Air-Stable p-n Junction Diodes Based on Single-Walled Carbon Nanotubes Encapsulating Fe Nanoparticles

著者	金子　俊郎
journal or publication title	Applied Physics Letters
volume	90
number	17
page range	173127-1-173127-3
year	2007
URL	http://hdl.handle.net/10097/34856

Air-stable *p-n* junction diodes based on single-walled carbon nanotubes encapsulating Fe nanoparticles

Y. F. Li,[a)] R. Hatakeyama, J. Shishido, T. Kato, and T. Kaneko
Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan

(Received 8 March 2007; accepted 4 April 2007; published online 27 April 2007)

The authors report electrical transport properties of *p-n* junction based on semiconducting single-walled carbon nanotubes (SWCNTs). The formation of *p-n* junction is realized in SWCNTs, which are encapsulated with Fe nanoparticles at low filling fractions. The devices exhibit an excellent rectifying behavior, and no current down to 10^{-14} A level flows when the device is biased in reverse. During measurements performed in the temperature range from 10 to 300 K, the devices maintain high reproducibility. More importantly, even after exposure to air, the rectifying characteristic keeps stable, which strongly suggests that ideal *p-n* junction diodes can be fabricated by SWCNTs. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2734509]

Over the past decade, single-walled carbon nanotubes (SWCNTs) have been widely studied due to many of their unique properties at the nanoscale and potential applications in lots of fields. For electronic applications, a number of nanodevices with unique transport properties, such as field effect transistors (FETs), single-electron transistors, memory devices, and sensors based on SWCNTs have been realized experimentally.[1–4] Encapsulating foreign atoms or molecules in SWCNTs has become one of attractive ways in controlling their transport properties. Compared with *p*-type pristine SWCNTs, *n*-type semiconductiong SWCNTs can be created by doping a large variety of electron donors.[5–8] Up to now, SWCNTs can be directly doped under a designed doping profile along its length, resulting in the formation of nanosized junctions, which exhibit interesting transport properties. For example, a *p-n* junction has been formed by partly doping potassium on the outside surface of SWCNTs but a leakage current is found at reverse biases.[9] Therefore, there is still a challenge whether ideal junction diodes can be fabricated with SWCNTs by foreign material encapsulation. Here we demonstrate that a *p-n* junction can be formed with SWCNTs by means of Fe encapsulation at low filling fractions. Our results reveal that the fabricated devices exhibit an air-stable rectifying characteristic, and no current down to 10^{-14} A level is found during the whole measurements in the temperature range from 10 to 300 K.

In this study, pristine SWCNTs with a diameter of about 1.4 nm are prepared by an arc discharge using Fe/Ni as a catalyst. In order to fill Fe nanoparticles in SWCNTs, ferrocene was selected as a starting material and firstly filled in SWCNTs by a chemical vapor diffusion method. Then ferrocene-filled SWCNTs are rapidly annealed in vacuum to release Fe atoms inside SWCNTs, which has been described elsewhere.[10,11] Fe-filled SWCNTs with different filling levels are prepared by adjusting the reaction time (from 2 to 48 h) of ferrocene vapor with SWCNTs. The amount of encapsulated Fe in SWCNTs is estimated by x-ray fluorescence spectroscopy. For the reaction time of 48 h, the filling fraction (number of the filled Fe atom per carbon atom of SWCNTs) is $f=2.8\times10^{-3}$ which corresponds to a high filling level, and in this case most Fe-filled SWCNTs exhibit unipolar *n*-type characteristics. In contrast, at low filling fractions with $f\leqq1\times10^{-3}$, in addition to *n*-type behavior, a *p-n* junction is significantly observed in SWCNTs due to partial Fe encapsulation.

The device preparation is similar to that used for making typical SWCNT-FETs. Samples of SWCNTs are dispersed by sonication in *N*,*N*-dimethylformamide (DMF) solvent for over 10 h, and then spin coated on FET substrates, which consist of Au electrodes with thickness of 150 nm. Each pair of Au electrodes with a channel length of 500 nm is made on a SiO_2 layer with a thickness of 500 nm. A heavily doped Si wafer is used as a back gate. A baking process at 400 K is finally carried out in air for 30 min to remove the excess DMF solution on the FET substrates. Electronic transport measurements are performed in both vacuum and air-conditions from 10 to 300 K using a semiconductor parameter analyzer (Agilent 4155C). It is worthy to mention that the fabrication procedure for making the *p-n* junction in our present study is relatively simple compared with those described in previous reports (Refs. 9 and 12–14), where half of SWCNTs is usually covered by polymethylmethacrylate and their opposite part remains uncovered.[12,13]

