JNBT
ⓒ2006INBDK

JNBT, Vol 3, No 1, pp. 24-29

Carrier conversion in double wall carbon nanotube transistors induced by change in metal work function

Donghun Kang and Wanjun Park*

Nano Devices LAB Samsung Advanced Institute of Technology Mt. 14-1,
Neongseo-Ri, Giheung-Eup, Yongin City, Gyeonggi-Do, Korea 449-71

ABSTRACT

Complete carrier conversion from p- to n-type was observed in double wall carbon nanotube field effect transistors under different vacuum conditions. In atmosphere, holes are the majority carrier whereas electrons become the majority carrier as pressure decreases. It is believed that the carrier conversion is associated with the different band alignment at the interface between the CNT and Pd electrode. The variation of metal work function sufficiently rearranges the band alignment at the carbon nanotube/metal electrode in vacuum and results in carrier conversion from p- to n-type transport. Band gap of carbon nanotube is an important factor for carrier conversion.

Key words : carbon nanotube, electrical propertie

Introduction

In recent years, intensive studies have been carried out to demonstratepractical nanodevices using semiconducting single wall carbon nanotubes (SWCNT) as channels, taking advantage of their promising physical properties (1, 2). To realize practical electronic devices with CNT, control of carrier type is a critical issue to be resolved in the near future. In the microelectronics era, types of carrier were generally controlled by the incorporation of impurities in semiconductor lattices (3). For carbon nanotube (CNT) devices, many unconventional approaches have been attempted to control carrier types of CNT field effect transistor (FET), such as chemical bonding with polymers and reactive gases or insertion of molecules inside CNTs (4-6). Interestingly, a previous study (7) reported that carrier type can be controlled electrostatically by engineering the band alignment in source and drain (8, 9). The concept of electrostatic doping gives a new insight in understanding the transport behavior of CNT FETs. In this letter, we intentionally choose double wall carbon nanotube and Pd asa channel materials and electrodes, respectively, in order to investigate the influence of band alignment at the interface.

Experimental

A conventional back gate structure was chosen and heavily doped p-type silicon was used as an electrode underneath of thermally grown SiO_2 of 130 nm. A synthesized double wall CNT whose typical length was 2-3 μm in length were suspended in a solvent by ultra sonic agitation for one hour. A small amount of the suspension was dropped and spin-coated on thermally grown SiO_2 for 40 seconds with the speed of 5000 rpm. Scanning probe microscopy (SPM) was used to locate the position of the wires dispersed on the active area containing pre-fabricated electrodes. Bilayer of electron beam sensitive polymer resists (PMMA/Copolymer)

* Corresponding author :
Wanjun Park
Tel : +82-31-280-9305
Fax : +82-31-280-9308
E-mail : wanjun@samsung.com

spin-coated and baked at 170 °C for two minutes. After the pattern generation for metal contacts by an electron beam lithography on the polymer resist was performed, Pd metal electrodes (~100nm) were defined by a lift-off process in acetone for 24 hours. Electrical measurements were carried out in a probe station connected to an Agilent 4156C, followed by rinsing in flowing deionized water for couple minutes and blowing with nitrogen gas. The probe station chamber was equipped with a N_2 purge line and pumping unit, which could pump down the chamber to ~10^{-6} Torr.

Results and discussion

Fig 1(a), (b) and (c) represent images of CNT FET captured by scanning electron microscope (SEM) and transmission electron microscope, respectively. The length of the CNT was about 1 mm and the typical diameter is about 3-4 nm. Fig 2(a) - (e) shows a series of I_{ds}-V_g curves in different vacuum conditions where I_{ds} is the current flowing between source and drain and V_g is the bias applied to the gate. Applied voltage at the drain (V_{ds}) was varied from 2 mV to 10 mV in increments of 2 mV. The family of I_{ds}-V_g curves in ambient air shows p-channel characteristics with a significant amount of current at V_g=0 V. As the pressure of the chamber goes down to low 10^{-5} Torr, the p-channel current decreases by 40% to that of air, and finally disappears at 6 × 10^{-6} Torr with the emergence of a high electron current. At 6 × 10^{-6} Torr, electrons predominantly contribute to I_{ds} current with insignificant contribution from holes. This indicates that the ambient pressure change causes a remarkable impact in carrier transports of double walled CNT-FETs, as shown in Fig 2. It is notable that with only pressure variation complete conversion of the carrier type from p- to n-type without post treatments can be achieved. This fact manifests itself clearly with the comparison of I_{ds} current in Fig 2(a) and (d) at V_g = 4 V. Measured hole current in air was about 70 nA at V_{ds} = 10 mV in Fig 2(a) while 100 nA of electron current is detected in vacuum at the same V_{ds} without any hole current. Interestingly, the conversion is a reversible process, which can be supported by the recovery of hole current after re-exposure to ambient air, as shown in Fig 2(e). Similar carrier conversions are also observed in several DWCNT-FETs whose typical I_{ds}-V_{ds} results are shown in Fig 3(a) and (b). All devices show conversion from p- to n-type under air and vacuum. For comparison with DWCNT-FETs, SWCNT-FETs were fabricated in the same conditions and the results are plotted in Fig 4. The most crucial difference is that carrier conversions are not observed in the SW-CNTFET. A previous study on CNT-FET suggested

