n-type carbon nanotube field-effect transistors fabricated by using Ca contact electrodes

Yosuke Nosho, Yutaka Ohno,[a] Shigeru Kishimoto, and Takashi Mizutani
Department of Quantum Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

(Received 21 July 2004; accepted 20 December 2004; published online 7 February 2005)

We have fabricated *n*-type carbon nanotube field effect transistors by choosing the contact metal. Single-walled carbon nanotubes were grown directly on a SiO_2/Si substrate by chemical vapor deposition using patterned metal catalysts. Following the nanotube growth, Ca contacts with a small work function were formed by evaporating and lifting off the metal. The devices showed *n*-type transfer characteristics without any doping into the nanotube channel. In contrast, the devices with Pd contacts showed *p*-type conduction. These results can be explained by taking into account the work functions of the contact metals. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1865343]

Semiconducting single-walled carbon nanotubes (SWNTs) are promising materials for nanoscale electron devices, such as nanotube field-effect transistors (FETs), for ultrahigh-density integrated circuits and quantum-effect devices for intelligent circuits, which are expected to bring a great breakthrough in the present silicon technology.[1,2] In order to realize such highly functional nanotube circuits, there are many issues to be addressed. One of the most important issues for nanotube FETs is to control the conduction type of devices. For example, nanotube FETs usually show *p*-type transfer characteristics,[3,4] even though *n*-type devices are indispensable for nanotube integrated circuits of low-power dissipation similar to Si complementally metal-oxide-semiconductor devices. Bockrath *et al.*[5] proposed the doping of potassium on the nanotube channel surface to fabricate *n*-type nanotube FETs. Although the potassium doping on the nanotube surface is a promising technique to change the conduction type of nanotube FETs from *p*-channel to *n*-channel characteristics, it is necessary to control the doping density. In addition to that, the ionized impurities would have some influences on the electron transport through the doped nanotube channel.

Recently, the operation mechanism of the nanotube FETs has been explained by Schottky barrier modulation model, in which the gating action is dominated by the Schottky barrier formed at the contact between the nanotube and the source metal.[6–8] Javey *et al.*[9] reported that the contact resistance of the electrode/nanotube contact can be reduced by using Pd as the contact metal in *p*-type nanotube FETs, since Pd has a large work function and hence the Schottky barrier height for holes is low. Taking these reports into account, if we use materials with a small work function as contact electrodes of nanotube FETs, the Schottky barrier height for electrons would be low. In this case, it is expected that electrons are injected from the contact electrode into the nanotube and *n*-type nanotube FETs will be realized without any doping into the nanotube channel.

In this letter, we have fabricated *n*-type nanotube FETs by using Ca with a small work function as the contact electrodes. The temperature dependence of the device characteristics has been measured to investigate the interfacial electronic structure at the Ca/SWNT contact.

Figure 1 shows schematic band structures of the interface at the source contact. If a metal with a work function larger than that of the SWNT, ~4.8 eV,[10] is used as the source electrodes, the Fermi energy (E_F) of the source electrode will be located close to the valence-band edge of the SWNT (E_v) as shown in Fig. 1(a). In this case, the Schottky barrier height for holes is low, and holes are easily injected from the electrode into the SWNT. On the other hand, in the case of a metal with a smaller work function than that of the SWNT, the E_F is located close to the conduction-band edge of the SWNT (E_c) as shown in Fig. 1(b), and electrons will be injected into the nanotube. We have chosen Ca as a contact metal with small work function of 2.8 eV in order to realize *n*-type devices.

Figure 2 shows a schematic device structure of the fabricated nanotube FET with Ca contact electrodes. A heavily doped p^+-Si wafer with thermally oxidized SiO_2 (100 nm) was used as the substrate. The SWNT was grown directly on the Si substrate by utilizing the position controlled growth technique.[11,12] The metal catalysts consisting of a double layer of Co (2 nm) on Pt (10 nm) were patterned on the substrate using photolithography, electron-beam evaporation, and lift-off process. A mixture of ethanol (10 sccm) and argon (100 sccm) was used as a source gas for the alcohol catalytic chemical vapor deposition.[13] The total pressure in the furnace was 1.3 Torr. The growth temperature and time

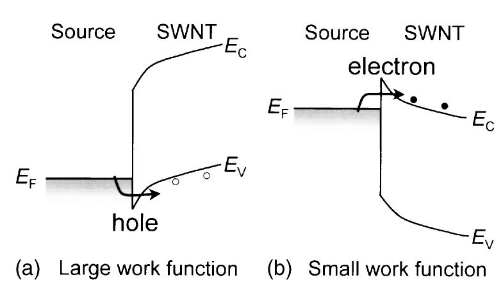

FIG. 1. Schematic band structures of the interface at the source contact. (a) For contact metal with large work function, and (b) for contact metal with small work function.