Prior to Fe encapsulation, the pristine SWCNTs exhibit the well-known *p*-type semiconducting behavior, and the unipolar *n*-type SWCNTs have been proven to be formed by Fe encapsulation at the high filling fraction,[11] as shown in a source-drain current versus gate bias (I_{DS}-V_G) characteristic of Fig. 1 for a source-drain voltage of $V_{DS}=1$ V. At low filling fractions with f in the range of $\sim3\times10^{-4}-10^{-3}$ (the corresponding reaction time is 2–6 h), apart from *n*-type SWCNTs the *p-n* junction is found to be formed in some Fe-filled SWCNTs. A typical transport characteristic for the *p-n* junction observed in SWCNTs is shown in Fig. 2, in which the I_{DS}-V_G curves are measured at different biases V_{DS} ranging from 0.4 to 1 V in steps of 0.1 V at room temperature. Obviously, the present transport feature is different from the normal monotonic increase or decrease with increasing the gate voltage, which is observed in simple *n*- or *p*-type transport characteristics. For $V_G<-13$ V, each I_{DS}-V_G curve shows a monotonic increase with increasing the negative gate bias, similar to the *p*-type behavior, and the current with V_G between −13 and −5 V is suppressed to near zero (on the order of 10^{-14} A). A current hump region is interestingly observed at $-5\ V<V_G<5$ V, which is known

[a)]Author to whom correspondence should be addressed; FAX: +81-022-263-9225; electronic mail: yfli@plasma.ecei.tohoku.ac.jp

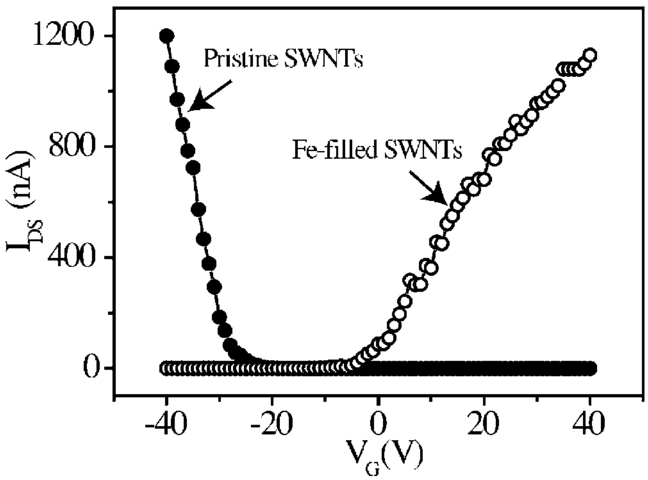

FIG. 1. I_{DS}-V_G characteristics (V_{DS}=1 V) for *p*-type pristine SWCNTs and *n*-type Fe-filled SWCNTs which are prepared at high filling fraction $f=2.8\times10^{-3}$.

as the formation of the *p*-*n* junction in SWCNTs, according to the previous descriptions.[9] When the gate bias is larger than 5 V, the current is suppressed to zero again until the gate voltage reaches 40 V. As the applied bias V_{DS} is larger than 0.5 V, the interesting hump current can repeatedly be observed in each I_{DS}-V_G curve. In contrast, when the applied bias is less than 0.5 V or becomes negative, the current tends to be reduced to zero.

To further assess the performance of the *p*-*n* junction device, we investigate the output characteristic of I_{DS}-V_{DS} curves with V_{DS} ranging from −1 to 1 V by applying different gate voltages, as shown in Fig. 2(b), which correspond to the gate voltage positions (A, B, C, D, and E) in Fig. 2(a), respectively. It can be seen clearly that all the measured I_{DS}-V_{DS} curves exhibit excellent rectifying characteristics, i.e., the current can flow only at the forward bias and diminish under the reverse bias. In agreement with observations of Fig. 2(a), the current designates a significant decrease at the gate voltages of both −10 and 10 V, and a small current is detected at V_{DS}=1 V in the *p*-*n* junction region (V_G=0 V) in contrast with the current measured at V_G=−40 and −20 V. It has been found that the current measured at the negative bias is of the order of 10^{-14} A, which is different from the previous descriptions.[9] In addition, we compare the diode behavior of SWCNTs with that of ideal diodes, of which the current-voltage curve is described by the following equation: $I_{DS}=I_0(e^{qV_{DS}/nK_BT}-1)$, where I_0 is the reverse bias saturation current, *e* is Euler constant (∼2.7183), *q* is the charge of electron (1.6×10^{-19} C), V_{DS} is an applied bias voltage, *n* is

