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Fabrication of n-type carbon nanotube field-effect transistors by Al doping

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We report the effect of an Al layer, covering the central part of the nanotube channel, on the electrical transport properties of carbon nanotube field-effect transistors (CNFETs). The CNFETs, consisting of single-walled carbon nanotube or double-walled carbon nanotube between two Pd electrodes on top of SiO2 layer, which showed p-type or ambipolar transport behaviors, exhibit clear n-type characteristics after the Al deposition. We ascribe such conversions into n-type behaviors to the electron doping in the Al-covered nanotube region, which results in the bending of the nanotube bands nearby the edges of the Al layer. This technique, Al deposition under a high vacuum, may give rise to a practical fabrication method for the n-type CNFET, which may enable us to develop complementary logic nanotube electronic devices. © 2006 American Institute of Physics.

A carbon nanotube (CNT), a graphitic tube with nanometer-scale diameter,1 has strong mechanical stiffness2 and excellent electrical transport properties.3–5 Such advantageous material properties may lead to many potential applications; nanotube electron emitter for flat-panel displays with extremely low-power consumptions,6 highly sensitive chemical sensors,7 and nanoscale electronics devices, such as memory and logic circuits.8–10 These nanoelectronics may give rise to future breakthroughs in the electronics industry when the Si-based semiconductor technology reaches its scaling limit.

Since the first CNT field-effect transistor (CNFET) (Refs. 11 and 12) was developed, quite a few studies have been devoted to understanding and controlling the conduction type of the CNFET. It has been known that most of the CNFETs are likely to show p-type characteristics, which is either due to the hole doping by the environmental oxygen or a lower Schottky barrier for hole current at the metal-CNT contact. In order to achieve operations similar to complementary metal-oxide-semiconductor devices, well-defined n-type transistors as well as p-type ones are needed. A few successes in the fabrication of the n-type CNFET have utilized potassium doping in the CNT channel13–16 or a calcium contact as an electrode with a low work function.17 However, these alkali elements are chemically very active, and usually very hard to control. Thus more practical and reliable method to fabricate n-type CNFET is required.

In this work, we show that an Al layer on top of a CNT, deposited by sputtering under a high vacuum, gives rise to n-type transport properties in the CNFET. We first fabricated a CNFET with an individual single-walled carbon nanotube (SWNT) or double-walled carbon nanotube (DWNT) between Pd electrodes. Before Al deposition, the devices show p-type or ambipolar behaviors, which may be due to the Fermi-level alignment at the contacts for SWNT or the small band gap for DWNT. However, once the Al layer was deposited on the CNT, the device became a clear n-type CNFET. We describe these changes in the transport behaviors with the band bending, caused by the electron doping in the CNT region under the Al layer.

For our experiment, high-purity DWNTs and SWNTs were synthesized by a hydrogen arc discharge method.18 Atomic force microscope (AFM) study indicated that the diameters of DWNTs were in the range of 2–4 nm and those of SWNTs were 1–2 nm. A droplet of dichloroethane containing CNTs was spun over a Si substrate with a 300 nm thick thermally grown SiO2 layer. Individual CNTs were located by AFM and conventional electron-beam lithography was used to generate electrical lead patterns onto a selected CNT. To form source and drain electrodes, 30 nm of Pd was deposited by magnetron sputtering at a base pressure of 10−8 Torr, followed by a standard lift-off process. Then, the electrical transport properties were measured at room temperature in the vacuum condition. A back gate was used for gating. After confirming the FET behavior of the device, we have generated the second pattern for Al deposition in the middle of the CNT. A 30 nm thick Al film was deposited by the same method as Pd. Then, the electrical transport properties of the device, between two Pd electrodes, were measured at room temperature in the vacuum condition.

The schematic device structure is shown in Fig. 1, where L is the separation between the source and drain electrodes and w is the width of the Al layer. Thickness of Pd and Al film is about 30 nm.

![FIG. 1. Schematic device structure. L is the distance between the Pd electrodes and w is the width of the Al layer. Thickness of Pd and Al film is about 30 nm.](image-url)
and \( w \) is the width of the Al layer. We have found that a high-energy deposition, such as sputtering, at a high vacuum (\( 10^{-8} \) Torr) is required to achieve \( n \)-type transport behaviors. For a comparison, we have also performed the same experiment with the Al layer deposited by an electron-beam deposition method at the base pressure of \( 10^{-6} \) Torr. We have found that such a method did not lead to any noticeable change of the field effect transistor (FET) behavior; original \( p \)-type CNFET exhibited \( p \)-type behavior even after the deposition of Al layer. Below, we report the three samples which exhibit \( p \)- to \( n \)-type conversion. For samples S1, \( L \) =\( 1.0 \mu m \) and \( w = 0.64 \mu m \), for sample S2, \( L = 0.70 \mu m \) and \( w = 0.47 \mu m \), and for sample S3, \( L = 5.3 \mu m \) and \( w = 1.3 \mu m \).

Figure 2(a) shows the gate modulation of sample S1 without Al deposition. An apparent \( p \)-type FET behavior is observed. The conductance at the bias voltage of \( V_{sd} \) =\( 0.5 \) V is about 150 nA/V. After the deposition of the Al film in the middle of CNT, the transfer characteristics change into a \( n \)-type FET, as shown in Fig. 2(b). The conductance at the bias voltage of \( V_{sd} =0.5 \) V is about 1 nA/V, which means a two orders of magnitude decrease in the conductance by the Al deposition. Such a conductance decrease after the Al deposition was commonly observed in other samples of ours as well as in other’s work.\(^{19}\) Similar behavior was also observed for the sample S2. Figures 2(c) and 2(d) show the gate modulations of sample S2. For sample S2, the conductance decreases by about one order of magnitude after the Al deposition.

