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Transport Properties of *p-n* Junctions Created in Single-Walled Carbon Nanotubes by Fe Encapsulation

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Abstract—**Electronic properties of single-walled carbon nanotubes (SWNTs) filled with Fe nanoparticles are studied by fabricating them as the channels of field-effect transistors (FETs). Our results reveal that Fe-filled SWNTs at low filling levels can exhibit high-performance *p-n* junction diode behavior. The synthesis of Fe-filled SWNTs is confirmed by transmission electron microscopy (TEM) observation, and magnetic properties of Fe encapsulated SWNTs are characterized by means of SQUID measurements.**

Keywords — ***carbon nanotubes, encapsulation, magnetic, p-n junction***

I. Introduction

Over the past decade, single-walled carbon nanotubes (SWNTs) have widely been studied due to many of their unique properties at the nanoscale and potential applications in lots of fields. For electronic applications, various nanodevices with novel transport properties, such field-effect transistors (FETs), single-electron transistors (SETs), memory devices, and sensors based on SWNTs have been realized experimentally. Many studies have demonstrated that SWNTs filled with foreign atoms or molecules represent a possible way to control their properties of SWNTs. Compared with *p*-type pristine SWNTs, *n*-type semiconductiong SWNTs can be created by doping a kind of electron donor. In addition, SWNTs can directly be doped under a designed doping profile along its length, resulting in the formation of nano-sized junctions which exhibit interesting properties. A *p-n* junction diode has ever been realized by partly doping potassium on the outside surface of SWNTs but its electrical properties show leakage current at reverse biases [1]. Therefore, it remains an open question whether ideal junction diodes can be fabricated with SWNTs by the foreign material encapsulation. Here we demonstrate that the *p-n* junction can be formed with SWNTs by means of the Fe encapsulation at low filling levels. Our results reveal that the SWNT-based diodes exhibit an air-stable rectifying behavior, similar to the characteristics for ideal diodes and almost no leakage current is found down to 10^{-4} A level during the whole measurements in the range from low to room temperature.

II. Experimental

Before Pristine SWNTs are prepared by an arc discharge using Fe/Ni as catalyst. The raw SWNTs are purified by filtration and acid treatment. The preparation of Fe-filled SWNTs is carried out using ferrocene as a starting material at 180 °C [2]. The encapsulation of Fe particles inside SWNTs has been confirmed by a Hitachi HF-2000 transmission electron microscope (TEM) operated at 200 kV and Raman spectroscopy (Jovin Yvon T-64000) with an Ar laser at 488 nm. Magnetic properties of samples are examined by a Quantum Design MPMS-5 SQUID magnetometer over a temperature range of 5-300 K. Electronic properties of Fe-filled SWNTs are measured by fabricating them as the channel of field-effect transistors. The measurements are performed on a semiconductor parameter analyzer (Agilent 4155C) in vacuum.

III. Results and Discussions

TEM images of (a) pristine, (b) ferrocene-filled, and (c) Fe-filled individual SWNTs are shown in Fig. 1. Compared with the pristine SWNT, Fig. 1(b) indicates clearly that ferrocene molecule clusters have been filled inside a SWNT with diameter of ~1.4 nm. In contrast, Fig. 1(c) reveals several Fe particles, which are imaged as discrete dark spots in a SWNT. In addition, the existence of Fe has further been confirmed by energy dispersive X-ray spectrometry.

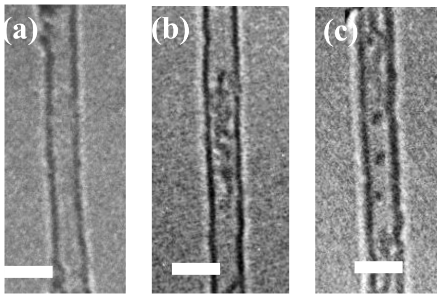

Fig. 1 TEM images of (a) pristine SWNT (b) ferrocene filled SWNT and (c) Fe filled SWNT (Scale bar: 2 nm).