[a]Also at: PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan; electronic mail: yohno@nuee.nagoya-u.ac.jp

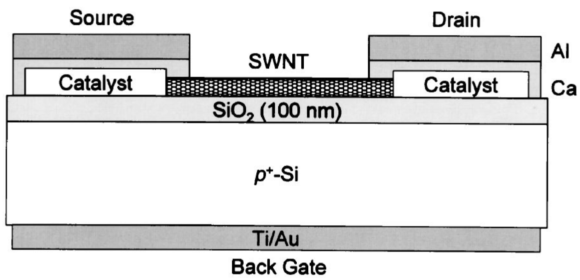

FIG. 2. Schematic device structure of fabricated *n*-type carbon nanotube FET.

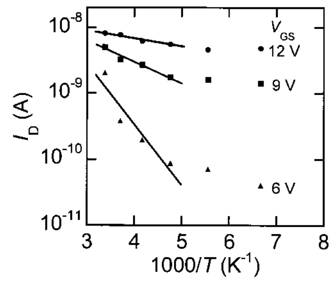

FIG. 4. Temperature dependence of I_D of the nanotube FET with Ca contact electrodes at $V_{DS}=0.1$ V.

were 800 °C and 1 h, respectively. The Au/Ti for the back gate electrode was deposited on the back side of the substrate. Ca (3 nm) and subsequent Al (500 nm) were deposited by electron-beam evaporation for the source and drain contact electrodes. The Al was used to prevent the oxidation of the Ca thin film. The channel length is 3 μm.

Figure 3(a) shows the drain current (I_D) as a function of the gate-source voltage (V_{GS}) of the fabricated nanotube FET with Ca contact electrodes. Here, the drain-source voltage (V_{DS}) was 0.1 V. The I_D increased with increasing V_{GS}, and hence *n*-type transfer characteristics were obtained. We have also fabricated the devices with Pd contact electrodes for comparison. The device had *p*-type transfer characteristics as shown in Fig. 3(b). These results show that, by changing the material used as the contact electrodes, the conduction type of nanotube FETs can be controlled without any doping into the nanotube. The drain current of the *n*-type FET was smaller than that of the *p*-type FET. This is probably because there exists a barrier at the Ca/SWNT interface larger than that for holes at the Pd/SWNT interface as it will be described later.

In order to investigate the interface between the SWNT channel and the Ca contact electrode, the temperature dependence of the I_D of the *n*-type nanotube FET was measured. Figure 4 shows the I_D in log scale as a function of $1000/T$ at $V_{GS}=6$, 9, and 12 V and $V_{DS}=0.1$ V. The I_D increased with increasing temperature above ~200 K. This suggests the existence of a potential barrier against electrons at the contact between the SWNT and the Ca electrode.

The barrier height was estimated from the slope of the Arrhenius plot as a function of V_{GS} as shown in Fig. 5. In the regime of $V_{GS}>10$ V, the barrier height was a small constant value of ~25 meV. In the regime of $V_{GS}<10$ V near the threshold voltage, on the other hand, the measured barrier height increased with decreasing V_{GS}. These behaviors of the barrier height can be understood if we take into account that the thermally assisted tunneling process of electrons dominates the current through the Schottky barrier formed at contact of the nanotube FET.[6] At $V_{GS}>10$ V, where the device was biased enough at the on state, the thickness of the Schottky barrier decreases, and electrons are injected from the Ca electrode into the SWNT by the thermally assisted tunneling process, in which thermally excited electrons tunnel through the thin Schottky barrier. Then, the measured barrier height corresponds to an effective barrier height for the thermally assisted tunneling of electrons as reported by Martel *et al.*[6] On the other hand, at $V_{GS}<10$ V near the threshold voltage, the thickness of the Schottky barrier increases, and hence the tunneling current component is suppressed. Therefore, the measured barrier height approaches the true Schottky barrier height with decreasing V_{GS}. The obtained results strongly suggest the existence of the Schottky barrier at the Ca/SWNT contact. The Schottky barrier height for electrons is estimated from Fig. 5 to be about 200 meV if we assume that the potential barrier is thick enough to suppress the tunneling current component at V_{GS} near the threshold voltage.

