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Oxygen-induced p-type doping of a long individual single-walled carbon nanotube

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Abstract

The effect of oxygen adsorption on a nanotube-based field effect transistor have been controversial as to whether it induces p-type doping of the nanotube body or the work function increase in the metal electrode. Here we report a transport measurement showing that a long individual single-walled nanotube can be doped as p-type upon oxygen adsorption. We discuss that, despite the fact that the charge transfer between the nanotube and O₂ adsorbator has not been agreed to date, the effect of oxygen adsorption should still be interpreted as inducing p-type doping in the nanotube body. The n-type doping by NH₃ adsorption is also measured for the purpose of comparison. Based on these observations, we suggest that, while the Schottky barrier management could be more effective for the transistor with a short nanotube, the doping effect could be more influential in devices with longer nanotubes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The carbon nanotube (CNT) has been considered as the most promising building block for future electronic devices because of its unique one-dimensional geometry, mechanical and chemical robustness, and its excellent transport property [1, 2]. The unprecedented high carrier mobility, large current density, and a delicate response to the gate bias have been demonstrated in CNT field effect transistors (FETs) [3–5]. Natural research trends nowadays are directed toward integration techniques [6] and designing device structures with a desired carrier type. Transistors with n- and p-type transport behaviour operating under the same voltage range are indispensable for the development of nanotube-based logic and large scale integrated circuit devices [7, 8].

However, the decisive mechanism of the carrier type of CNT-FETs has remained in a substantial controversy. Common observations of the p-type behaviour of the nanotube devices have been attributed to the doping by the adsorbed

oxygen from the ambient air [9–11]. It was shown theoretically [12] and experimentally [13] that electronic properties of CNT-FETs are sensitive to the absorption of oxygen molecules attributed to charge transfer and gas induced charge fluctuation. Meanwhile, Derycke *et al* have suggested that the main effect of the oxygen adsorption lies in the adjustment of the Schottky barrier rather than the bulk doping of the CNT body [14, 15], which is consistent with subsequent studies showing a negligible charge transfer between oxygen adsorbator and the nanotube wall [16–18]. Despite this apparent controversy, we here note that bundles or networks of nanotubes may react differently from an individual nanotube upon oxygen adsorption. The thermoelectric power measurement proved that the networks of CNTs could be doped as p-type upon oxygen adsorption, irrespective of the contact metal [9, 10]. On the other hand, the transfer character of a transistor with a single and short nanotube could sensitively depend on the Schottky barrier rather than doping [14, 15].

In this work, we investigate the effect of gas adsorption on the transport properties of a long individual single-walled carbon nanotube through transport measurements as well as *ab initio* electronic structure calculations. Measured $I_{ds}-V_g$

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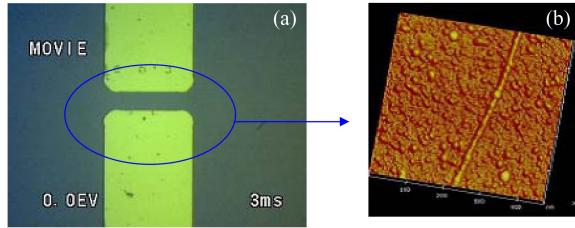


Figure 1. (a) The image of a long nanotube between a Ti/Au electrode by optical microscope and scanning electron microscope (SEM). (b) An enlarged view by SPM of a region of the nanotube.

curves apparently show that main effect on the transport is the doping of the CNT body by the adsorbed gas species. Through the *ab initio* electronic calculations, we show that, even though the electron transfer between the nanotube and absorber is negligible, the effect of the adsorption should be interpreted as a bulk doping of the CNT body.

2. Experimental procedure

Single-walled carbon nanotubes were grown by the patterned catalyst method [16]. Electron beam-sensitive resist was spin-coated on the thermally grown SiO_2 of 500 nm at 5000 rpm and baked for 2 min at 170 °C. The catalyst islands with the size of $1 \mu\text{m} \times 1 \mu\text{m}$ were formed by e-beam lithography. Metal catalysts suspended in solvent were dropped onto the patterned wafer which was spun to cover the open patterns on the SiO_2 substrate. After lift-off in a solvent, the wafer was rinsed in deionized water and dried with pressured nitrogen. CH_4 gas was introduced in a thermal CVD furnace at 905 °C for 10 min with hydrogen gas after loading the wafer. Most of the CNTs were single walled, with diameters in the range 2–3 nm determined by AFM measurements. After defining the metal contact patterns with the conventional photolithography technique, the Ti/Au electrodes were deposited on the patterns by using thermal evaporation. A second lift-off process was carried out to form metal contacts with the CNTs. The distance between source and the drain electrode was fixed at 10 μm .

