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Electronic transport properties of Cs-encapsulated single-walled carbon nanotubes created by plasma ion irradiation

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The electronic transport properties of Cs-encapsulated single-walled carbon nanotubes (Cs@SWNTs), which are created by a plasma ion irradiation method, are experimentally investigated at both room and low temperatures by fabricating field-effect transistor devices with these modified SWNTs. It is found that Cs@SWNTs exhibit air stable *n*-type transport characteristics at room temperature, where Cs atoms function as an electron donor. Moreover, Coulomb oscillations are observed under a low temperature, which is derived from the electronic structure modulated mainly by the encapsulated Cs atoms. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2339862]

Due to their outstanding electronic properties such as ballistic transport and low scattering rates, single-walled carbon nanotubes[1] (SWNTs) have attracted much attention. They have been expected to be a promising candidate for next-generation electronic devices, such as field-effect transistors[2,3] (FETs) and logic circuits. Therefore, it is very important to modify and control their electronic structure.

In order to modify electronic properties of SWNTs, several methods such as alkali-metal doping have been investigated.[4,5] However, although alkali metals can work as a good electron donor, the alkali metals doped on the SWNTs surface cannot maintain their *n*-type behavior under ambient condition due to their inherent air instability. In this regard, SWNTs encapsulating alkali metals (A) (A@SWNTs) are expected to be immune from property degradation of inner alkali-metal atoms even under air exposure. Based on this background mentioned above, a plasma ion irradiation method has been developed to realize the encapsulation of alkali-metal atoms and fullerene molecules inside SWNTs.[6–8] This plasma ion irradiation method enables us to select species of ionized atoms or molecules and control their flux or energy by changing dc biases (ϕ_{ap}) applied to SWNTs, yielding A@SWNTs for $\phi_{ap} \ll 0$ and C_{60}@SWNTs for $\phi_{ap} > 0$. In this letter, our concern is concentrated upon the electronic properties of A@SWNTs (A=Cs) obtained via the Cs-plasma ion irradiation process.

Nanotubes used here are prepared by an arc-discharge method. Then, the purified SWNTs are deposited on a substrate (1.5×1.5 cm^2) which is exposed to Cs positive ions or negative C_{60} ions during plasma irradiation process, which is well described in our previous literatures.[6,9] Cs positive ion irradiation process is carried out by applying a deeply negative dc-bias voltage ($\phi_{ap} \ll 0$) (Refs. 7 and 8) usually for 1 h in a vacuum chamber, as drawn schematically in Fig. 1(a). After this process, Cs@SWNTs are obtained and their properties are investigated under a FET configuration by measuring drain-source currents (I_{DS}) as a function of gate voltage (V_G) or drain-source voltage (V_{DS}). In order to make SWNT-FET devices Cs@SWNTs are firstly dispersed by supersonic treatment for several hours in *N*,*N*-dimethylformamide (DMF) solvent. Then, the SWNT suspensions are spin coated on a FET substrate manufactured prior to the application of SWNTs. The excess DMF solution on the FET substrates is removed by a baking process at 400 K carried out in air for 30 min. The source and drain electrodes used are made of Au placed on a SiO_2 layer (thickness of 500 nm) and have a channel length of 500 nm.