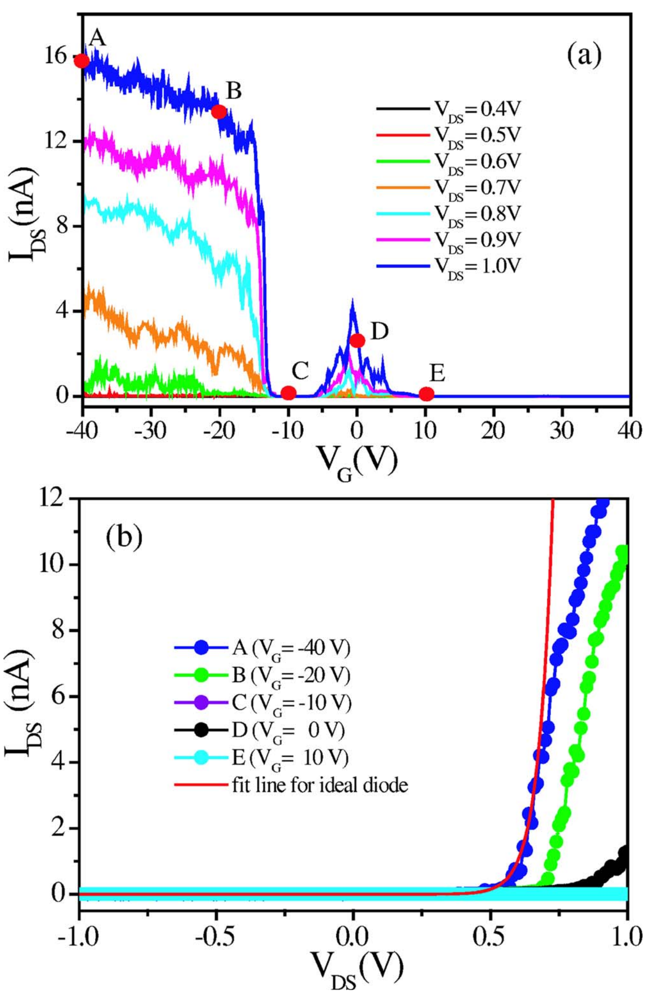

FIG. 2. (Color online) (a) I_{DS}-V_G curves measured with V_{DS} ranging from 0.4 to 1 V for *p*-*n* junction device. Here Fe-filled SWCNTs are prepared at filling fraction $f=1\times10^{-3}$. (b) I_{DS}-V_{DS} curves exhibiting rectifying behavior for gate voltages ranging from −40 to 10 V, which correspond to the voltage positions (A, B, C, D, and E) marked in (a), respectively. The fit line for the ideal diodes is calculated with n=1.2, $I_0=10^{-14}$, and T=300 K.

