulai, L.W. Chen, J. Liu and R. B.. Weisman, "Do Inner Shells of Double-Walled Carbon Nanotubes Fluoresce," *Nano Letters*, Vol. 9, No. 9, 2009, pp. 3282-3289.

[3] T. Shimada, T. Sugai, Y. Ohno, S. Kishimoto, T. Mizutani, H. Yoshida, T. Okazaki and H. Shinohara, "Double-Wall Carbon Nanotube Field-Effect Transistors: Ambipolar Transport Characteristics," *Applied Physics Letters*, Vol. 84, No. 13, 2004, pp. 2412-2414.

[4] K. Liu, W. Wang, Z. Xu, X. Bai, E. Wang, Y. Yao, J. Zhang, and Z. Liu, "Chirality-Dependent Transport Properties of Double-Walled Nanotubes Measured in Situ on

Copyright © 2011 SciRes.

Their Field-Effect Transistors," *Journal of the American Chemical Society*, Vol. 131, No. 1, 2008, pp. 62-63.

[5] S. Wang, X. L. Liang, Q. Chen, Z. Y. Zhang and L. M. Peng, "Field-Effect Characteristics and Screening in Double-Walled Carbon Nanotube Field-Effect Transistors," *The Journal of Physical Chemistry B*, Vol. 109, No. 37, 2005, pp. 17361-17365.

[6] Y. F. Li, R. Hatakeyama, T. Kaneko, T. Izumida, T. Okada and T. Kato, "Transport Properties of Cs- Encapsulated Double-Walled Carbon Nanotubes," *Applied Physics Letters*, Vol. 89, No. 9, 2006, pp. 093110-1-3.

[7] Y. F. Li, R. Hatakeyama, T. Kaneko, T. Izumida, T. Okada and T. Kato, "Synthesis and Electronic Properties of Ferrocene-Filled Double-Walled Carbon Nanotubes," *Nanotechnology*, Vol. 17, No. 16, 2006, pp. 4143-4147.

[8] S. Abe, G. Sato, T. Kaneko, T. Hirata, R. Hatakeyama, K.Yokoo, S. Ono, K. Omote and Y. Kasama, "Effects of Ion Energy Control on Production of Nitrogen–C_{60} Compounds by Ion Implantation," *Japanese Journal of Applied Physics*, Vol. 45, No. 10B, 2006, pp. 8340-8343.

[9] Y. F. Li, R. Hatakeyama, T. Kaneko, T. Izumida, T. Okada and T. Kato, "Electrical Properties of Ferromagnetic Semiconducting Single-Walled Carbon Nanotubes," *Applied Physics Letters*, Vol. 89, No. 8, 2006, pp. 083117-1-3.

[10] T. Izumida, R. Hatakeyama, Y. Neo, H. Mimura, K. Omote and Y. Kasama, "Electronic Transport Properties of Cs-Encapsulated Single-Walled Carbon Nanotubes," *Applied Physics Letters*, Vol. 89, No. 8, 2006, pp. 093121-1-3.

[11] A. N. Khlobystov, D. A. Britz, A. Ardavan and G. A. D. Briggs, "Observation of Ordered Phases of Fullerenes in Carbon Nanotubes," *Physics Review Letters*, Vol. 92, No. 24, 2004, pp. 245507-1-3.

[12] T. Kaneko, Y. F. Li, S. Nishigaki and R. Hatakeyama, "Azafullerene Encapsulated Single-Walled Carbon Nanotubes with *n*-Type Electrical Transport Property," *Journal of the American Chemical Society*, Vol. 130, No. 9, 2008, pp. 2714-1715.

Copyright © 2011 SciRes.