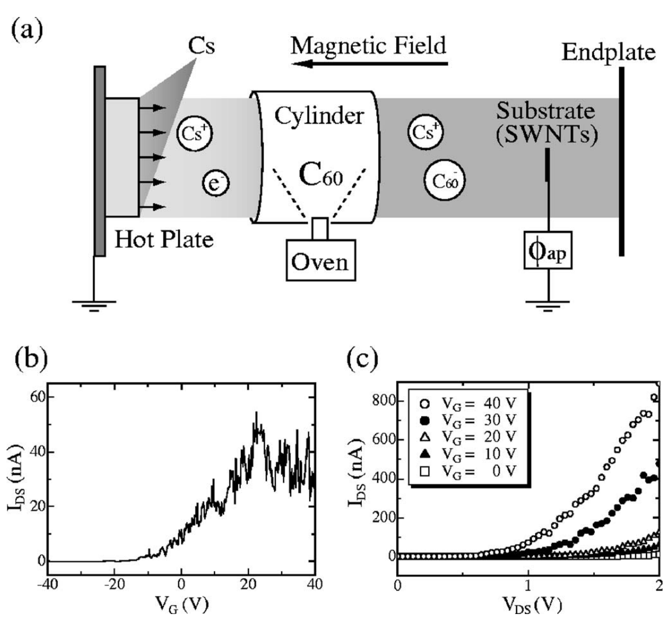

FIG. 1. (a) Schematic diagram of the experimental unit. (b) Typical I_{DS}-V_G characteristic of Cs@SWNTs measured in vacuum at room temperature with V_{DS}=1 V. (c) Typical I_{DS}-V_{DS} characteristics of Cs@SWNTs in vacuum at room temperature with V_G varying from 0 to 40 V. Plasma ion irradiation time is 1 h in both the cases (b) and (c).

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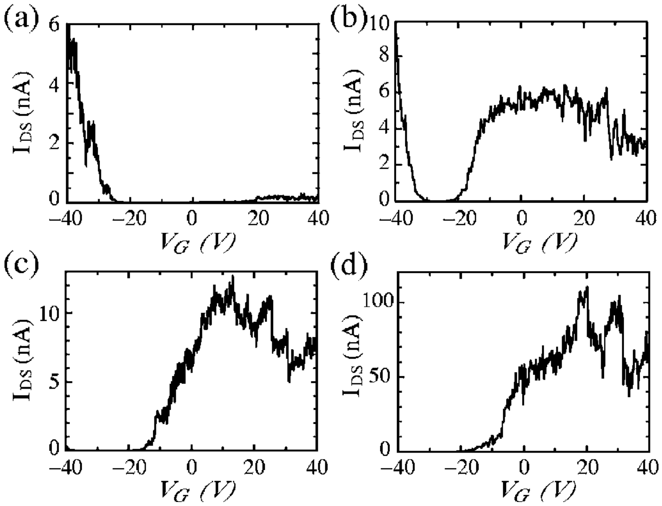

FIG. 2. I_{DS}-V_G characteristics of Cs@SWNTs measured at $V_{DS}=1$ V in vacuum by varying Cs ion irradiation time. The numbers of Cs atom irradiated to SWNTs are (a) $D=2.2\times10^4/\mathrm{nm}^2$ (15 min), (b) $D=4.3\times10^4$ nm^2 (30 min), (c) $D=6.5\times10^4/\mathrm{nm}^2$ (45 min), and (d) $D=8.6\times10^4$ nm^2 (60 min).

A heavily doped Si substrate is used as a back gate, and the back-gate electrode is prepared by Al evaporation. Figure 1(b) shows a typical I_{DS} vs V_G characteristic of a Cs@SWNT-FET at room temperature with $V_{DS}=1$ V. A clear off state is observed in the FET device when V_G is smaller than −15 V. In Fig. 1(c) I_{DS} vs V_{DS} characteristics of the Cs@SWNT-FET are given for different V_G varying in steps of 10 V, where conduction is suppressed as the gate voltage decreases. These results demonstrate that Cs@SWNT behaves as a *n*-type semiconductor. This fact evidently indicates that Cs atoms encapsulated inside SWNTs act as an electron donor to local areas of SWNTs.

Figure 2 presents an evolution of electronic properties of Cs@SWNTs created by changing plasma ion irradiation time from 15 to 60 min. While plasma irradiation is carried out, the current I flowing to the substrate applied with SWNTs is about 860 μA. The total number of injected Cs atoms per unit area D is estimated by $D=tI/SC$, where t, $S(1.5\times1.5\ \mathrm{cm}^2)$, and $C(1.6\times10^{-19}\ \mathrm{C})$ are the irradiation time, the substrate size, and the electrical charge of a Cs ion, respectively. Then, Figs. 2(a)–2(d) show the I_{DS}-V_G characteristics of Cs@SWNTs measured with $V_{DS}=1$ V in vacuum. The samples are prepared by Cs ion irradiation process during which the concentrations of Cs^+ are about 2.2×10^4, 4.3×10^4, 6.5×10^4, and 8.6×10^4 Cs ions/nm^2, respectively. Ambipolar properties remain in the range of low doping level, as seen in Figs. 2(a)–2(c), respectively. A threshold gate voltage for *p*-type conductance tends to shift more negatively from −22.2 to −35.6 V, and the conductance region of *n*-type gradually increases with increasing the total amount of irradiated Cs atoms. Finally, Cs@SWNTs change to show the complete *n*-type behavior, as described in Fig. 2(d). It is easily anticipated that charge transfer from Cs atoms to SWNTs takes place when Cs atoms are encapsulated inside SWNT.[10,11] As a result, the conduction band of SWNTs is believed to approach the Fermi level of the electrodes (Au), and electrons easily come to be conducted.