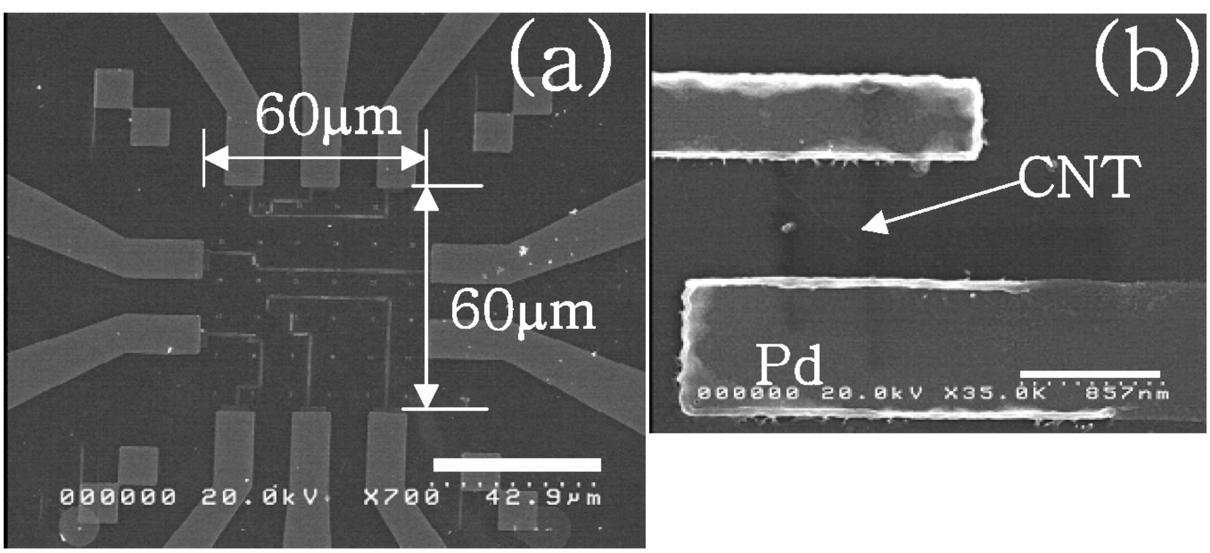

Fig 1. Scanning microscope electron images of double wall carbon nanotube transistors (a) and (b). Transistors are fabricated in 60 mm × 60 mm area by electron lithography. Pd was used for the electrodes.