Electrical properties were measured in a chamber of a probe station which is connected with Agilent 4156C. Gas doping was executed in the chamber, which can be pumped down to lower 10^{-6} Torr with a pumping unit. The pressure inside the chamber was measured with different pressure gauges depending on the chamber pressure. The flows of doping gases, O_2 and NH_3 were controlled through mass flow devices and a pressure control unit with a precision of 1 sccm. Each measurement was taken 10 min after flow started.

3. Result and discussion

Figures 1(a) and (b) show the images captured by optical microscope and scanning probe microscope (SPM) of CNT FETs, respectively. An overview of the transistor structure is shown in figure 1(a). It simply has two metal electrodes with a heavily doped p-Si back gate. The small black dots on the metal electrodes in figure 1(a) are the trace of catalysts, and are patterned by electron beam lithography. The distance between

the two metal electrodes is 10 μm . The SPM was used to image the area between the two electrodes and the result in figure 1(b) shows an individual long CNT on the substrate with negligible remains of residual particles. The diameter of the CNT was estimated to be 2.5–3.0 nm through the measurement of the height difference between the substrate and the CNT.

Figure 2(a) shows transfer characteristics of our CNT-FET under various oxygen pressures. The transistor was loaded in the chamber of the probe station, equipped with the pumping unit of a turbo-molecular pump. After evacuating the chamber down to 1×10^{-6} Torr, oxygen gas flowed into the chamber, whose pressure is maintained at 3.4–50 Torr. The $I_{ds}-V_g$ curves, as shown in figure 2, have typical ambipolar behaviour, which is commonly observed in an FET with double-walled nanotubes or large-diameter SWNTs. This ambipolar behaviour has been ascribed to their small band gap [17, 18]. Here the diameter of our nanotube is about 3 nm, and thus the band gap is estimated to be 0.2 eV, according to the formula $E_{\text{gap}} = 2\gamma_0 a_{\text{C-C}}/d$ [19].

Under a high vacuum of 1×10^{-6} Torr, the n-channel almost turns on at $V_g = 0$. This could be ascribed to the fact that the Fermi level of Ti aligns with the conduction band edge of the nanotube [14]. We note that the overall $I_{ds}-V_g$ curves shift right, as the oxygen pressure increases from 3.4 to 50 Torr. In addition, the slope of the $I_{ds}-V_g$ curves change as well, as noted in the inset of figure 2(a). For example, a comparison between the 1×10^{-6} and 50 Torr cases shows that the n-channel current is more suppressed, while the p-channel current is enhanced. These observations bring important discussions about the origin of the change: doping of CNT and metal work function change in metal electrode. Derycke *et al* discussed that the carrier type of the nanotube transistor can be engineered by doping as well as by the Schottky barrier control at the metal–nanotube contact [14]. They noted that the slope of the $I_{ds}-V_g$ curves changes upon Schottky barrier variation, while the curves shift with negligible slope change upon doping. In this regard what we mainly observed from the oxygen exposure is rather closer to a doping effect than modulation of the Schottky barrier. As the oxygen pressures increases to 50 Torr, the $I_{ds}-V_g$ curves shift right by about 7 V, as shown in figure 2(a).

For the purpose of comparison with oxygen adsorption, the same transistor was exposed to ammonia gas, as shown in figure 1(b). As the ammonia pressure increases, the $I_{ds}-V_g$ curves shift left, while the curvatures remain almost intact. This is an indication of n-type doping by the adsorbed NH_3 molecules, in consistency with the calculation by Chang *et al* [20]. A comparison of figures 2(a) and (b) tells us that, while the $I_{ds}-V_g$ curves simply shift left upon NH_3 exposure, the case of oxygen exposure is rather more complicated than NH_3 . The overall rightward shift of the $I_{ds}-V_g$ curves in figure 2(a) should be ascribed to the hole-doping induced by the adsorbed oxygen molecules. However, there are other details which were not observed from NH_3 doping: a slight change in $I_{ds}-V_g$ slope and the increase of the off-stage range where the device effectively turns off. The small changes in the slope of the $I_{ds}-V_g$ curves are believed to indicate the increase in the work function of the electrode due to the adsorbed oxygen on the metal surface.