Since the Cs@SWNT-FET belongs to a microscopic system, its conduction is predicted to be suppressed at low temperatures because of the charging energy by a single

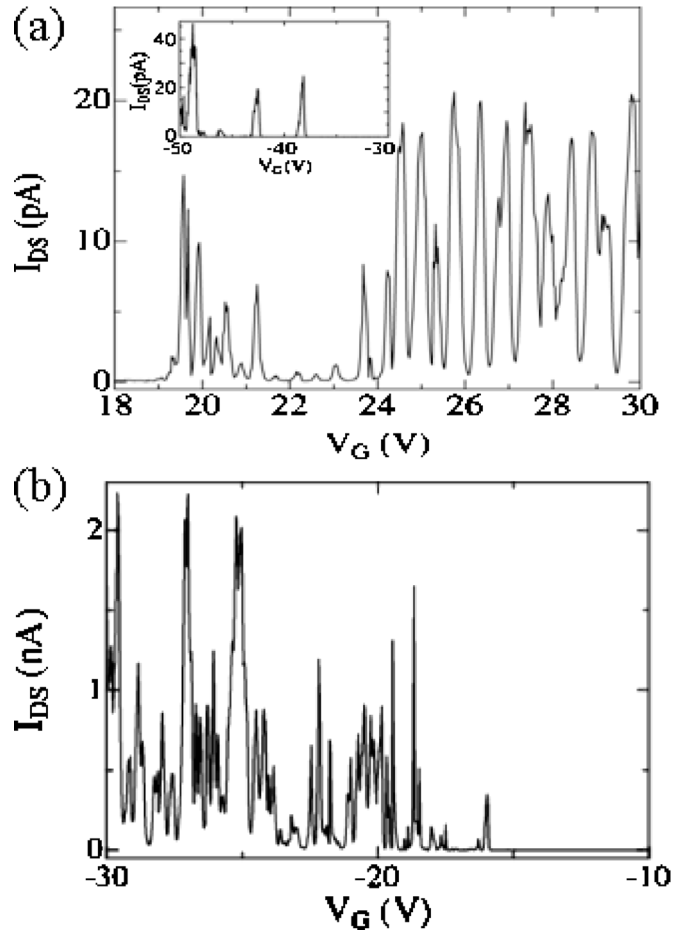

FIG. 3. (a) Coulomb oscillation characteristic of Cs@SWNTs measured with $V_{DS}=10$ mV at 11.5 K and the inset showing Coulomb oscillation characteristic of C_{60}@SWNTs measured with $V_{DS}=20$ mV at 11.5 K. (b) Coulomb oscillation characteristic of pristine SWNTs measured with $V_{DS}=10$ mV at 11.5 K.

electron,[12] which leads to the appearance of some singular phenomena at low temperatures. Here we pay attention to the phenomenon of Coulomb oscillations especially. In this case it is to be emphasized that we can gain further insight into an encapsulated profile of alkali metals inside SWNTs, because it is possible to estimate a quantum dot size made due to potential barrier by observing Coulomb oscillations. Figure 3(a) shows an I_{DS} vs V_G characteristic of Cs@SWNTs measured with $V_{DS}=10$ mV at 11.5 K. Each current peak splits into two or three subpeaks with different amplitudes, which indicates that the system evidently consists of multiple quantum dots. Focusing on a periodic element of the oscillations, a periodic spacing ΔV_G is determined to be about 0.5 V. However, considering the 500-nm-thick oxide back gate in our case, the efficiency of gate voltage can be estimated to be about 10% or less. Since ΔV_G corresponding to 10% efficiency is about 0.05 V, then the dot size can be estimated using a relation of $\Delta V_G/e\approx\ln(2L/d)/2\pi\varepsilon\varepsilon_0L$,[13,14] where L, d, and ε are the dot size, diameter of SWNT, and dielectric constant, respectively. This formula with the values of $d=1.4$ nm and $\varepsilon=3.9$ yields about 200 nm as a dot size, which is smaller than 500 nm of the tube length between the source and drain electrodes. Thus, the encapsulation profile along the nanotubes is considered to build a potential barrier between an encapsulated part and an unencapsulated part. It is natural that Cs ion irradiation possibly causes some defects

