Air-Stable Chemical Doping of Carbon Nanotube Transistors

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Much progress has been made on carbon nanotube (CN) based transistors recently in terms of both fabrication and understanding of their performance limits[1,2]. Nevertheless, there are still key issues to be addressed for potential technological applications. In particular, there has been no efficient and process-compatible p-doping method for CN field effect transistors (CNFET). Unlike doping in CMOS processes, CNFET can not be doped substitutionally via ion implantation which immediately damages the CN lattice. A nanotube can be doped substitutionally, electrostatically, or via charge transfer. It's known that CNFETs fabricated from as-grown CNs on thick gate dielectric and under ambient conditions show p channel conduction due to oxygen interactions at the metal-CN interface[3]. However, the oxygen content at the metal-CN interface can be easily changed by standard fabrication processes (e.g., any post processing involving vacuum pumping such as thin film deposition). In fact, a p-CNFET can be easily converted to an ambipolar or N-CNFET via vacuum pumping[3]. P-doping of CN using gaseous NO_2 has been reported[4], but it requires the device to be kept under controlled environment to prevent dopant desorption. N channel conduction CNFET has been realized either by annealing/out-gassing oxygen at the contacts[3] or by doping with electron-donating alkali metals[3] or gases (NH_3)[4], both require controlled environment and degrade quickly upon exposure to air. To make CNFETs technologically viable, it is therefore crucial to find stable and consistent doping methods. Here we report for the first time a novel air-stable chemical p-doping scheme which, in addition to introducing tunability of the threshold voltage V_{th}, leads to improved device performance in both on- and off-states, increasing the drive current 2-3 orders of magnitude, transforming CNFET from ambipolar to unipolar, suppressing minority carrier injection and improving I_{off}, exhibiting excellent drain induced barrier lowering (DIBL)-like behavior.

We have fabricated CNFETs with palladium source and drain electrodes separated by 300 nm on top of 10 nm SiO_2 and Si backgate as shown in Fig. 1. We immerse the fabricated devices to a dilute solution (0.01 to 0.1 mg/mL) of triethyloxonium hexachloroantimonate $(C_2H_5)_3O^+SbCl_6^-$ in methylene chloride or dichlorobenzene for 12 hrs. It is a one-electron oxidant which is known to oxidize aromatic compounds and form charge transfer complexes[6]. Interaction of CN with this reagent results in the formation of charged (radical cation) moiety on CN (Fig. 2). Let **1** represent the benzene ring(s) on a CN, we describe the interaction as in (1). Excess dopant is then removed by rinsing with solvent.

$$2\,\mathbf{1} + 3\,[(C_2H_5)_3O^+SbCl_6^-] \longrightarrow 2\,[\,\mathbf{1}^{+\cdot}\,SbCl_6^-\,] + 3\,C_2H_5Cl + 3\,(C_2H_5)_2O + SbCl_3 \qquad (1)$$

A typical transfer characteristics (I_d *vs.* V_{gs}) at $V_{ds} = -0.5V$ of a CNFET before and after doping is shown in Fig. 3. We found: i). V_{th} for hole conduction increased from -1.55V (intrinsic CNFET) to -0.85V, indicative of electron transfer from the nanotube to $(C_2H_5)_3O^+SbCl_6^-$, moving the nanotube Fermi level E_F toward valence band, and V_{th} tuned to a technologically relevant gate bias range; ii). the drive current I_{on} improved by 2 orders of magnitude, greatly reducing contact resistance between tube and metal; iii). the characteristic transformed from the original ambipolar to pure p-conduction (unipolar). CNFETs are known to be Schottky barrier (SB) FETs, whose switching is dominated by the SBs formed at the metal/nanotube interface[7] and operate as p-type FETs in air[3]. As gate dielectric thickness scaled down, due to the quasi 1D-channel of the nanotube and the ultrathin CN body thickness, the SB can be thinned sufficiently to allow thermally-assisted tunneling of electrons or holes, and CNFETs operate as ambipolar FETs in air. The simultaneous injection of electrons and holes into CN channel and exponentially deteriorating I_{off} with an increasing drain field[8] is unacceptable in a scaled FET for potential logic gates applications. After doping, we successfully suppressed the minority carrier (electron current) injection at the drain and transformed the CNFET from ambipolar to unipolar, as clearly shown from Fig. 4, the I_d-V_{gs} characteristic at various V_{ds} (-0.1 to -0.5 at -0.1V step). The complete suppression of drain field induced minority carrier injection and excellent DIBL-like behavior by doping suggests possible stronger affinity/absorption of the dopants to the metal contact/tube interface, generating a non-uniform doping profile along the length of the tube. We propose that there are more dopants aggregating at the nanotube/metal interface causing strong band bending to suppress minority carrier (electron) injection at the off state. A decreased subthreshold swing $S=dV_{gs}/d(\log I_d)$ from 120 to 85 mV/decade (post doping *Id-Vg* shown in Fig. 4) shows improved switching and excellent gate control of the CN channel. Fig. 5 shows the output characteristics (I_d *vs.* V_{ds}) of a p-doped device. Its transconductance g_m (dI_d/dV_g) at $V_{ds} = -1.32V$ is *2uS*, outperfporming those of the best p-CNFET with small diameter CNs and the gate dielectric used. The above results are reproducible with 20 independent CNFETs and the devices are stable in air for weeks. These devices preserve their doping characteristics after solvent washing and vacuum pumping, and the absorption of dopants on devices is irreversible.