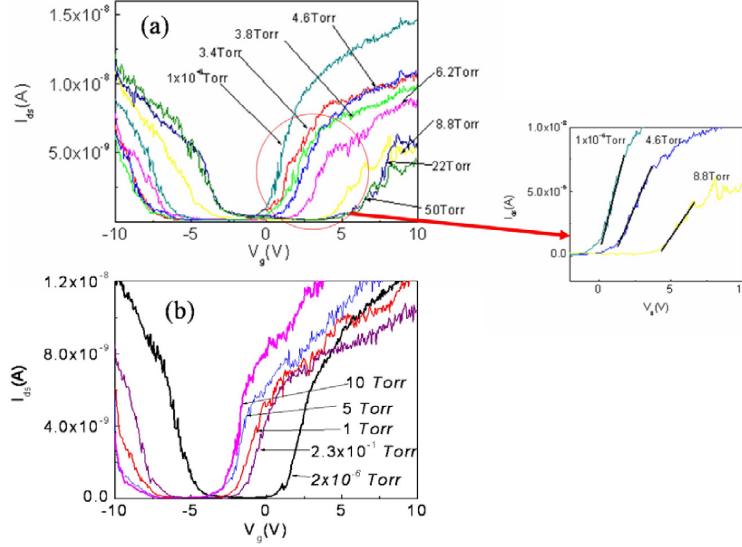


Figure 2. The I_{ds} - V_g curves of the CNT-FET under (a) oxygen pressures and (b) ammonia pressures. In (a) the curves for 1×10^{-6} , 4.6, and 8.8 Torr are magnified in the right panel to highlight the changes in the slope of the I_{ds} - V_g curves.

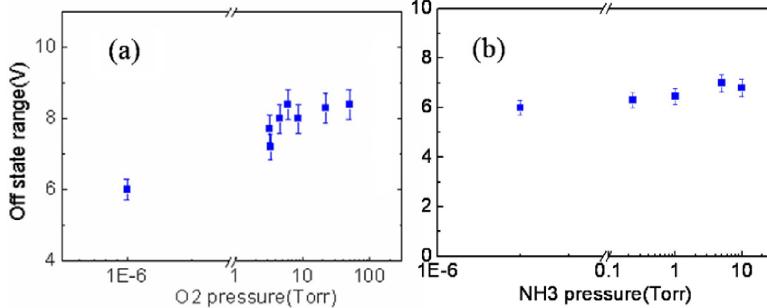


Figure 3. The off-state range in the I_{ds} - V_g curves of the CNT-FET under (a) oxygen pressures and (b) ammonia pressures.

The other details we observed in O_2 exposure are related to the off-stage range of this device. In figure 2(a), the off-state range of the I_{ds} - V_g curves, where we define the off-state by the extrapolation of I_{ds} - V_g tangential lines to the gate bias, increases as the oxygen pressure increases without a significant change in p-channel current. For instance, a comparison of the curves of 1×10^{-6} and 6.2 Torr shows that the n-channel current is reduced while the p-channel current is almost unchanged. The off-state versus with variation of gas pressure is plotted in figure 3. There is no apparent change in the off-state range change upon exposure to the ammonia gas, while it increases about 2 V upon oxygen exposure. This feature could not be explained by p-type doping of the nanotube body or work function increase in the electrode surface. This should be ascribed to the n-channel current suppression by the trapped negative charges on the LUMO level of the O_2 molecules near the nanotube surfaces or the surface of the gate dielectric.

In the previous paragraph, we discussed that the effects of oxygen on the transport properties of CNT-FET are complicated, including the doping of the nanotube body, work function increase in the metal surface, and the increase in the off-state range. However, theoretical studies to date have not

agreed on the effect of O_2 adsorption on the electronic structure of a carbon nanotube. Jhi *et al* [11] suggested that O_2 could strongly adsorb on the wall of a carbon nanotube, inducing a non-negligible hole-doping. Two subsequent theoretical works argued that such kind of local-density-approximated calculation overestimates the O_2 binding energy, and claimed that the hole-doping intensity as well as the binding energy could be negligible. In experimental aspects, the suggested p-type doping by environmental oxygen has been reported for networks of nanotubes [9, 10]. Meanwhile, Derycke *et al* have suggested that the main effect of the oxygen adsorption lies in the adjustment of the Schottky barrier rather than the bulk doping of the CNT body, through measurements with a single-nanotube FET [14, 15]. Thus we note that there has been no clear demonstration of the O_2 -induced p-type doping of an individual carbon nanotube.

