Self-aligned Carbon Nanotube Transistors with Novel Chemical Doping

Jia Chen, Christian Klinke, Ali Afzali, Kevin Chan, Phaedon Avouris
IBM T. J. Watson Research Center, Yorktown Heights, NY 10598

ABSTRACT

We report an unconventional chemical p- and n- doping scheme utilizing novel materials and a charge transfer mechanism to obtain air-stable, self-aligned, unipolar carbon nanotube transistors. This scheme in addition to introducing the tunability of the threshold voltage $V_{th}$ increases the drive current 2-3 orders of magnitude, transforms CNFET from ambipolar to unipolar, suppresses minority carrier injection and yields an excellent $I_{on}/I_{off}$ ratio of $10^6$.

INTRODUCTION

Much progress has been made on carbon nanotube (CN) based field effect transistors (FET) recently, in terms of both fabrication and understanding of their performance limits [1-3]. Nevertheless, there are still key issues to be addressed. In particular: 1) There has been no process-compatible doping method for CNs. Conventional Si substitutional doping (e.g., by ion implantation) destroys the CN lattices. Current methods to obtain p- or n- CNFETs suffer from severe process-limitations, e.g., a p-CNFET can be easily converted to an ambipolar or a n-FET under any fabrication processes involving vacuum pumping (through the change of the oxygen content at the metal-CN interface) [4]. Efforts utilizing alkali metals [4] or gas-phase (NH$_3$) [5] doping to obtain n-CNFETs require controlled environment to prevent dopant desorption and devices degrade quickly upon exposure to air. 2) Performance-wise, the Schottky barriers (SB) formed between the CN and the source/drain metal contacts lead to large subthreshold swing $S$ ($dV_{gs}/d(logI_d)$), and to strong ambipolar conduction when the transistor is scaled down vertically. The resulting SB-limited drive current ($I_{on}$), slow switching, and exponentially deteriorating $I_{on}$ with an increasing drain field [6] is unacceptable for logic gates applications. To make CNFETs technologically viable, it is therefore crucial to find novel doping methods/materials that are both process-stable and meet the performance challenges. Here we report on an unconventional chemical p- and n- doping scheme utilizing novel materials and a charge transfer mechanism to obtain self-aligned, air-stable and unipolar CNFETs. We demonstrate an ability to change carrier injection properties; to tune $V_{th}$, and to improve device performance in both ON- and OFF-states.

EXPERIMENT

A. p-DOPING

Fig. 1. Schematics of a CNFET on 10nm SiO$_2$ using Si backgate, overlaid by a SEM image of a CN under Pd contacts.

The fabricated devices were then immersed in a 1mg/mL solution of triethyloxonium hexachloroantimonate (OA) ($C_2H_5)_3O^-SnCl$_6$$^2$- in dichlorobenzene. OA is a one-electron oxidant whose interaction with CN leads to hole injection in CN [7]. Let $\alpha$ represent the benzene ring(s) on a CN. We describe the interaction as:

$$2\alpha + 3\text{OA} \rightarrow 2[\alpha^{+} \cdot \text{SnCl}_6^{2-}] + \text{volatile products.}$$

We have fabricated CNFETs with 1.4nm diameter laser ablation CNs, palladium source and drain electrodes separated by 300 nm, 10 nm gate oxide and a Si backgate as shown in Fig. 1.

Fig. 1. Schematics of a CNFET on 10nm SiO$_2$ using Si backgate, overlaid by a SEM image of a CN under Pd contacts.

We found: i) $V_{ph}$ for hole conduction increased from intrinsic -0.6V to -0.35V, indicative of electron transfer from the CN...
Fig. 2b. Transfer characteristics of the above CNFET after p-doping under various $V_d$ (-0.1 to -0.6V @ -0.1V step), with $S$ -85mV/dec.

to OA, moving the CN $E_F$ toward valence band, and $V_{th}$ tuned to a technologically relevant gate bias range; ii) $I_m$ increased by 2 orders of magnitude, greatly reducing CN-metal contact resistance; iii) $S$ decreased from 200 to 85 mV/decade, showing improved switching and SB reduction; iv) the minority carrier (electron current) injection at the drain was successfully suppressed after doping and the transistor characteristics transformed from ambipolar to unipolar, as is clearly shown in Fig. 2b. To further understand the dopant-CN interaction, we selectively doped CNFETs in a section of the channel (Fig. 3a) and at the vicinity of the contacts (Fig. 3b). Negative ebeam resist Hydrogen silsesquioxane (HSQ) was used to mask 50nm at the CN-source(drain) interfaces for channel doping and 200nm of the channel for contacts doping, respectively. The transfer characteristics before and after selective doping (channel vs. contacts) are shown in Fig. 4 and Fig. 5. Table I compares the key device characteristics post selective doping. In the case of contacts doping, the simultaneous increase of $I_m$ and decrease of $S$ imply SB height reduction, which in turn reduces $V_{th}$. When only the central section of the FET channel is doped, there is insignificant change in both $I_m$ and $S$, and thus the SB is not significantly affected. The $V_{th}$ shift reflects a long 1-D carrier depletion length. When both the contacts and the channel are doped, $V_{th}$ is further reduced via bulk doping where the carrier concentration in the tube is increased and $E_F$ shifted toward the valence band. Both the SB lowering and the