Raman spectroscopy has been used to characterize the filled carbon nanotubes because it is well known as one of the most powerful tools for investigating the vibration properties of the SWNTs and filled SWNTs in relation to their structural and electronic properties. Figure 2(a) displays the radial breathing modes (RBM) for the pristine SWNTs, ferrocene-filled and Fe-filled SWNTs. The pristine SWNTs show standard Raman peaks at 161 cm^{-1} and 178 cm^{-1} which correspond to the SWNTs with diameters of *ca.* 1.54 nm and *ca.* 1.40 nm, respectively. Compared with the empty sample, the intensity and shape of the RBM profile in the ferrocene-filled SWNTs change markedly. It can be observed that the absolute intensities of both peaks at 161 cm^{-1} ($I_{\omega 161}$) and 178 cm^{-1} ($I_{\omega 178}$) decrease, and in particular, the peak at 161 cm^{-1} corresponding to nanotubes with large diameters shows a

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strong reduction and a little upshift compared with the peak at 178 cm^{-1} related to nanotubes with small diameters. More importantly, a striking change in RBM profile between the pristine sample and the ferrocene-filled SWNTs can be identified by the appearance of a distinct Raman peak at a high frequency of 197 cm^{-1} attributed to thin nanotubes with diameters of 1.26 nm. This result can possibly be interpreted as an evidence for diameter selective filling. The diffusion speed of ferrocene vapor in thick SWNTs would be higher than that in thin SWNTs. Therefore, the high filling rate can easily be obtained in large-diameter nanotubes, which results in a strong intensity loss of Raman resonance. In contrast, it is more likely that only a small effect on the Raman intensity occurs in the case of SWNTs with small diameters due to the low filling rate, and this may consequently lead to a relative increase in the intensity of the high-frequency peak ($I_{\omega 197}$) compared with $I_{\omega 161}$ and $I_{\omega 178}$ in the entire RBM profile.

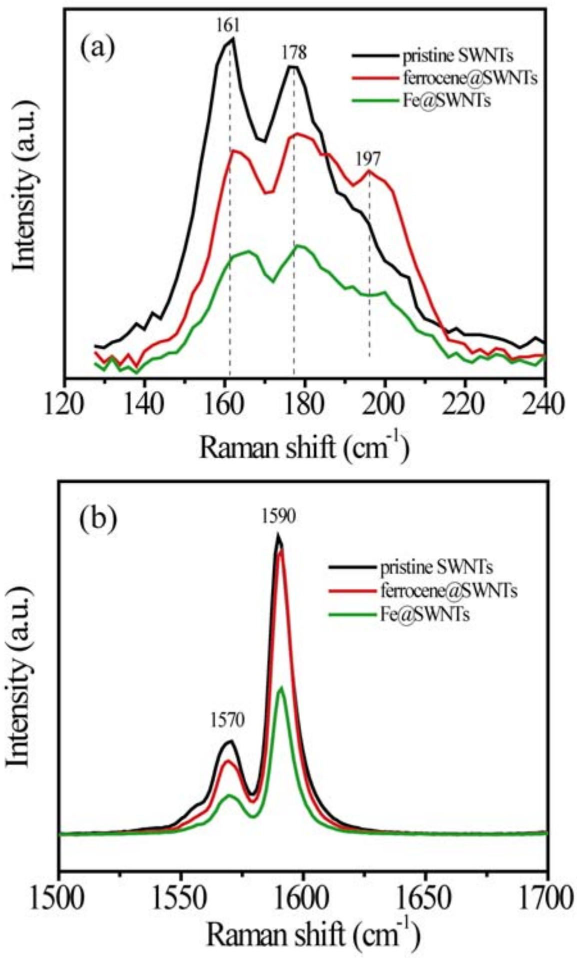

Fig.2 Raman spectra of pristine SWNTs, ferrocene-filled SWNTs and Fe-filled SWNTs: (a) RBM region; (b) high frequency region

By comparison, in the case of the Fe-filled SWNTs, interestingly, a marked reduction in the intensity of the peak at 197 cm^{-1} is observed. This change is more obvious than those of peaks near 161 and 178 cm^{-1}, namely, the ratios of $I_{\omega 197}/I_{\omega 161}$ and $I_{\omega 197}/I_{\omega 178}$ significantly decrease compared with their values for the ferrocene-filled SWNTs. This result indicates that the thin SWNTs are very sensitive to the nano-sized clusters, although the filling yield in these tubes is low, which is consistent with the descriptions in a reference [3]. In addition, as previously determined, the intensity changes in the Raman peak also mirror the changes in the position of the Fermi level. When Fe clusters are formed within SWNTs, the electron charge transfer from Fe atoms to the SWNTs affects the density of states (DOS) near the Fermi level. According to the experimental results, it seems that the interaction between Fe and small-diameter nanotubes is stronger compared with that between Fe and large-diameter nanotubes, which agrees well with the related theoretical results [4]. Furthermore, the hybridization between the C π orbital and the Fe d orbital is easily enhanced in thin nanotubes, which leads to a strong Fe-C bond formation between Fe atoms and SWNTs. On the other hand, the electronic properties of SWNTs, such as the band gap, will be changed due to the bonding state of Fe and C atoms. Since the line shape and intensity of G-band are very sensitive to whether the SWNT is metallic or semiconducting [5], the intensity loss of the G-band when compared with the G-band of pristine sample may give another indication for charge transfer between the encapsulated Fe clusters and the SWNTs.