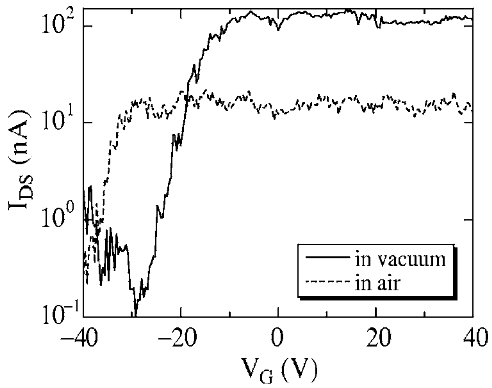

FIG. 4. I_{DS}-V_G characteristics of Cs@SWNTs in vacuum (black line) and in air (dashed line) measured at room temperature with $V_{DS}=6$ V. Titanium carbide is formed between SWNTs and electrodes.

on SWNTs, which may lead to forming quantum dots between potential barriers. In order to elucidate which mechanism is dominant in the present situation, the same measurement is performed for the case of C_{60} encapsulated SWNTs (C_{60}@SWNT-FET), as shown in the inset of Fig. 3(a). For the sake of comparison, a clear difference between ΔV_G or L of Cs@SWNT-FET ($L=200$ nm) and C_{60}@SWNT-FET ($L=40$ nm) is observed even under the same condition concerned with ion irradiation effect on the defect of SWNTs. Furthermore, when we compare the transport characteristics of pristine SWNTs at low temperatures with those of Cs@SWNTs and C_{60}@SWNTs, the observed ΔV_G for pristine SWNTs at 11.5 K is found to be about 0.126 V, much smaller than those in the cases of Cs@SWNTs and C_{60}@SWNTs, as shown in Fig. 3(b). Therefore, the observed Coulomb oscillation transport behavior of Cs@SWNTs is possibly due to the encapsulation profile inside SWNTs.

Let us focus a special concern upon air stability of Cs@SWNT-FET. Figure 4 shows I_{DS} vs V_G characteristics (measured with $V_{DS}=6$ V) of Cs@SWNTs at room temperature both in vacuum and air conditions, respectively. In this case the device is fabricated by Ti electrodes instead of Au ones and annealed in high vacuum at about 1000 °C in order to form titanium carbide, i.e., firm contact between SWNTs and electrodes. The I_{DS} dependence on V_G in vacuum is shown by the black line in Fig. 4, confirming that the Cs@SWNT-FET behaves as a n-type semiconductor also in this case. After this Cs@SWNT-FET is exposed to air, its I_{DS}-V_G characteristic is measured as represented by the dashed line in Fig. 4. The n-type behavior of Cs@SWNT still persists even in air. It is to be emphasized strongly that the above I_{DS}-V_G characteristics in air and vacuum are repeatedly observed many times during the alternating measurements on the same sample of Cs@SWNTs. On the contrary, although the Cs doping method on the outside of SWNTs has been known to be available for changing p-type SWNTs to n-type SWNTs, the doped Cs atoms on their surface have no role in maintaining the n-type behavior in air. According to this comparison, it can be concluded that the reactive Cs atoms are protected against oxidation by the carbon layers because the Cs atoms are encapsulated inside SWNTs.

In summary, the electronic transport properties of Cs@SWNTs effectively created by the plasma irradiation method have been investigated in detail at temperatures ranging from room to low ones. Cs@SWNTs are verified to show the n-type behavior even in air, implying that the electronic structure of SWNTs can effectively be modified by the Cs-plasma irradiation method. Moreover, Coulomb oscillations are observed to come into existence in the performance of Cs@SWNT-FET at low temperatures. This phenomenon indicates that quantum dots with the size smaller than the SWNT length are generated in Cs@SWNTs and potential barriers appear to be formed mainly by inhomogeneity of encapsulated Cs-atom profiles along the nanotubes.

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