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Fabrication of *n*-type nanotube transistors with large-work-function electrodes

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The authors found experimentally that carbon nanotube field-effect transistors (CNFETs) could exhibit *n*-type characteristics even though their electrodes consist of a large-work-function metal such as Co. To explain their result, which is contrary to the general belief that CNFETs with large-work-function electrodes always lead to *p*-type characteristics, *ab initio* electronic structure calculation for the metal-carbon nanotube junction was performed, which showed that the Fermi level alignment at the junction could sensitively depend on microscopic structures of the metal-carbon nanotube junction. This suggests that deposition method of electrodes as well as the metal type could be utilized to obtain *n*-type CNFETs. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2709934]

The carbon nanotube field-effect transistor (CNFET), which employs a semiconducting carbon nanotube (CNT) as an electron channel, could potentially be utilized in the nanoscale electronics in the future. Many studies on CNFETs, both theoretical and experimental, have been performed to improve the device performance as well as to understand the underlying physics of electron transport in nanoscale.[1,2] One of the main challenges in this field is controlling the conduction type of CNFETs. Both *n*-type and *p*-type transistors, operating within the range of manageable gate voltage, are required for logic devices. It is well known, however, that the CNFETs commonly exhibit the *p*-type operation only. Such characteristic *p*-type behavior of the CNFET has long been an issue of debate.[3–5] But the most fundamental reason has been attributed to the lower Schottky barrier for the hole transport at the metal-CNT contact interface.[4,5] Many researchers have tried low-work-function metals, such as K and Ca, for the electrodes and succeeded to achieve a *n*-type CNFET.[6,7]

In this letter, we report that even a large-work-function electrode could lead to a *n*-type CNFET, depending on how the metal electrode is constructed. We found that the occurrence of a *n*-type behavior in our CNFETs with Co/Au electrodes is closely related to how the metal electrode is deposited. High-kinetic-energy deposition, such as sputtering, resulted in a higher chance of getting *n*-type CNFETs. In order to explain our observation, we have performed *ab initio* electronic structure calculations. We found that the positioning of the metal Fermi level in the band gap of the semiconducting CNT could depend on the local atomic structure at the metal-CNT interface. This means that in addition to the type of the electrode material, the specific electrode-

deposition process could affect the overall conduction behavior of the device.

For our experiment, high-purity single-wall carbon nanotubes and double-wall carbon nanotubes were synthesized by either arc discharge or chemical vapor deposition. A droplet of dichloroethane containing CNTs was spun over a highly doped Si substrate with a 300 nm thick thermally grown SiO_2 layer. Once an individual CNT was located by atomic force microscope (AFM), conventional electron-beam lithography was used to generate electrical lead patterns onto the selected CNT. To form source and drain electrodes, layers of 40 nm Co and 10 nm Au were deposited successively by magnetron sputtering at a base pressure of 2×10^{-7} Torr, followed by a standard lift-off process. We used a Au layer to prevent oxidation of Co. Then, the electrical transport properties were measured at 2 K in the vacuum condition. A back gate was used for gating. A total of six samples exhibited field-effect transistor behavior. Listed in Table I are the sample parameters for three *n*-type, two ambipolar, and one *p*-type CNFETs. We note that the growth method, the diameter of the CNT, and the channel length have no correlation with the transport type of the CNFET. In a later paragraph, we discuss that such difference in the conduction type should be ascribed to the difference in the bonding configuration at the metal-carbon nanotube interface.

Figure 1 shows the gate modulations of three *n*-type CNFETs. As mentioned in previous paragraphs, researchers have believed that the large-work-function metal should always lead to *p*-type behaviors.[7,8] In this regard, the occurrence of the *n*-type FETs with the Co/Au electrode, which is a typical large-work-function metal ($\approx$5 eV), is quite remarkable.[9] Sample N1 clearly displays *n*-type behavior with *n*-channel threshold voltage of −3.4 V, as shown in Fig. 1(b). In samples N2 and N3, as shown in Figs. 1(c) and 1(d), the *p* channels are not suppressed completely, but the *p*-channel conductance is about two orders of magnitude

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TABLE I. Device parameters. Three *n*-type CNFETs are denoted by N1, N2, and N3. Two ambipolar CNFETs are labeled by AP1 and AP2, and P1 represents one *p*-type CNFET. Here, length means the interelectrode distance.

