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Creation of Functional Double-Walled Carbon Nanotubes by Plasma Processing

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We investigate the transport properties of double-walled carbon nanotubes (DWNTs) encapsulating various molecules or atoms via a plasma-ion irradiation method. The pristine DWNTs are found to exhibit ambipolar semiconducting behavior due to their small bandgap. In contrast, Cesium (Cs)-encapsulated DWNTs exhibit high performance n-type behavior, while fullerene (C_{60})- or Iodine (I)-encapsulated DWNTs indicate p-type semiconducting behavior, since they can operate as electron donor and acceptors, respectively. In addition, our measurements reveal that it is possible to make p-n junctions in DWNTs by adjusting the filling levels and types of encapsulated electron dopants.

Keywords: carbon nanotube, plasma, encapsulation, electronic, transport properties

1. Introduction

Over the past years, double-walled carbon nanotubes (DWNTs) consisting of two concentric cylindrical graphene layers have attracted increasing interests because of their advantages over other types of carbon nanotubes in size, electrical and mechanical properties. For instance, owing to their large diameter, pristine DWNTs usually exhibit the ambipolar semiconducting characteristic compared with the p-type characteristic of pristine single-walled carbon nanotubes (SWNTs) [1]. More recently, n-type or p-type DWNTs have been formed by encapsulating either electron donors or acceptors [2]. Due to the fact that they have their narrow bandgap, it may be easy to construct p-type or n-type DWNTs by encapsulating single electron dopant. Also, encapsulating two kinds of atoms or molecules, namely, both electron donor and acceptor in one DWNT provides a possibility of creating ideal p-n junctions. Although a theoretical work on such kind of doped nanotubes with both electron donors and acceptors has been proposed [3], experimental works on this interesting topic have remained to be less investigated so far.

In this paper, we report the transport properties of the DWNTs encapsulating various atoms or molecules at different filling levels, which is realized by a plasma-ion irradiation method. Unipolar n-type or p-type DWNTs are found to be created by encapsulating electron donors or acceptors, respectively. Importantly, our findings suggest that p-n junctions in DWNTs can be realized by Cs, I, or C_{60} fullerene encapsulation at low filling levels. More importantly, the transport properties of DWNTs encapsulating two types of dopants are also explored. It is worthwhile to point out that the possibility of p-n junction formation in DWNTs encapsulating a pair of electron dopants is much higher than that observed in DWNTs by encapsulating single dopant.

2. Experimental

The DWNTs used in this work are fabricated by an arc discharge method with Fe as catalyst. High-resolution transmission electronic microscopy (HRTEM) observations have confirmed that most pristine DWNTs have high purity and a uniform outer diameter of 4 ~ 5 nm. For the purpose of encapsulating Cs, C_{60} or I into DWNTs, a novel plasma irradiation method is used, which is similar to the experimental process of Cs or C_{60} encapsulation into SWNTs described in our previous work, and the experimental setup of the system and details of preparation process have been described elsewhere [4]. When negative DC substrate biases ($\phi_{ap} < 0$) are applied to a DWNT-coated substrate with respect to a grounded plasma-source electrode, positive Cs ions ($n_i \sim 1\times10^{10}$ cm^{-3}, n_i: ion density) are substantially accelerated by a plasma sheath in front of the substrate and finally bombard the nanotubes. On the contrary, when positive DC biases ($\phi_{ap} >$ 0 V) are applied to the substrate, negative C_{60} or I ions are accelerated toward DWNTs. Because the acceleration energy of Cs toward DWNTs is proportional to the DC bias voltage, different filling levels of Cs-encapsulated DWNTs can be obtained by adjusting the plasma irradiation time or applied substrate bias voltages. In the case of Cs encapsulation, different DC ϕ_{ap} during the same experimental time (60 min) is applied to synthesize different filling-level samples. 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

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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 [2, 5]. The transport property measurements are carried out at room temperature in a vacuum using a semiconductor parameter analyzer (Agilent 4155C).

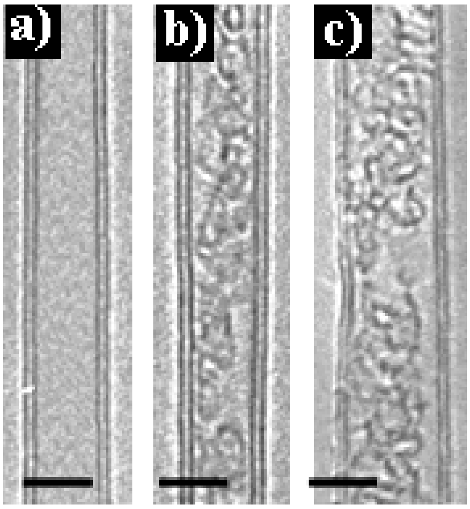

Fig. 1 TEM images for a (a) pristine DWNT (b) Cs-encapsulated DWNT and (c) C_{60}-encapsulated DWNT (Scale bar: 4 nm).