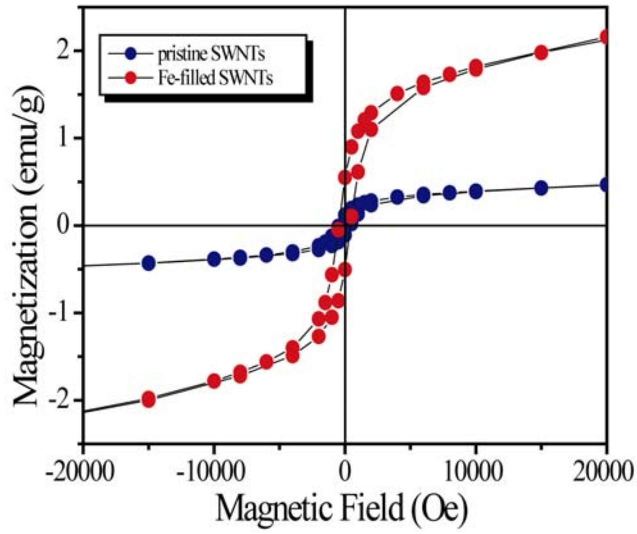

Fig. 3 Magnetic properties of pristine and Fe-filled SWNTs

Figure 3 presents the magnetization vs. applied magnetic field for pristine SWNTs and Fe-filled SWNTs measured at 5 K. Our results indicate clearly that the magnetization of Fe-filled SWNTs is much larger than that of pristine SWNTs. It is necessary to mention that the magnetization of pristine SWNTs is attributed to the existence of magnetic catalyst. This result provides an indirect evidence for the encapsulation of Fe nanoparticles in SWNTs since they are easily oxidized and lose their magnetization without the protection of SWNTs. In addition, the Fe-encapsulated nanotube samples show saturation of magnetization much slower compared to the

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pristine nanotube samples, suggesting some Fe particles are in a superparamagnetic state [6].

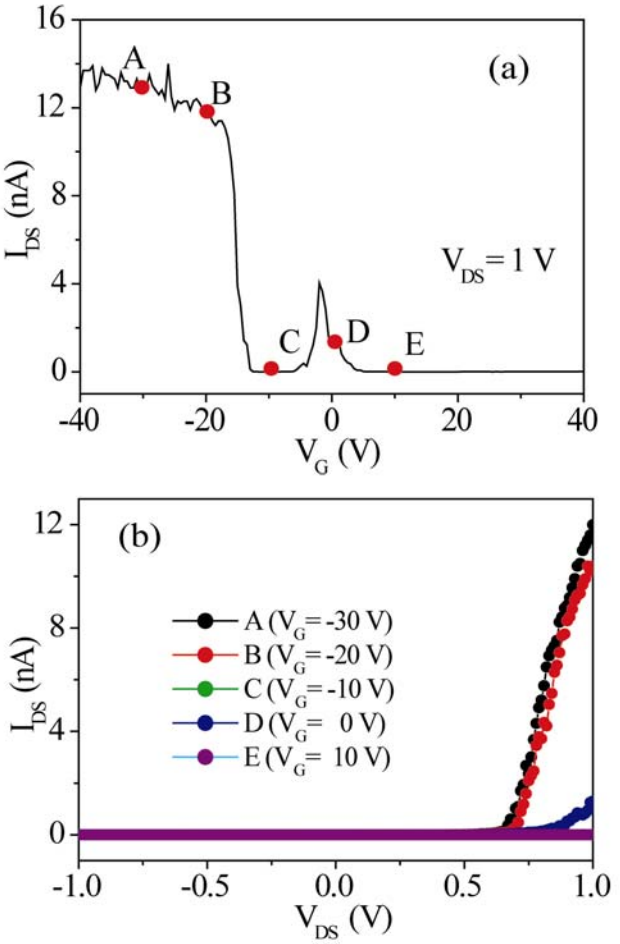

Fig. 4 (a) A I_{DS}-V_G curve measured at room temperature for *n-p* junction diode fabricated by Fe-filled SWNT at a low filling level, in which a hump conductance feature is observed at -5 V < V_G < 5 V. (b) By applying gate voltages from -30 to 10 V, corresponding to the positions (A, B, C, D and E) marked in Fig. 4(a), respectively, I_{DS}-V_{DS} curves exhibiting excellent rectifying behavior.