Sample name	Growth method	Diameter (nm)	Length (nm)	FET type	Threshold voltage (V)
N1	Arc	1.9	350	*n*	−3.4
N2	CVD	2.9	600	*n*	1.4
N3	CVD	1.8	1000	*n*	2.5
AP1	Arc	2.1	300	Ambipolar	−2.4, 0.9
AP2	Arc	1.9	280	Ambipolar	−1.8, 2.0
				p	8.5
P1	CVD	1.7	780	*p*	6.3

smaller than that of the *n* channel. The CNT diameters, measured by AFM, were in the range of $1.7–2.9$ nm. The CNT with the larger diameter is likely to be double walled, whereas the tube with the smaller diameter is likely to be single walled.[10]

In contrast to the aforementioned samples, sample P1 shows *p*-type characteristics. At first, this sample, of which resistance was greater than 1 GΩ at room temperature, had negligible conductance. We have performed rapid thermal annealing (RTA), known to enhance the conductance of the CNT-metal junction. After annealing the sample at the temperature of 500 °C in a vacuum condition (1×10^{-6} Torr) for 60 s, the sample resistance went down to 0.3 MΩ and it exhibited a clear *p*-type gate modulation, as shown in Fig. 2(a). The *p*-channel threshold voltage was found to be 8.5 V, as denoted by an arrow in Fig. 2(a).

In order to investigate the effect of annealing on the CNFET characteristics, we have also performed a second RTA with the same conditions. After the second RTA, the sample resistance went down to 0.24 MΩ, implying further improvement of the metal-CNT contact interface. Figure 2(b) shows the gate modulation of sample P1 after the second RTA. Note the overall similarity between Figs. 2(a) and 2(b). Both gate modulation curves are quite similar, exhibiting quasiperiodic current modulations, attributed to the Coulomb oscillation. One noticeable change after the second RTA is
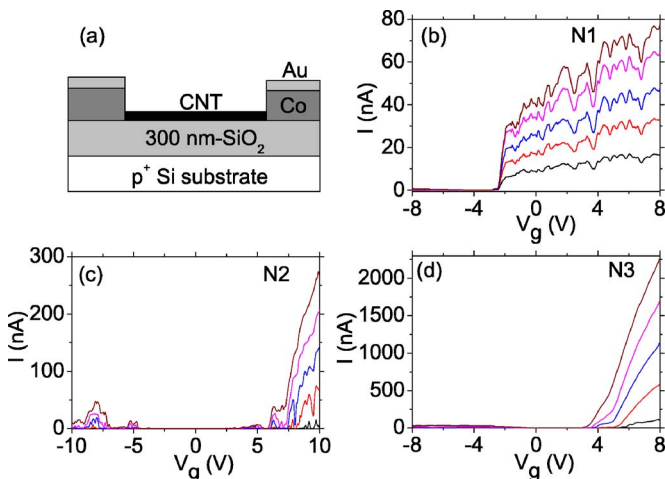
the shift of the *p*-channel threshold voltage. It is shifted to the negative direction, from 8.5 to 5.9 V. For sample P1, the conductance enhancement by the second RTA is accompanied by a negative shift of the gate modulation curves. The negative shift of the *p*-channel threshold voltage indicates the weakening of the *p*-type characteristics or the strengthening of the *n*-type characteristics. Though we have not observed *p*-type to *n*-type conversion since sample P1 is broken during the third RTA, we expected that a further improvement of the metal-CNT contact interface may have resulted in an ambipolar or *n*-type CNFET.

In the previous paragraph, we discussed that the difference in the conduction type among our CNFETs could not be correlated with the CNT diameter, the types of electrode metal, or the CNT growth method. We suggest that such difference may be ascribed to the difference in the metal-carbon bond strength, in other words, the strength of the interface dipole. It is very hard to obtain direct experimental information about the metal-carbon bond, and there are many uncertain parameters in the metal-CNT interface. In this regard, the *ab initio* electronic structure calculation could be a great help.

When the CNT is weakly physisorbed on the metal surface, the positioning of Fermi level is strongly dependent on the work function of the metal.[11] This indicates that when the metal-CNT forms a weakly physisorbed contact, the Schottky barrier could be controlled by the choice of metal. However, it was also shown that the Fermi level of the large-work-function metal could be aligned at the conduction band edge of the semiconducting CNT, when the deposited metal layer exerts a substantial pressure on the wall of the carbon nanotube.[12] Moreover, in this work, we show that the Fermi level of the metal could be strongly pinned at the midgap of the CNT when there are strong metal-carbon bonds at the
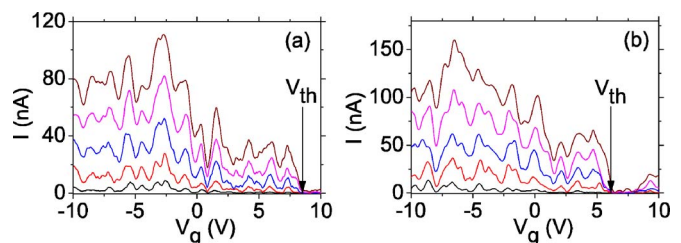

FIG. 1. (Color online) Device schematics and the gate modulation curves of three *n*-type CNFETs (N1, N2, and N3) with varying source-drain bias voltage (V_{sd}). In (b), V_{sd} is changed from 0.2 to 1.0 mV, from bottom to top, respectively. In (c) and (d), V_{sd} is changed from 40 to 200 mV, from bottom to top, respectively. All of the measurements were done at 2 K.