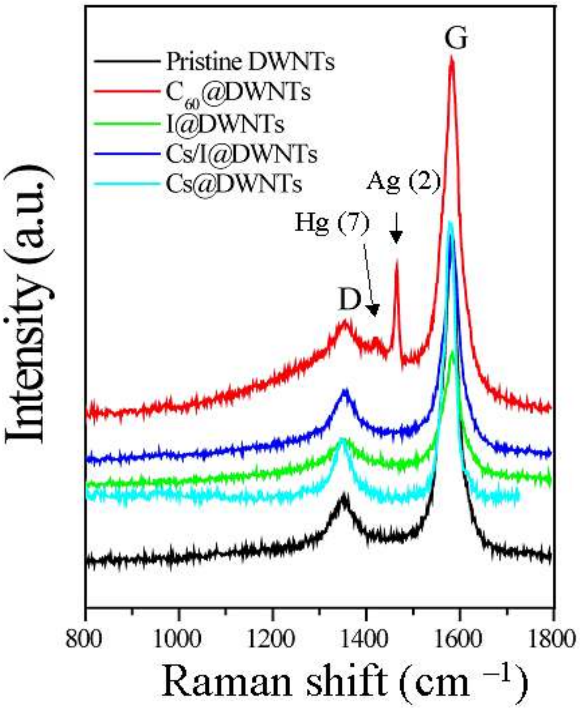

Fig. 2 Raman spectra of various kinds of DWNTs

3. Results and Discussion

A pristine DWNT with inner diameter 4 nm and outer diameter 4.8 nm is first shown as a TEM image in Fig. 1(a).

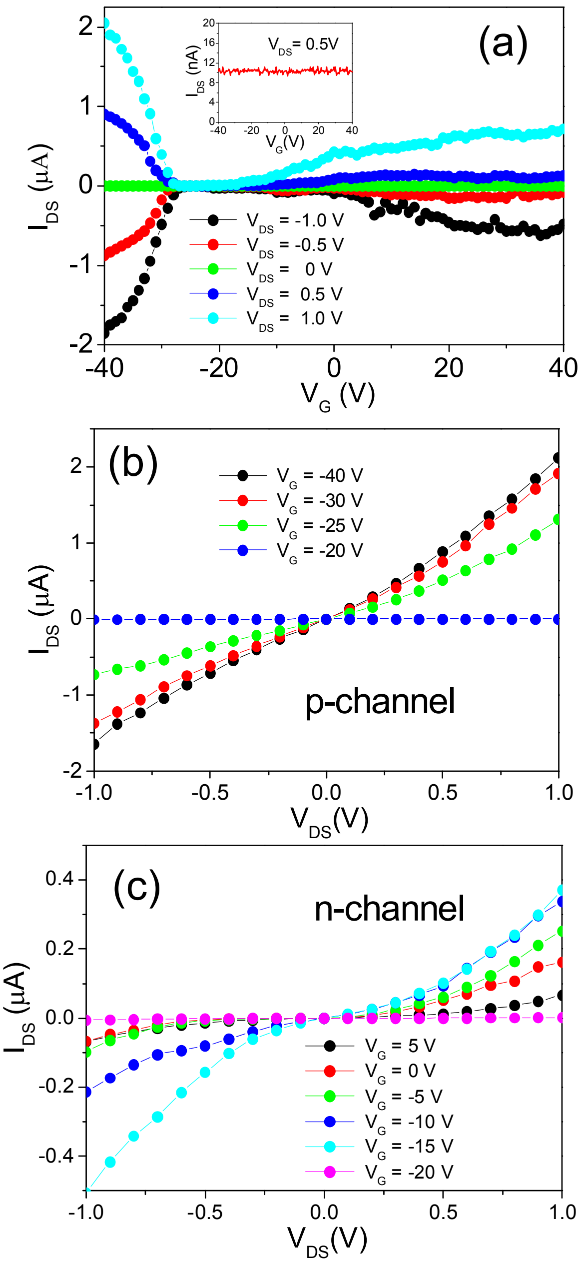

Fig. 3 (a) I_{DS}-V_G curves measured with bias voltage (V_{DS}) ranging from -1 to 1 V in steps of 0.5 V for an ambipolar DWNT. Inset of (a) showing a metallic DWNT measured at V_{DS} = 0.5 V. (b) I_{DS}-V_{DS} output characteristics under p-channel. (c) I_{DS}-V_{DS} output characteristics under n-channel.