To realize air-stable N-doping of CNs, we use amine-rich electron-donating polyethyleneimine (PEI). Its use was first reported by Shim et al.[8], however, their devices were built on thick gate dielectric and did not scale properly. Interestingly, we observed similar device performance improvement among the PEI-doped CNFETs. Fig. 6 shows a transfer characteristics at $V_{ds}=0.5V$ of a CNFET before and after PEI doping. Comparing the electron current branch, we notice: i). V_{th} decreased from the intrinsic 1.25V to 0.6V, ii). I_{on} improved by 3 orders of magnitude, iii). the minority carrier (hole current) injection was suppressed, improving I_{off}. The highest g_m measured among PEI-doped devices at a very moderate V_{ds} of *0.5V* is 220nS, almost 2 orders of magnitude higher than reported previously[9] (4nS).

In conclusion, we have successfully demonstrated for the first time air-stable chemical p-doping of CNFET via charge transfer; introduced tunability of the V_{th}, transformed scaled CNFETs from ambipolar to unipolar, improved I_{on} by 2-3 orders of magnitude, suppressed minority carrier injection (immunity from drain induced I_{off} degradation from intrinsic SB CNFET), yielding an excellent I_{on}/I_{off} ratio of 10^6, and demonstrated excellent DIBL-like behavior. The authors thank P. Solomon and J. Appenzeller for stimulating and insightful discussions, and B. Ek for expert technical assistance.

[1] A. Javey et al., Nat. Mater. **1**, 241 (2002);
A. Javet et al., Nature **424**, 654 (2003).
[2] S. J. Wind et al., Appl. Phys. Lett. **80**, 3817 (2002).
[3] V. Derycke et al., Appl. Phys. Lett. **80**, 2773 (2002).
[4] J. Kong et al., Science **287**, 622 (2000).
[5] M. Bockrath et al., Phys. Rev. B **61**, 10606(R) (2000).
[6] R. Rathore et al., J. Org. Chem. **63**, 5847 (1998).
[7] J. Appenzeller et al.,Phys. Rev. Lett. **89**,126801 (2002).
[8] M. Radosavljevic et al., Appl. Phys. Lett. **83**, 2435 (2003).
[9] M. Shim et al., J. Am. Chem. Soc. **123** 11512 (2001).

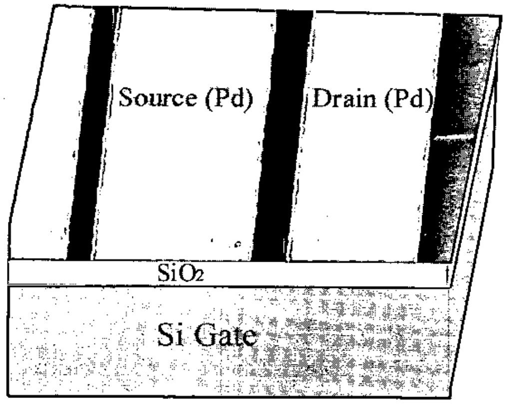

Fig. 1. Schematics of a CNFET on 10nm SiO_2 using Si backgate, overlayed by a SEM image of a CN under Pd contacts.