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**Table 1. Comparison of major device characteristics with selectively doped CNFETs.**

<table>
<thead>
<tr>
<th>Doping Scheme</th>
<th>$\Delta V_{th}$</th>
<th>$I_m$</th>
<th>$S$</th>
<th>$\Phi_{SB}$</th>
<th>Carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully Doped</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Contacts Doped</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Channel Doped</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

- ✓ means significant change.
- - means insignificant change.
suppression of minority carrier injection (Fig. 2b) after doping can be understood in terms of the modification of workfunction of the source and drain electrodes. When the OA molecules interact with the electrodes, charge transfer takes place and the stable counter-ions, SbCl₄⁻, remain at the surface of the metal electrodes. They generate an outwards directed surface dipole that reinforces the intrinsic surface dipole thus raising the metal workfunctions. An increased workfunction favors hole injection at one electrode (high \( I_m \) and low \( S \)), while it suppresses electron injection at the other electrode. In fact, modification at the metal-CN interface band lineup (SB) due to local variation of substrate work function induced by oxygen adsorption has been observed directly in electrostatic force microscopy and Kelvin probe experiments [8].

When one increases doping concentration, a p-CNFET can be converted to an almost metallic tube (Fig. 6). In this case, the SBs are ultimately minimized so the transport through the CNTFET is not limited by the contacts rather by the bulk of the tube, as in a conventional MOSFET. To test the efficiency of doping, a top-gated device with self-aligned 'extension-like' OA doping was realized by covering the CN and source/drain electrodes with 12 nm low temperature oxide (LTO) [3] and ebeam patterned tungsten (W) gates (insets of Fig. 7). To reduce the electrostatic coupling from the bottom gate, the top-gated devices were fabricated on a 100nm oxide substrate. The source/drain separation is 2um and the top-gated region is 1.66um with 170nm on each side for 'extension'-doping where the LTO was etched by diluted HF using the top W-gate as the etch mask. Fig. 7 shows the transfer characteristics before and after OA doping. The transistor was completely off due to the ungated regions before doping; afterwards, p-type characteristic with a \( V_{th} \) of -0.2V, a sharp \( S \) of 69 mV/dec, and an excellent \( I_{on}/I_{off} \) ratio of \( 10^6 \) was obtained. This is the first realization of a self-aligned top-gated CNFET utilizing novel chemical doping.

B. n-DOPING

To realize air-stable n-doping of CNs, we introduced a novel amine-containing compound (different from ref. 10) and we observed similar device performance improvement in the doped CNFETs. Fig. 8 shows a transfer characteristics at \( V_d=0.5V \) of a CNFET before and after doping.

We have: i) successfully converted a p- to a n-CNFET; ii). improved \( I_m \) by 3 orders of magnitude; iii). suppressed the minority carrier (hole current) injection; iv) obtained the sharpest \( S \) (87 mV/dec) among n-doped devices (compared with both K-doping [9] and using Al as source/drain contacts [2]). The \( V_{th} \) dependence shown in Fig.9 exhibits excellent DIBL-like behavior. Chemical doping allows us to tune the device \( V_{th} \) by varying the doping concentration, and to obtain enhancement as well as depletion mode transistors. Shown in Fig.10 are the transfer characteristics of an enhancement mode CNFET after polyethyleneimine (PEI) [10] doping and
the inset shows a depletion mode n-CNFET post stronger PEI doping where the estimated linear electron doping density is 0.5e/nnm (corresponding to a bulk doping density of 10^{20}/cm^3), which is similar to the extension doping concentration of current CMOS FETs. In addition to the analogous characteristics improvement, we obtained a transconductance almost 2 orders of magnitude higher than reported previously [10].

CONCLUSIONS

In summary, we have successfully introduced novel materials for stable chemical p- and n-doping of CNFETs via charge transfer; realized for the first time a self-aligned CNFET with chemical doping; introduced tunability of the $V_{th}$; transformed scaled CNFETs from ambipolar to unipolar; improved $I_{on}$ by 2-3 orders of magnitude; and yielded an excellent $I_{on}/I_{off}$ ratio of $10^6$.

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REFERENCES


Fig. 9. Transfer characteristicsof a CNFET after n-doping at $V_{g}=0.1$ to 0.5V @ 0.1V step.

Fig. 10. Transfer characteristicsof a CNFET after PEI-doping at $V_{g}=0.5V$ which converted a p-type to a n-type CNFET. The inset shows a depletion mode CNFET after stronger PEI doping.