In contrast, Figs. 1(b) and (c) show TEM images of individual DWNT filled with Cs atoms and that filled with C_{60} molecules, respectively. The above observations indicate that amorphous phases of Cs atoms or C_{60} molecules have been filled in DWNTs, which are different from the chain-like morphologies of Cs or C_{60} molecules observed in SWNTs due to their large diameter of DWNTs [6]. Although they have similar morphologies during TEM observations, Raman spectra reveal some difference between pristine DWNTs and encapsulated samples, as seen in Fig. 2, in which the intensity ratio of G/D band is decreased from 6.5 for the case of pristine DWNTs to 3.3 ~ 5 for the case of encapsulated DWNTs. Specially, for C_{60}-encapsulated DWNTs, 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 D-band can be attributed to the Hg (7) mode of C_{60} molecules [7]. Therefore, both TEM observations and Raman spectra indicate evidently that foreign materials have been encapsulated inside DWNTs.

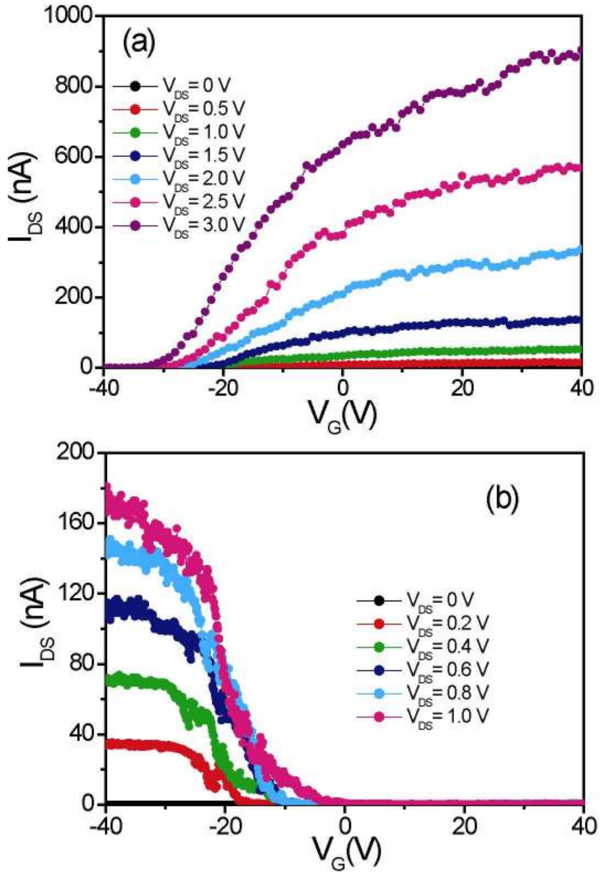

Fig. 4 (a) I_{DS}-V_G characteristics for Cs-encapsulated DWNTs measured with V_{DS} varying from 0 to 3 V in steps of 0.5 V, indicating excellent n-type behavior. (b) I_{DS}-V_G characteristics for unipolar p-type C_{60}-encapsulated DWNTs with V_{DS} varying from 0 to 1 V in steps of 0.2 V.

Transport properties of pristine DWNTs are found to be either metallic (inset) or ambipolar, as shown in Fig. 3(a). 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 -1 V to 1 V are applied. The region on the left-hand for V_G < -25 V corresponds to p-type conduction, and n-type conductance is observed on the right-hand region for V_G > -25 V. The current-voltage characteristics of the device indicate that the source-drain current increases strongly with increasing the negative gate voltage in p-channel and increasing the positive gate voltage in n-channel, respectively. Particularly, the observed saturated conductance in p-channel typically appears to be two or three times larger than that observed in n-channel for pristine DWNT-FET. In addition, ambipolar behavior of DWNT-FET can also be observed from the I_{DS}-V_{DS} characteristics measured with different gate voltages. For gate voltage in the range of -40 V < V_G < -20 V, the conductivity of DWNT is gradually suppressed by increasing the V_G in p-channel, as shown in Fig. 3(b), showing a signature of p-type behavior. While for V_G > -20, the current dependence of the positive V_G can be clearly observed in n-channel, as seen in Fig. 3(c), and the conductance also appears to be lower than that of the p-channel, which agrees with the characteristics of I_{DS}-V_G curves. Therefore, the output characteristics well confirm that the DWNT-FETs can show both p- and n- type semiconducting behavior over a large span of gate voltages.