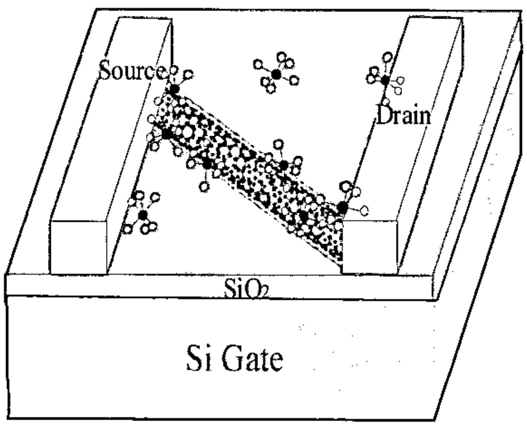

Fig. 2. Schematics of a doped CNFET, with $SbCl_6^-$ as counter ion.

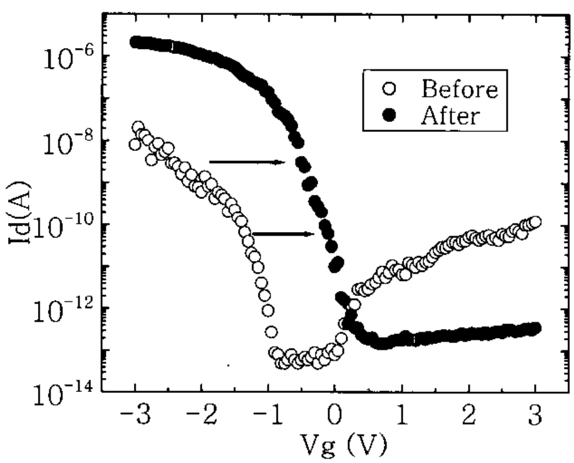

Fig. 3. Transfer characteristics of a CNFET before and after p-doping at $V_{ds} = -0.5\ V$

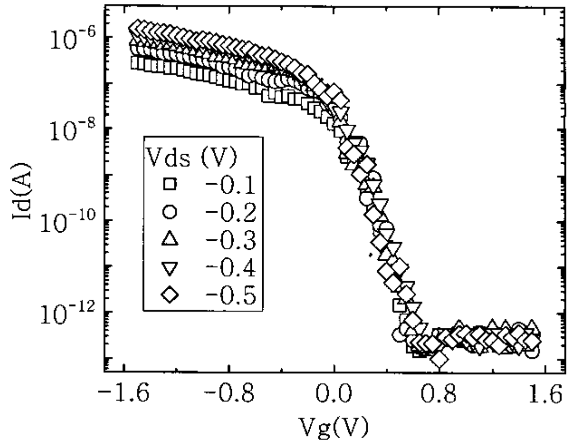

Fig. 4. Id-Vg of a p-doped CNFET under different Vds (-0.1V to -0.5V @ -0.1V step), with S= 85mV/dec.

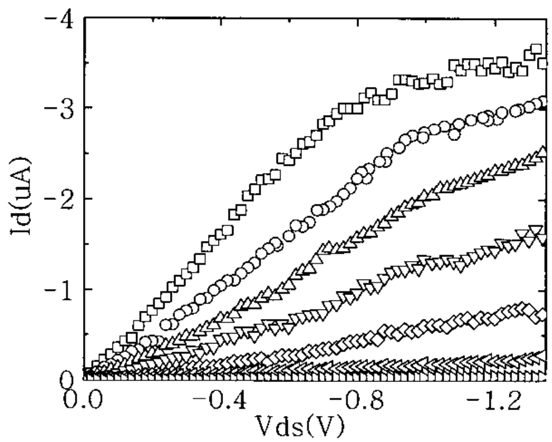

Fig. 5. Output characteristics of a CNFET after p-doping with V_{gs} from -3 to –1.2 V at a step of 0.3V.

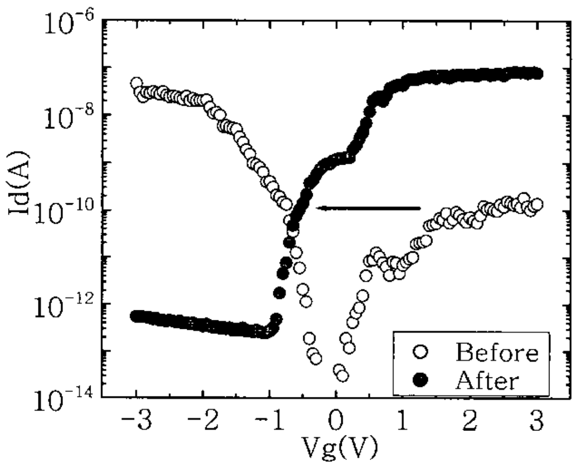

Fig. 6. Transfer characteristics of a CNFET before and after n-doping with $V_{ds} = 0.5V$.