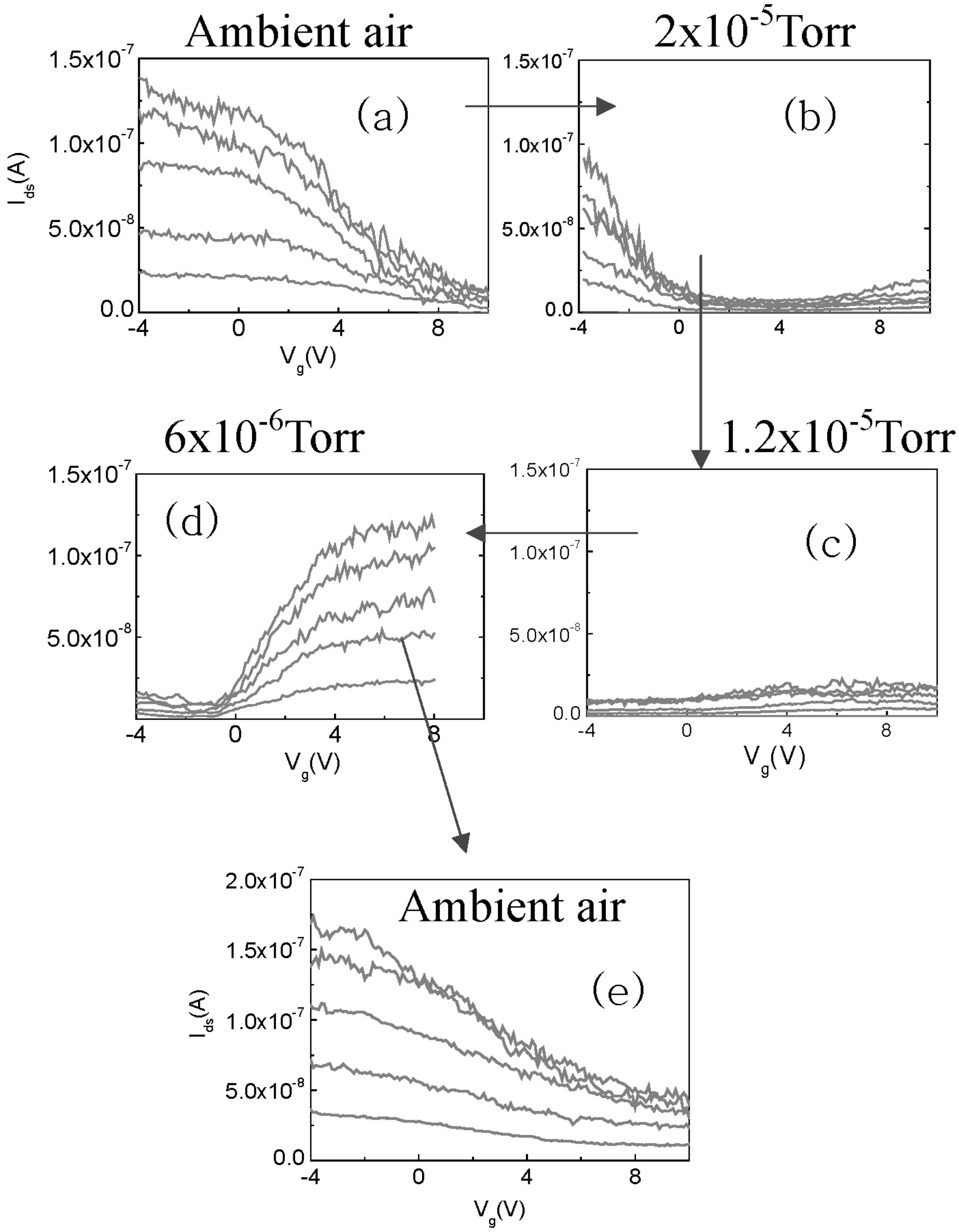

Fig 2. Evolution of I_{ds}-V_g curves at different vacuum pressure where V_{ds} varies from 2 to 10 mV. Carrier conversion from p- to n-type occurs at 1×10^{-6} Torr. The process of conversion is reversible with the pressure.

the variation of metal work function causes ambipolar transport in high vacuum (10) which means that two types of carriers exist at different gate bias.

However, the dramatic conversion of carrier type was not observed from the their work without thermal annealing of 200 °C in high vacuum (10). In addition, carrier conversion at certain gate bias (V_g = 4 V), which was discussed before in Fig 2(a) and (d) are not observed in their experiments.

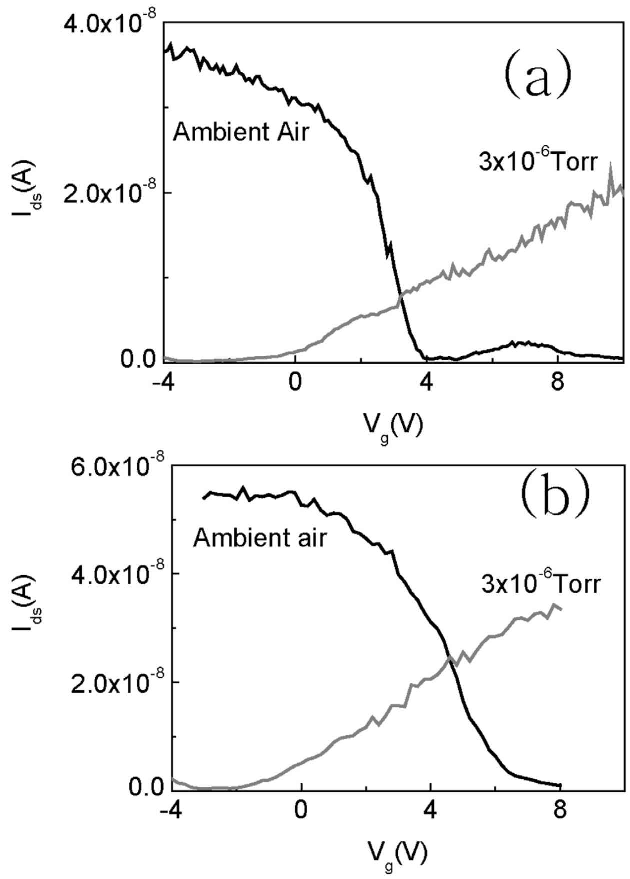

Fig 3. I_{ds}-V_g curves from different double wall CNT FETs at V_{ds} = 30 mV and 160 mV, respectively. All show the carrier conversion from p- to n-channel with the change in pressure.