Figure 4(a) shows the unipolar n-type semiconducting DWNT which is prepared by Cs-encapsulation, where the characteristics of source-drain current versus gate voltage I_{DS}-V_G measured at different V_{DS} ranging from 0 to 3 V in steps of 0.5 V indicate clearly that the FET device exhibits excellent n-type semiconducting behavior, that is, no ambipolar behavior is found due to the strong electron-donating property of Cs. The threshold voltage (V_{th}) necessary to completely deplete the nanotubes is about -30 V at V_{DS} =1 V, which is similar to the value of V_{th} for the n-type region in pristine ambipolar DWNTs. A high I_{on}/I_{off} ratio around 10^6 is achieved at each given bias voltage, and this drastic switching is much higher than that in the case of Cs-encapsulated SWNTs (10^3~10^4) measured under the same condition [8]. This excellent characteristic of DWNTs is possibly due to their larger diameter which results in the formation of the Ohmic contact between the nanotubes and the source-drain Au electrodes. For SWNTs, only Schottky contact is considered to be formed, which is considered to be caused by their small diameter according to recent works [9, 10]. Interestingly, for C_{60} or I encapsulation, the transport characteristic is just opposite to that observed for Cs-encapsulated DWNTs, and unipolar p-type C_{60} encapsulated DWNTs are obtained at high filling levels, as given in Fig. 4(b). 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 0 ~ 1 V. The observed V_{th} near 0 V at V_{DS} =1 V shows a clear upshift compared with that observed for the p-type region of pristine DWNTs, suggesting that C_{60} molecules exert a strong electron-withdrawing effect on DWNTs. Therefore, based on charge-transfer modulation the original p- or n-region of ambipolar DWNTs can selectively be suppressed, depending on the type of encapsulated dopants.

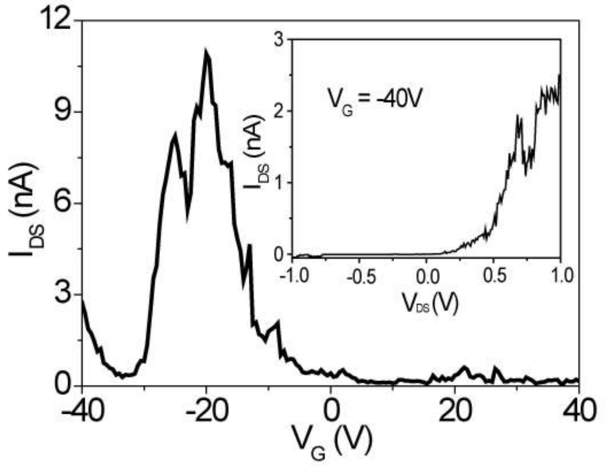

Fig. 5 I_{DS}-V_G characteristic curve for a Cs/C$_{60}$ encapsulated DWNT together with the inset showing a rectifying I_{DS}-V_{DS} characteristic measured with V_G = -40 V.

In the case of our electrical transport measurements, it is found that unipolar n-type Cs-encapsulated DWNTs can be prepared with $\phi_{ap} < -100$ V during the plasma irradiation process. As the absolute value of negative ϕ_{ap} is smaller than 100 V, ambipolar or p-n junction behavior is found to be shown in DWNTs due to encapsulation of a smaller amount of Cs. As a result, p-n diode features have ever been found in some encapsulated DWNTs at low filling levels by reducing the plasma irradiation time or applied substrate biases. Furthermore, in order to construct nano p-n junctions with high efficiency, hereto molecules/atoms are encapsulated inside DWNTs by changing the polarity of substrate biases during plasma processing. As a result, more DWNTs are found to exhibit p-n junction characteristics by encapsulating a pair of dopants in contrast to the case of encapsulating single dopant. Figure 5 gives the I_{DS}-V_G characteristic measured with V_{DS}= 1 V for a Cs/C$_{60}$ encapsulated DWNT, which is prepared under the plasma irradiation of both Cs (30 min) and C$_{60}$ (30 min) ions for 1h by instantaneously changing the polarity of the substrate bias. Different from normal n- or p-type transport characteristics, the I_{DS}-V_G curve displays a hump-like characteristic at –30 V < V_G < 0 V, which indicates that Cs/C$_{60}$ encapsulation inside the DWNT leads to a p-n junction formed in the nanotube. Furthermore, the I_{DS}-V_{DS} characteristic measured at V_G = -40V in the inset of Fig. 5 shows a clear rectifying characteristic, providing direct evidence for the p-n junction formation.