Pristine SWNTs exhibit the well-known *p*-type behavior. While unipolar *n*-type SWNTs can be realized by the Fe encapsulation at high filling levels (number of the filled Fe atom per carbon atom of SWNTs is f = 2.8 × 10^{-3}) [7]. Interestingly, *p-n* junctions are found to be created in some Fe-filled SWNTs at low filling levels ($f \leq 10^{-3}$) due to the Fe partial encapsulation [8]. A typical *p-n* junction characteristic is shown in Fig. 4. Figure 4(a) displays the drain-source current versus gate bias (I_{DS}-V_G) measured at room temperature with drain bias V_{DS} = 1 V. Obviously, an unusual transport behavior is observed, which is different from the normal monotonic increase or decrease for simple *n*- or *p*-type transport characteristics under increasing gate voltages. For V_G < -13 V, the conductance show a monotonic increase by increasing the negative gate bias, and the conductance with V_G between -13 V and -5 V is near zero. A conductance hump structure is clearly observed at -5 V < V_G < 5 V, which is known as the formation of *p-n* junction in SWNTs, according to the previous description [1]. When the gate bias is larger than 5 V, the conductance is suppressed to zero again until the gate voltages reach 40 V. Importantly, the similar *p-n* junction characteristic can be observed in other independent devices, although the position and shape of the hump conductance structure observed in the I_{DS}-V_G curves vary from device to device. To further assess the performance of the above 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. 4(b), corresponding to the positions (A, B, C, D, and E) in Fig. 4(a), respectively. It can be seen clearly that these I_{DS}-V_{DS} curves exhibit ideal rectifying characteristics, namely, the current can flow at the forward bias and diminish under the reverse bias. In addition, at gate voltages V_G = -10 V and 10 V, the current is significantly suppressed to near zero, while at the *p-n* junction region (V_G = 0 V), a small current is detected at 1 V bias in contrast with that measured at V_G = -30 V and -20 V. Clearly, the observed results are just well consistent with the observations in Fig. 4(a). More importantly, at the reverse bias no leakage current of down to 10^{-14} A level is found during the whole measurements.

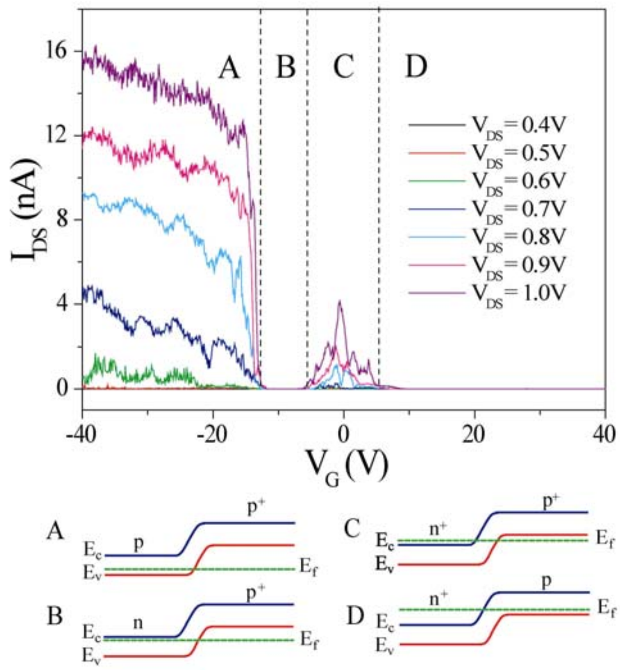

Fig. 5 I_{DS}-V_G curves measured with V_{DS} ranging from 0.4 to 1 V at room temperature, which can be divided into different regions A, B, C, and D, corresponding to pp^+, np^+, n^+p^+ and n^+p junctions, respectively, as shown in the bottom inset.