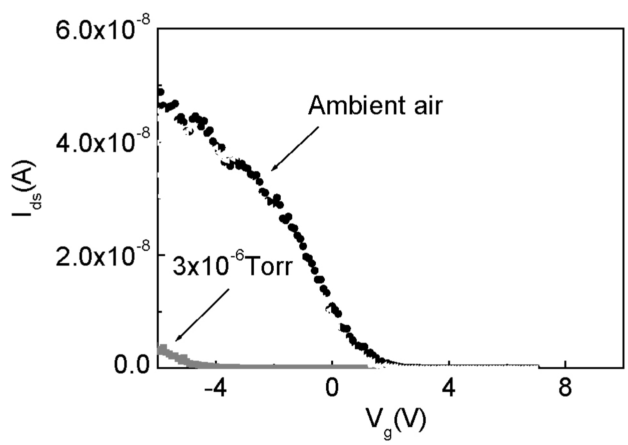

Fig 4. Ambient air effect on SWCNT-FET. The red dotted lines represent I_{ds}-V_g at 3 × 10^{-6} Torr and the black dotted shows I_{ds}-V_g in air.

We believe that this is the first observation of complete carrier conversion from p- to n-type in DWCNT-FETs without

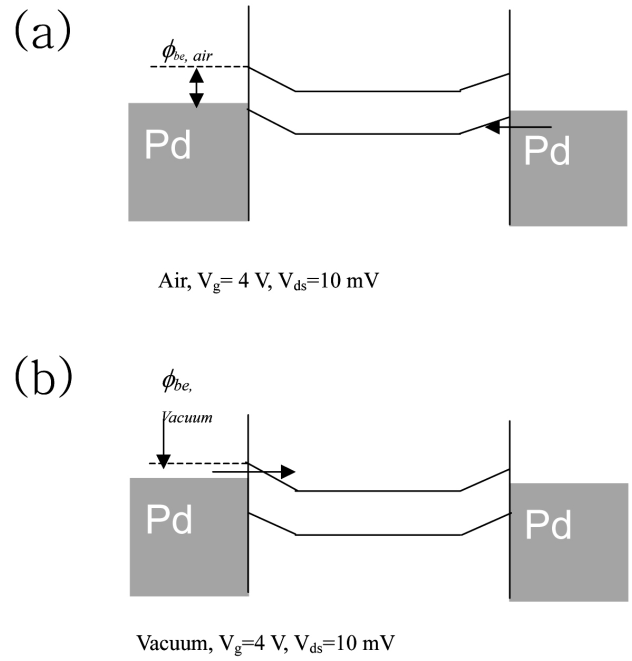

Fig 5. Schematic band diagrams show the band alignments for double wall CNT where (a) and (b) represents the band diagram in air and vacuum, respectively.

doping and vacuum annealing. This conversion may be associated with band alignment at the interface of the CNT and metal electrode. The expected band alignment for DWCNT was shown in Fig 5(a) and (b) which represent the alignment of DWCNT in air and vacuum. For the ambient air case, the barrier for hole transport is minimal due to the higher work function of Pd while the electron barrier is high enough to block electron current from the drain. At the high vacuum, the metal work function is reduced (1), providing a favorable situation for the flow of electron rather than that of hole. The explanations which discussed above can be understood by using a schottky barrier equation (11), $J \sim exp(-e\phi_{be}/kT)$, where ϕ_{be} means the electron barrier from metals and can be expressed by the difference between ϕ_{metal} and χ_{CNT}. ϕ_{metal}, χ_{CNT}, k and T are the metal work function, electron affinity of carbon nanotube, Boltzmann constant and temperature, respectively. Since ϕ_{be} varies with the pressure of measurement systems, it can be rewritten as the function of pressure, $\phi_{be}(p)$ = [$\phi_{Pd}(p)$ - χ_{CNT}], where $\phi_{Pd}(p)$ is palladium work function at a certain pressure, p. As shown in Fig 5(a), $\phi_{be}(p)$ in air is larger than that of vacuum (Fig 5(b)) and electrons undergoa higher barrier to flow. In contrast, holes feel a lower transport barrier in air, which provides a favorable condition for the hole current. As the pressures decreases, $\phi_{be}(p)$ becomes smaller coupled with the reduction in Pd work function, resulting in the band rearrangement at the interface. It affects the realignment with the shift-up of the Fermi level close to the conduction band of DWCNT. In fact, the possibility of carrier conversion can be predicted by the comparison of two parameters, $\Delta\phi_{be}(p)$ and E_g where $\Delta\phi_{be}$ p represents the difference between $\phi_{be}(p)$ in air and a certain pressure, p_1, that is $\Delta\phi_{be}(p)$ = $\phi_{be}(air)$ - $\phi_{be}(p_1)$. For the single-wall case, it seems that the amount of $\Delta\phi_{be}(p)$ is much smaller that its band gap (13), resulting in no conversion. This argument is well supported by the experimental results in Fig 4, where conversion was not observed. However, the story develops differently for DWCNT case due to its smaller band gap. The identical magnitude of $\Delta\phi_{be}(p)$, which did not cause the conversion on the SWCNT, can actually brings the conversion to DWCNT. It seems that a work function change of 0.3 eV (band gap of 3 nm CNT) can be considered meaningful for DWCNT which is a reasonably achievable number considering a previous work (13).