Similarly, p-n junctions are also found in many of DWNTs encapsulating both Cs and I for 30 min, respectively, during plasma irradiation. In order to confirm the performance of fabricated FET devices, typical I_{DS}-V_G characteristics are measured at different biases V_{DS} ranging from 0.6 to 1 V in steps of 0.1 V for Cs-I encapsulated DWNTs, as shown in Fig. 6(a). Obviously, an interesting hump current at –10 V < V_G < 40 V can repeatedly be observed in each I_{DS}-V_G curve, similar to the results observed for Cs-C$_{60}$ encapsulated DWNTs except the different hump position. In the hump current region, electron conductance can occur by quantum-mechanical tunneling through the p-n junction formed by n-type (Cs) and p-type (I) encapsulation.

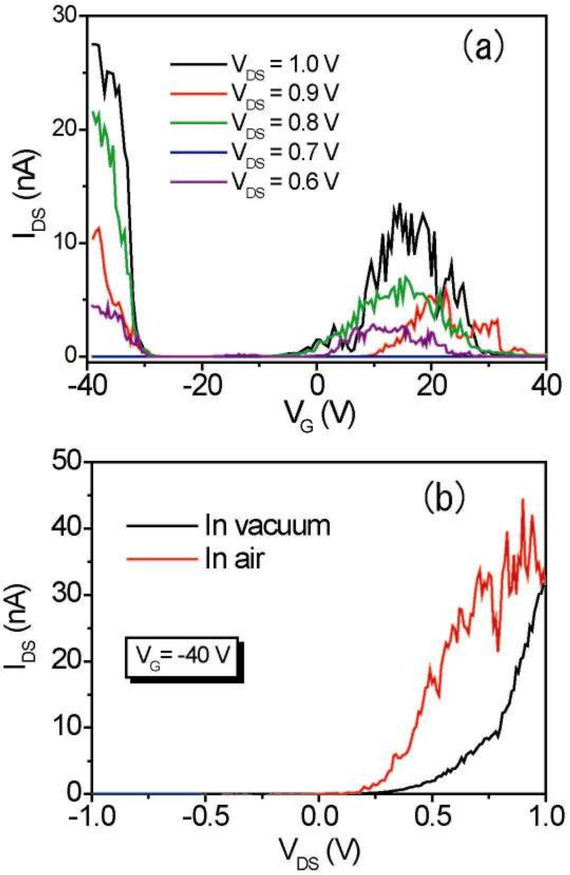

Fig. 6 I_{DS}-V_G curves measured with V_{DS} ranging from 0.6 V to 1 V. (b) I_{DS}-V_{DS} curves measured at V_G = -40 V in vacuum and air, respectively, demonstrating the excellent rectifying characteristic.

It is worth noting that rectifying transport behavior can remain stable in air, as shown in Fig. 6(b), where the characteristic of I_{DS}-V_{DS} curves are measured in both vacuum and air with V_{DS} ranging from -1 to 1 V. The data indicate that the measured I_{DS}-V_{DS} curves exhibit a clear rectifying characteristic. In other words, the current rises sharply at only the forward bias, and is blocked at the reversely applied bias. It is found that the rectifying characteristic remains stable even in air although the flowing current shows an increase compared the current measured in vacuum, which suggests that the adsorption of oxygen may cause the change of barrier height in the depletion region formed inside DWNTs. The current rectification is the result of p-n junction formed in the

DWNT by Cs-C_{60} or Cs-I encapsulation, which also coincides with the theoretical predication [3]. It is important to mention that such rectifying transport characteristics are observed in more than ten of Cs-I encapsulated DWNT devices, and highly reproducible and scalable compared to the those observed in single material encapsulated nanotubes at low filling levels [2], suggesting a promising way in making the nano p-n junction.

4. Conclusions

The formation of various atoms or molecules encapsulated DWNTs has been realized via a plasma ion-irradiation method. Electrical transport measurements indicate pristine DWNTs can exhibit metallic or ambipolar semiconducting behavior. While unipolar n-type or p-type semiconducting DWNTs are significantly observed by doping electron donors or acceptors, indicating the electronic structure of DWNTs is easily modified by selectively encapsulating electron dopants. The fabrication of p-n junctions in DWNTs is realized by encapsulating heteromaterial encapsulation via the different-polarity plasma ion-irradiation method. It is also found that p-n junctions can be created in DWNTs by controlling the filling levels of dopants. More importantly, the possibility of creating the p-n junction with air stability is greatly enhanced by encapsulating both electron donors and electron acceptors in DWNTs. Our studies may provide a promising way in the design of nanotube-based functional nanodevices.

5. References

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