However, we note here that, irrespective of whether the binding energy of the O_2 on the wall is strong or not, *ab initio* calculation should predict the existence of the LUMO level of O_2 just above the valence band edge of the semiconducting nanotube [20, 21]. Here we performed *ab initio* density-functional calculations using the Vienna

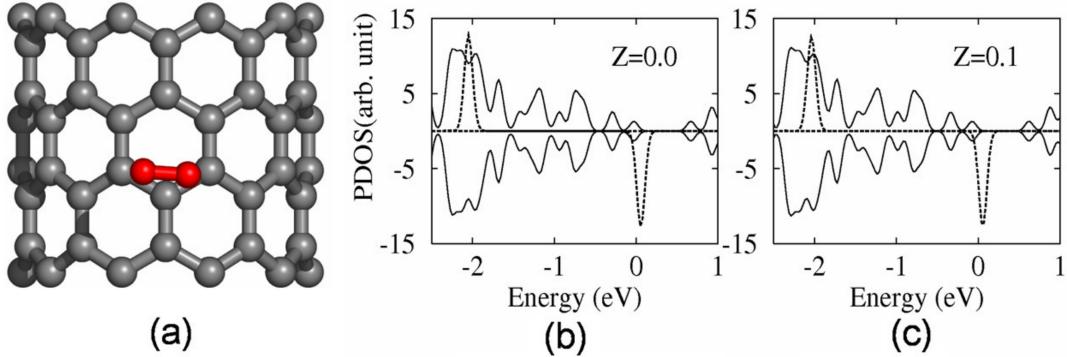


Figure 4. (a) Adsorption geometry of an oxygen molecule on the wall of the (10, 0) nanotube. The electronic density of states for (b) the O₂ adsorbed carbon nanotube and (c) that with excess charge of 0.1 electrons. The upper panels in (b) and (c) are for the spin-up electrons, while the lower panels are for the spin-down electrons. Dotted lines and solid lines in (b) and (c) are the projected density of states for the oxygen molecule and the carbon nanotube, respectively.

simulation package (VASP) [22–24]. The spin-polarized gradient-corrected approximation is adopted for the exchange–correlation potential [25]. The ionic potentials are described by the projector augmented wave (PAW) method as provided with VASP [26], and the energy cutoff for the plane-wave basis is set to 400 eV [27]. In figure 4, we present the adsorption geometry of an oxygen molecule on the (10, 0) nanotube and the electronic density of states. To simulate an isolated single nanotube, we assumed a large two-dimensional lattice in the plane perpendicular to the tube axis, where the distance between the nanotube and its replica is larger than 10 Å. The unit cell along the axial direction is twice the minimal unit cell of the zigzag carbon nanotube ($\approx 8.49 \text{ \AA}$). The atomic positions are relaxed with residual forces smaller than 0.05 eV Å⁻¹ with the given unit cell parameters. The upper panels in figures 4(b) and (c) are for the majority-spin states and the lower panels are for the minority-down states. The dotted peaks in the upper panel at about -2 eV and that in the lower panel at just above 0 eV show the triplet ground state of the oxygen molecule. The LUMO level of O₂, which is the pp π^* with the minority-spin state, is just above the valence band maximum of the (10, 0) nanotube. In other words, the Fermi level of the oxygen adsorbed nanotube sits at the valence band edge rather than at the midgap. We increased the electron occupation to have 0.1 excess electrons in the unit cell (80 carbon atoms and 2 oxygen atoms). We find that the excess electrons occupy the LUMO of O₂ rather than the conduction band of the carbon nanotube. Thus, the turn-on voltage of the n-channel current will be increased by the presence of the oxygen molecule on the nanotube wall. This shift of the Fermi level, and the consequent unease in turning on the n-channel current, should be interpreted as p-type doping of the nanotube, regardless of whether the charge transfer is strong or not.

4. Summary

We have performed transport measurements of a long individual carbon nanotube under oxygen pressure and ammonia pressure. We found that the I_{ds} – V_g curves shift right as the oxygen pressure increases, while they shift left as the ammonia pressure increases. This indicates that oxygen

adsorption induces p-type doping while that of ammonia give rise to n-type doping of the nanotube. In contrast to the ammonia cases, the effect of oxygen is more complicated, including small changes in the slope as well as an increase in the off-state range. We suggest that the oxygen exposure of CNT-FETs could induce a work function increase in the metal surface, and p-channel current suppression, as well as hole-doping of the CNT body. However, such a doping effect would be dominant as the length of the nanotube increases.

Acknowledgment

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