If work function varies continuously under different vacuum conditions, we should see a sequential change in I_{ds} current from holes to electrons along with an intermediate-stage as the pressure goes down. Interestingly, there is an intermediate stage where both carriers are not dominant, as shown in Fig 2(c). This is a direct evidence that the Pd Fermi level sweeps up with the variation of pressure, and at 1.2×10^{-5} Torr, aligns at the midgap of CNT, resulting in an almost flat I_{ds} current. The existence of the intermediate state supports the band alignment illustrated in Fig 5. Even though n-type conversion happens at vacuum, the implication of this result is that the control of carrier type can be achieved in ambient air by the proper combination of CNT and metal electrodes. Recently, n-type carrier transport was achieved by using Ca as a metal electrode, which is conceptually coherent with our experimental results of carrier conversion (9). This study suggests that the carrier type can be controlled by the choice of metals, hence different work function. Besides that, we suggest that the band gap of carbon nanotubeshould be considered as another crucial factor to control carrier type.

Summary and conclusion

Carrier conversion was observed in vacuum for double-wall carbon nanotube transistors with Pd electrodes. P-type carriers in air were completely converted to n-type in vacuum of 6×10^{-6} Torr without a annealing. The conversion was not observed in single-wall carbon nanotube devices, which were fabricated with the same conditions. It is believed that the dramatic change in carrier type is induced by the rearrangement of the Schottky barrier, which is determined by the small band gap of DWCNT and the work function change in Pd electrodes. Selecting the right metal electrode and band gap of CNT seems very crucial in controlling the carrier types.

Acknowledgement

This research project was partially supported by the Terra-level Nanodevices, Korean National Program. The authors thank Prof. C. J. Lee in Hanyang University, Prof. Kim and J.R. Kim in Chonbuk National University for their cooperation.

References

(1) Javey A, Guo J, Wang Q, Lundstrom M, Dai H (2003) Nature **424**, 654
(2) Avouris Ph, Appenzeller J (2004) The Industrial Physicist, June/July, 18
(3) Sze SM. (1981) Physics of Semiconductor Devices 2nd ed., New York, John Wiley & Sons 20
(4) Radosavljevic M, Appenzeller J, Avouris Ph, Knoch J (2004) Appl Phys Lett **84**, 3693
(5) Shim M, Javey A, Kam NWS, DaiH (2001) J Am Chem Soc. **123**, 11512
(6) Lu J, Nagase S, Yu D, Ye H, Han R, Gao Z, Zhang S, Peng L (2004) Phys Rev Lett **93**, 116804
(7) Lee U, Gipp PP, Heller CM (2004) Appl Phys Lett **85**, 145
(8) Javey A, Guo J, Farmer DB, Wang Q, Wang D, Gordon RG, Lundstruom M, Dai H (2004) Nano Lett **4**, 1319

(9) Mizutani T (2004) 1st Japan-Korea Symposium on Carbon nanotubes, Jesoo Island, Korea, pp 29
(10) Deryke V, Martel R, Appenzeller J, Avouris Ph (2003) Appl Phys Lett **80(15)**, 2773
(11) Neamen DA (2003)Semiconductor Physics and Devices 3rd ed., New York, MacGraw-Hill, pp 338
(12) Wildoer JWG, Venema LG, Rinzler AG, Smalley RE, Dekker C (1998) Nature **391**, 59
(13) Kandasamy K, Surplice NA (1980) J. Phys. C, Solid St. Phys **13**, 689

(Received Feb 15, 2006; Accepted March 22, 2006)