Sample S3 exhibited ambipolar behavior before the Al deposition as shown in Fig. 3(a). Such ambipolar behavior is commonly observed in a DWNT or a large-diameter SWNT (Refs. 20 and 21) and is attributed to the small band gap of the large-diameter CNT. Through the AFM measurement, we have found that the diameter of the CNT in sample S3 was about 3.0 nm, larger than the diameters (\( \sim 1.5 \) nm) of the CNTs in samples S1 and S2. Like the other two samples, sample S3 also exhibits a transition to a \( n \)-type CNFET after the Al deposition. Figure 3 shows the gate modulations of the sample S3. Before the Al deposition [Fig. 3(a)], this device showed an ambipolar behavior. After the Al film deposition, the \( p \)-channel current was suppressed considerably, while the \( n \)-channel current was negligibly affected, as shown in Fig. 3(b).

As we mentioned before, when the Al layer was deposited with the electron-beam deposition method at a relatively low (\( \sim 10^{-6} \) Torr) base pressure, \( p \)- to \( n \)-type transition was observed. The absence of the type conversion can be explained by the oxidation of the Al layer during or after the film deposition. Recent theoretical study shows that the work function of the oxidized Al surface is close to that of Au and, therefore, the oxidized Al particles are likely to induce hole doping, rather than the electron doping, in the CNT.\(^{22}\) This means that the Al particle, once oxidized, may lead to \( p \)-type behavior in a CNFET, thus no type conversion would occur. Because we could not observe type conversion in CNFETs, where the Al layer was deposited by electron-beam evaporation, we suspect that Al layers deposited by electron-beam evaporation oxidize more than those deposited by sputtering. In the electron-beam evaporation process, Al particles can be substantially oxidized during evaporation under a low vacuum condition (\( 10^{-6} \) Torr) and low deposition rate (\( \sim 1 \) nm/s). Moreover, oxidation of Al layer may occur even after the evaporation process because non-negligible spacing could be formed between CNT and Al film, which may result in the oxidation of the Al layer after deposition. Therefore, we suggest that high-energy evaporation, such as sputtering, under a high vacuum would be crucial to growing an Al layer without oxidation, and in turn to achieve \( n \)-type CNFETs.

We now suggest a theoretical explanation on the type conversion of CNFET with Al deposition. It is well known that the \( p \)-type operations of CNFET (samples S1 and S2) are largely attributed to the large work function of the Pd electrodes. When the electrodes are large work-function metals, such as Pd or Au, the Fermi level of the electrodes is located close to the valence-band edge of the CNT, as shown in the band diagram of Fig. 4(a), resulting in a \( p \)-type CNFET.\(^{22}\) However, the ambipolar behavior of sample S3 [Fig. 3(a)] is likely due to the smaller band gap of the large diameter CNT. The channel length of sample S3 is much longer than those of samples S1 and S2.

![FIG. 2. The gate modulation characteristics for sample S1 (a) before and (b) after the Al layer deposition. The same characteristics for sample S2 (c) before and (d) after the Al layer deposition. Through the AFM measurement, diameters of the nanotubes are determined to be about 1.2 and 1.5 nm for sample S1 and S2, respectively.](image1)

![FIG. 3. The gate modulation characteristics for sample S3 (a) before and (b) after Al layer deposition. The diameter of the nanotube is about 3.0 nm.](image2)

![FIG. 4. The band diagrams along the axis of the nanotube (a) before and (b) after the Al layer deposition. C.B. and V.B. represent the conduction band and the valence band, respectively. The horizontal dashed line represents the Fermi level.](image3)
channel length, the CNT is more likely to be in a diffusive conduction regime and the CNT channel may contribute more to the resistance than the metal-CNT contacts.

The n-type behaviors, as shown in Figs. 2(b), 2(d), and 3(b), could be ascribed to the electron doping by the deposited Al layers. It has been shown that electronic charge transfers from Al layer to the CNT when unoxidized Al particles are in the vicinity of the CNT. The overall band diagram after the Al deposition is described in Fig. 4(b). We note that the Fermi level is aligned at the valence-band edge near the Pd electrode, while it is at the conduction-band edge under the deposited Al layers. Thus, there must be a sharp band bending near the edges of the Al layer. For electrons to flow through the CNT, they need to be thermally excited or to experience interband tunneling near the edges of the Al covered region. If the deposited Al particles did not contaminate the metal-CNT contact, the Schottky barriers described in Figs. 4(a) and 4(b) would not change upon the Al deposition. Thus, the decreased current with deposited Al layer, as shown in Figs. 2(b) and 2(d), should be ascribed to the additional resistance near the edges of the Al layers.

In summary, we fabricated CNFETs with an individual CNT between two Pd electrodes and measured their transport properties. While most devices showed p-type transport behaviors, some large-diameter CNFETs showed ambipolar behaviors. After covering the CNT channel region with the 30 nm thick Al layer deposited by sputtering at a high vacuum, we achieved n-type transport behaviors in the aforementioned CNFETs. We explained such conversion from p-type to n-type behavior in terms of the bending of the conduction and valence bands, which originates from the electron doping in the CNT region under the Al layer. We suggest that the deposition of Al layers without oxidation would be a key technique to achieve n-type CNFETs, and could pave the way to a more practical fabrication method for n-type CNFETs.

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