In our case, the *p-n* junction diodes fabricated by Fe-filled SWNTs have shown good reproducibility during the measurements. Figure 5 demonstrates the I_{DS}-V_G curves measured at different biases V_{DS} ranging from 0.4 to 1 V in steps of 0.1 V at room temperature. The results indicate that the hump conductance feature can repeatedly be observed in

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the range about -5 V < V_G < 5 V when the applied bias is larger than 0.5 V, which has further confirmed the *p-n* junction formed in SWNTs. In contrast, when the applied bias is less than 0.5 V or negative, the current tends to be reduced to 10^{-14} A. To well understand the formation of the *p-n* junction formed SWNTs, energy band diagrams for different region A, B, C, and D of I_{DS}-V_G curves are shown in the bottom inset of Fig. 5, and they can be assigned as pp^+, np^+, n^+p^+ and n^+p junctions, respectively. In region A, the high negative gate voltage shifts the conduction band (*Ec*) and valance band (*Ev*) up relative to Fermi level (E_f), causing a electron density decrease in the left half for *n*-type nanotube (to *p*) and a degeneration of hole doping for right *p* side (to p^+). In this region, the current shows a sharp increase at about V_G= -15 V, and a slowly increase from V_G < -20 V when we increase the negative gate voltages. In region B, by decreasing the negative gate voltage E_f shows an up shift relative to *Ev* and *Ec*, resulting in the formation of np^+ band structure. In region C, which represents the interesting hump conductance area, an increase in V_G can enrich the electrons in the nanotube, so the negative gate is insufficient to deplete electrons in the left half of *n*-type tube, yielding a n^+p^+ junction. As a result, almost symmetrical I_{DS}-V_G curves at V_G = 0 V can be observed, as given in Fig. 5. Further increase in the gate voltage, reverts from p^+-type to *p*-type in the right half tube, and the current is suppressed again in this region.

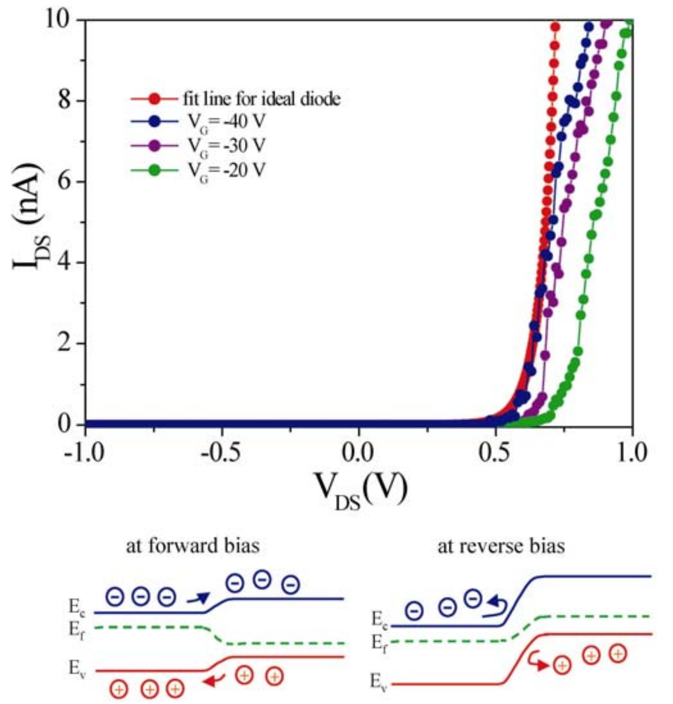

Fig. 6 I_{DS}-V_{DS} curves measured with V_G = -40 V, -30 V and -20 V, respectively. The fit line for the ideal diodes are calculated with n =1.2, I_o = 10^{-14} and T = 300 K. In the inset, the band diagram illustrating the band structures at forward and revere biases, respectively.