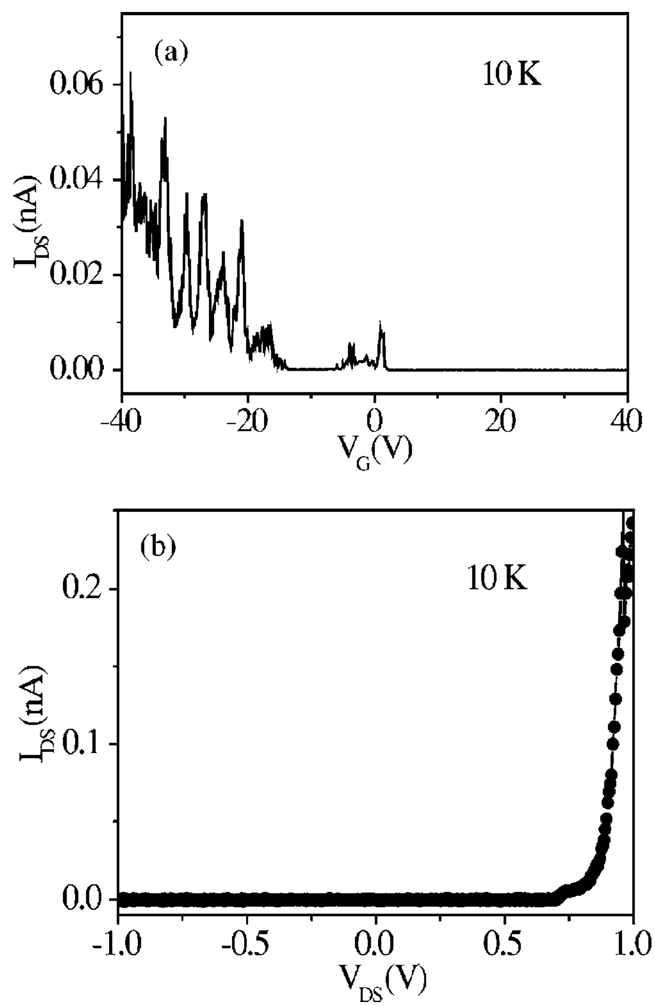

FIG. 3. (a) I_{DS}-V_G curve measured at 10 K with V_{DS}=0.6 V, showing the hump current feature keeps stable at V_G=0 V. (b) An I_{DS}-V_{DS} curve measured at 10 K with V_G=0 V showing the device remains the rectifying behavior.

the ideality factor (typically between 1 and 2), K_B and T are Boltzmann's constant (1.38×10^{-23}) and temperature, respectively. In our case, the parameters used for the fit line are $I_0=10^{-14}$ A, $n=1.2$, and $T=300$ K. The value chosen for n is typical of many devices, which has been mentioned previously.[15] By comparison, it is found that the measured I_{DS}-V_{DS} curves exhibit a good similarity to the fit line for the ideal diodes, and both of them display a sharp current increase feature with the applied bias more than 0.5 V. It is important to emphasize that similar rectifying characteristics have been observed in many independent devices. Therefore, our results reveal that ideal *p*-*n* junction diodes can possibly be fabricated by SWCNTs encapsulating Fe nanoparticles.

Temperature dependences of the I_{DS}-V_G characteristics for the diode device reveal that the observed rectifying characteristic can keep stable during the measurements ranging from 10 to 300 K. Figure 3(a) gives a I_{DS}-V_G curve measured at 10 K with $V_{DS}=0.6$ V, and the striking hump feature can also be found at about $V_G=0$ V although the current decreases by two orders of magnitude compared with that measured at room temperatures. This decrease is attributed to the increase of serial resistance at the two metal-nanotube contacts at low temperatures.[16] In addition, periodic Coulomb oscillations are observed at $V_G<-20$ V, indicating a signature of single-electron charging effect at low temperatures. The measured I_{DS}-V_{DS} curve in Fig. 3(b) indicates that the device remains the ideal rectifying behavior even at low temperatures. Furthermore, we examine the transport characteristics of *p*-*n* junction diode in air-condition, as indicated in Fig. 4(a), where the I_{DS}-V_G curve is measured at $V_{DS}=1$ V after the device is exposed to air for over 24 h. Interestingly, the hump current region disappears, and the current flow across the nanotube shows a great increase compared with the results observed in Fig. 2. However, the characteristic of I_{DS}-V_{DS} shown in Fig. 4(b) demonstrates evidently that the rectifying characteristic of device keeps stable in air. A reason for the above transport phenomenon can be explained in terms of the adsorption of oxygen during measurements performed in air. Since the oxygen acts as an electron acceptor, its adsorption on the outside of SWCNTs is considered to weaken the *n*-type part of the encapsulated nanotube. Consequently, the width of depletion region or height of potential barrier can possibly be reduced, which can give rise to a large current flowing through the thin *p*-*n* junction. To confirm this, we have examined the characteristics of the device again in vacuum at room temperature. As expected, a recoverable characteristic as a signature of the current decrease and hump current feature is repeatedly observed, similar to the results displayed in Fig. 2(a).

In summary, we have demonstrated that the *p*-*n* junction can possibly be created in SWCNTs through encapsulating Fe particles at the filling fraction $f\leqq1\times10^{-3}$. Our results reveal that the devices show excellent rectifying performance at various temperatures ranging from 10 to 300 K, which is similar to characteristics of ideal diodes. More importantly, the *p*-*n* junction characteristics of SWCNTs have proved stable even in air-condition. It is believed that we may offer a feasible approach to the fabrication of *p*-*n* junction nanodevice with SWCNTs.