FIG. 2. (Color online) Gate modulation curves of a *p*-type CNFET (P1) after (a) the first RTA and (b) the second RTA. The measured temperature was 2 K. In (a), the source-drain bias voltage is changed from 2 to 10 mV, from bottom to top, respectively. In (b), the source-drain bias voltage is changed from 3 to 15 mV, from bottom to top, respectively.
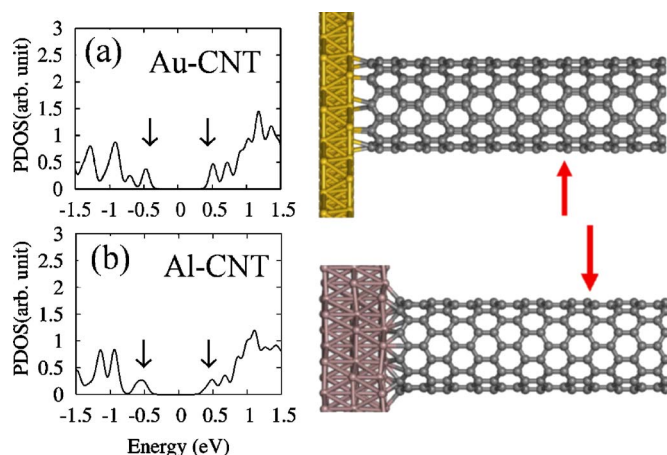
FIG. 3. (Color online) Electronic structure and bonding configuration for (a) two Au layers and (b) three Al layers in contact with the semiconducting (10,0) CNT. Partial densities of states (PDOSs) for 20 carbon atoms in the zigzag chain of the CNT, indicated by red arrows in atomic geometries, are presented with respect to the Fermi level of each configuration. Two downward arrows in PDOS indicate the valence and conduction band edges. In this calculation, the CNT of 10 nm length is connected to the metal at both ends, but only the part at one end is shown.

interface. The computational methods used in this work are the same as in previous works.[11,12] Figure 3 shows the results of the electronic structure calculation in the case of strong metal-carbon bonds. The Fermi level sits at the center of the band gap, irrespective of whether the work function of the metal is large (Au) or small (Al). Based on these results, we suggest that the microscopic differences in the metal-CNT interface are responsible for the different characteristics (*n* type, ambipolar, and *p* type) of the CNT with the same Co/Au electrode.

It should be addressed why we frequently observe *n*-type CNFETs, which are rarely seen by other groups. We believe that our method of electrode formation made such a difference. Directional deposition methods, such as electron-beam or thermal evaporations, are usually adopted for electrode metal deposition since they are compatible with the following lift-off process. In our experiment, however, we used magnetron sputtering to deposit electrode metals. Compared with thermally evaporated metals, sputtered ones have a much higher kinetic energy. We believe that such a high-energy deposition could result in the formation of strong chemical bonds between the electrode metal and the CNT, and thus a higher chance of obtaining *n*-type CNFETs. For comparison, we have also fabricated CNFETs by using the electron-beam evaporation. All of the six fabricated samples exhibited *p*-type characteristics, which also corroborate our suggestion.

In summary, we have fabricated nanotube field-effect transistors with an individual CNT and measured their electrical transport properties. We have shown that even a large-work-function electrode, such as Co/Au, could result in a *n*-type CNFET. This is in contradiction with the general belief that large-work-function electrodes always result in *p*-type FETs. We suggested that the formation of strong chemical bonds at the metal-CNT junction could explain our experimental observations. Through *ab initio* electronic structure calculations, we showed that the Fermi level could be pinned in the middle of the band gap or at the conduction band edge of the CNT, and thus ambipolar and even *n*-type CNFETs are allowed. Our results suggest that, in designing the conduction type of CNFETs, the metal work function could not be the only decisive parameter, but the local interface structure could be important as well. Thus, a precise control of the metal-carbon bonding configuration should be developed for a further improvement of nanotube electronics.

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