In Fig. 6, the characteristics of I_{DS}-V_{DS} curves are described by applying different V_G = -40 V, -30 V and -20 V, respectively, each of which indicates that the current can flow in only one direction. Furthermore, the performance of SWNT diodes is compared with that for ideal diodes in which the current-voltage curve is described by the following equation: $I_{DS} = I_o\left(e^{qV_{DS}/nK_BT} - 1\right)$, where I_o 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 the ideality factor (typically between 1 and 2), K_B and *T* are Boltzmann constant (1.38×10^{-23}) and temperature, respectively. In our case, the parameters used for the fit line are $I_o = 10^{-14}$ A, n = 1.2 and T = 300 K. As a result, 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 exhibit a sharp current increase feature with applied biases more than 0.5 V. A little deviation of the measured line compared with that for the ideal diode at high V_{DS} might be explained in terms of the poor contact between SWNT and Au electrodes. Therefore, the above results reveal that ideal *p-n* junction diodes can possibly be fabricated by SWNTs encapsulating Fe nanoparticles. The band structure for the *p-n* junction under forward and reverse bias is shown in the bottom inset of Fig. 6, respectively. The electrical properties of the SWNT diode can be understood as consequences of the formation of energy barrier or depletion zone around the *p-n* junction. At forward biases (V_{DS} > 0), the energy barrier or the width of depletion layer across the *p-n* junction decreases, the electrons can roll around the relative flat parts of the energy diagram and move from *n*-type to *p*-type across the junction. A similar reason can be applied to the free holes, which can flow in the opposite direction. As a negative bias (V_{DS} < 0) is applied, the potential barrier across the *p-n* junction increases, and as a result, the electrons and holes cannot flow through the junction. In other words, the conductance exhibits blocking characteristics when the diode is reversely biased.

Furthermore, we examine the transport characteristics of the *p-n* junction diode in air condition, as indicated in Fig. 7(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. 4. However, the characteristic of I_{DS} -V_{DS} shown in Fig. 7(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, and its adsorption on the outside of SWNTs 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 device again in vacuum at room temperature. As expected, a recoverable characteristic as signature of the current decrease and hump current feature is repeatedly observed, similar to the results displayed in Fig. 4(a).

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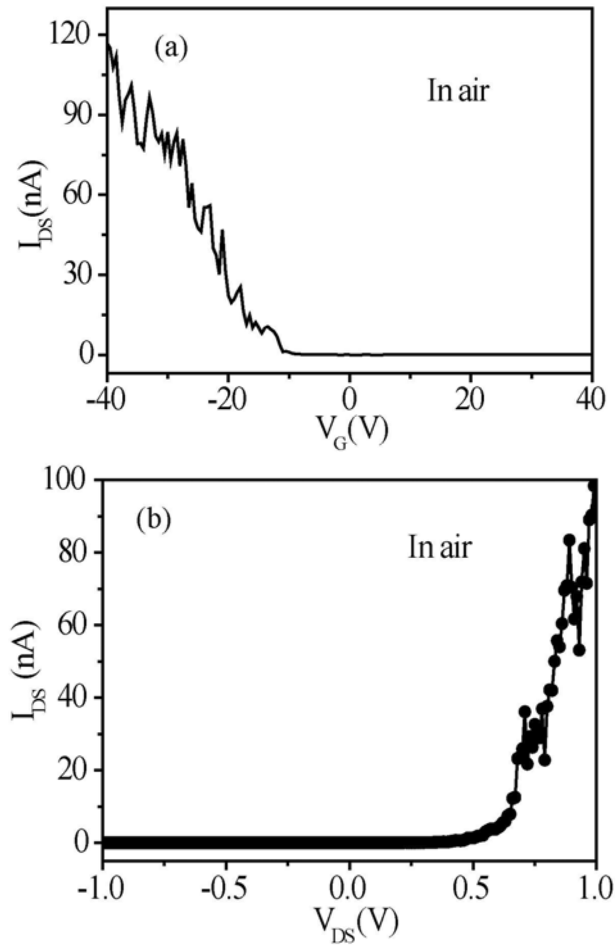

Fig. 7 (a) I_{DS}-V_G curve measured with V_{DS} = 1 V at room temperature in air, indicating the hump current region disappears. (b) A stable rectifying I_{DS}-V_{DS} characteristic measured at V_G = -40 V is observed in air condition.

IV. CONCLUSIONS

In conclusion, TEM observations, Raman spectra, and magnetic measurements have confirmed that Fe particles are filled in SWNTs by using ferrocene as a starting material. It is found that the *p-n* junctions can possibly be created in SWNTs through encapsulating Fe particles at the filling fraction $f \leqslant 1 \times 10^{-3}$. Our results reveal that the devices show the excellent rectifying performance, which is similar to characteristics of ideal diodes. More importantly, the *p-n* junction characteristics of SWNTs can keep stable even in air condition. It is believed that we may offer a feasible approach to the fabrication of the *p-n* junction nanodevice with SWNTs.

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