Now, we discuss the band structure of the Ca/SWNT interface of the fabricated *n*-type nanotube FETs. Since the work function of Ca, ~2.8 eV, is smaller than that of SWNTs, it is expected that E_F of the Ca electrodes is posi-

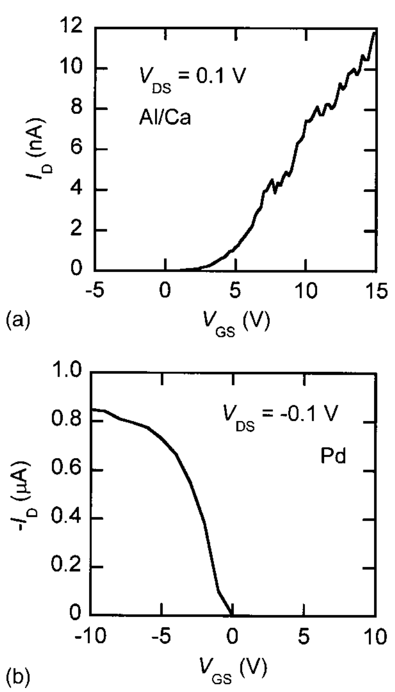

FIG. 3. I_D-V_{GS} characteristics of fabricated nanotube FETs with (a) Al/Ca and (b) Pd contact electrodes.

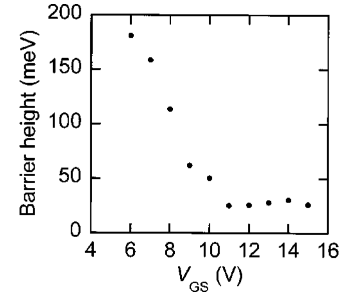

FIG. 5. V_{GS} dependence of barrier height obtained by slope of Arrhenius plot.

tioned above E_c of the SWNT if we assume the Mott–Schottky model. If this is the case, there is no barrier against electrons. However, the obtained results suggest the existence of a Schottky barrier at the Ca/SWNT contact as described above. A possible explanation for the reason why the Schottky barrier is formed at the Ca/SWNT contact is that a dipole layer formed at the Ca/SWNT interface causes an abrupt potential drop at the interface as reported for organic/metal interfaces.[14]

The interfacial property is dominated not only by the work function of the metal but also by the interfacial dipole as described above. The control of the interface dipole is essential to solve remaining issues such as the unbalance in the current drivability between the present *n*- and *p*-type FETs, and as the adjustment of the threshold voltage. By decreasing the charge density of the dipole at the Ca/SWNT interface, the Schottky barrier height for electrons would be lowered, and then the current in the *n*-type FET would be increased. For the threshold voltage adjustment, it is important to control energy level alignment at the electrode/SWNT interface.

In conclusion, we have fabricated *n*-type carbon nanotube FETs by using Ca contact electrodes without any doping into the nanotube channel. The idea to put the Fermi energy of the contact electrodes close to the conduction-band edge of the SWNT channel by using contact metal with a small work function was confirmed. The temperature dependence of the drain current suggested the existence of the Schottky barrier at the Ca/SWNT interface even though the work function of Ca was much smaller than that of SWNTs, probably due to the dipole layer formation at the Ca/SWNT interface.

This work was supported in part by the Special Coordination Funds of the Ministry of Education, Culture, Sports, Science, and Technology of the Japanese Government.

[1] C. Dekker, Phys. Today **52**, 22 (1999).
[2] M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Carbon Nanotubes*, Springer Series, Vol. 80 (Springer, Berlin, 2001).
[3] S. J. Tans, A. R. M. Verschueren, and C. Dekker, Nature (London) **393**, 49 (1998).
[4] R. Martel, T. Schmidt, H. R. Shea, T. Hertel and P. Avouris, Appl. Phys. Lett. **73**, 2447 (1998).
[5] M. Bockrath, J. Hone, A. Zettl, P. L. McEuen, A. G. Rinzler, and R. E. Smalley, Phys. Rev. B **61**, R10606 (2000).
[6] R. Martel, V. Derycke, C. Lavoie, J. Appenzeller, K. K. Chan, J. Tersoff and P. Avouris, Phys. Rev. Lett. **87**, 256805 (2001).
[7] A. Bachtold, P. Hadley, T. Nakanichi, and C. Dekker, Science **294**, 1317 (2001).
[8] S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller and P. Avouris, Phys. Rev. Lett. **89**, 106801 (2002).
[9] A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, Nature (London) **424**, 654 (2003).
[10] S. Suzuki, C. Bower, Y. Watanabe, and O. Zhou, Appl. Phys. Lett. **76**, 4007 (2000).
[11] H. T. Soh, C. F. Quate, A. F. Morpurgo, C. M. Marcus, J. Kong, and H. Dai, Appl. Phys. Lett. **75**, 627 (1999).
[12] Y. Ohno, S. Iwatsuki, T. Hiraoka, T. Okazaki, S. Kishimoto, K. Maezawa, H. Shinohara, and T. Mizutani, Jpn. J. Appl. Phys., Part 1 **42**, 4116 (2003).
[13] Y. Murakami, Y. Miyauchi, S. Chiashi, and S. Maruyama, Chem. Phys. Lett. **374**, 53 (2003).
[14] H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Adv. Mater. (Weinheim, Ger.) **11**, 605 (1999).