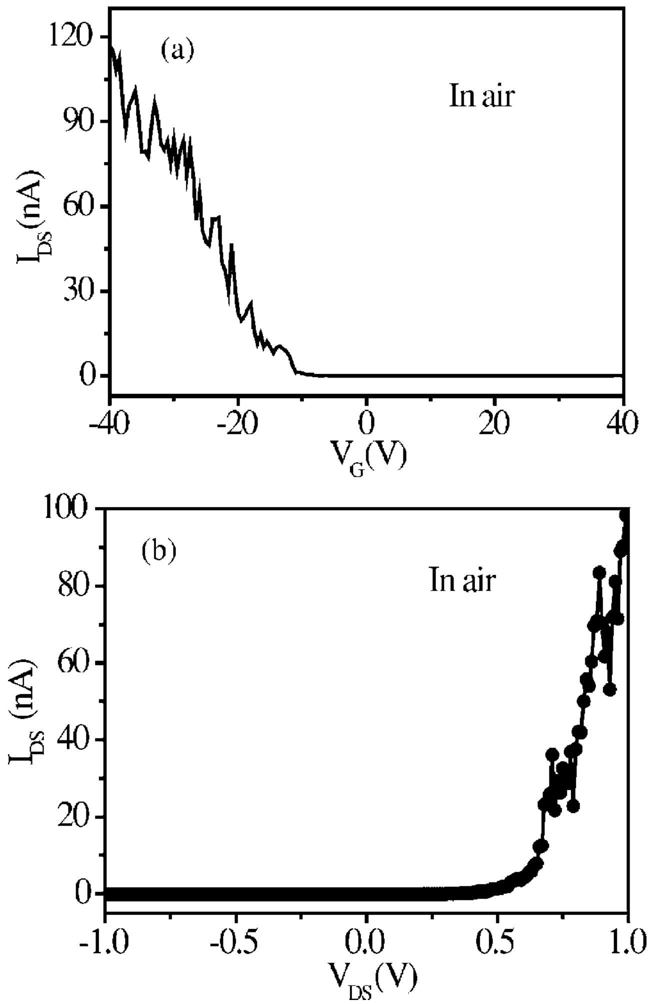

FIG. 4. (a) I_{DS}-V_G curve measured with $V_{DS}=1$ V at room temperature in air, indicating the hump current region disappears. (b) A stable rectifying I_{DS}-V_{DS} characteristic measured at $V_G=-40$ V is observed in air-condition.

This work was supported by Tohoku University 21st Century Center of Excellence (COE) Program, Research Fellowship of Japan Society for the Promotion of Science (JSPS) and JSPS-CAS Core-University Program on Plasma and Nuclear Fusion.

[1]R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, Appl. Phys. Lett. **73**, 2447 (1998).
[2]M. Bockrath, D. H. Cobden, P. L. McEuen, N. G. Chopra, A. Zettl, A. Thess, and R. E. Smalley, Science **275**, 1922 (1997).
[3]M. S. Fuhrer, B. M. Kim, T. Durkop, and T. Brintlinger, Nano Lett. **2**, 755 (2002).
[4]J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. J. Dai, Science **287**, 622 (2000).
[5]A. Javey, R. Tu, D. B. Farmer, J. Guo, R. G. Gordon, and H. J. Dai, Nano Lett. **5**, 345 (2005).
[6]J. Kong, C. Zhou, E. Yenilmez, and H. J. Dai, Appl. Phys. Lett. **77**, 3977 (2000).
[7]V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris, Appl. Phys. Lett. **80**, 2773 (2002).
[8]T. Izumida, R. Hatakeyama, Y. Neo, H. Mimura, K. Omote, and Y. Kasama, Appl. Phys. Lett. **89**, 093121 (2006).
[9]C. Zhou, J. Kong, E. Yenilmez, and H. J. Dai, Science **290**, 1552 (2000).
[10]Y. F. Li, R. Hatakeyama, T. Kaneko, and T. Okada, Jpn. J. Appl. Phys., Part 2 **45**, L428 (2006).
[11]Y. F. Li, R. Hatakeyama, T. Kaneko, T. Izumida, T. Okada, and T. Kato, Appl. Phys. Lett. **89**, 083117 (2006).
[12]J. Kong, J. Cao, and H. J. Dai, Appl. Phys. Lett. **80**, 73 (2002).
[13]J. Kong and H. J. Dai, J. Phys. Chem. B **105**, 2890 (2001).
[14]J. U. Lee, Appl. Phys. Lett. **87**, 073101 (2005).
[15]J. U. Lee, P. P. Gipp, and C. M. Heller, Appl. Phys. Lett. **85**, 145 (2004).
[16]C. Zhou, J. Kong, and H. J. Dai, Appl. Phys. Lett. **76**, 1597 (1999).