Charge Transferred Doping and Electroluminescence in Carbon Nanotube Transistors

Jia Chen, Marcus Freitag, Christian Klinke, Ali Afzali, James Tsang and Phaedon Avouris

IBM T. J. Watson Research Center, NY, 10598, USA

Abstract — We report an unconventional chemical p- and n- doping scheme utilizing novel materials and a charge transfer mechanism to obtain self-aligned, unipolar, stable carbon nanotube field effect transistor (CNTFET). This scheme introduces the tunability of the threshold voltage V_{th}, increases the drive current 2-3 orders of magnitude, transforms CNTFETs from ambipolar to unipolar, suppresses minority carrier injection and yields an excellent I_{on}/I_{off} ratio of 10^6. We utilize the ambipolar conduction in CNTFETs for optoelectronic applications, and demonstrate spatially-resolved electron-hole recombination in long channel transistors. This allows us to probe the carrier transport processes under varying bias conditions in nanotubes, determine the recombination lengths and recombination times, observe defects, etc.

Index Terms — Nanotechnology, carbon nanotube field effect transistors, charge transfer doping, Schottky Barrier, 1-D channel, electroluminescence, hot carriers, electron-hole recombination.

I. INTRODUCTION

Significant progress has been made recently on carbon nanotube based field effect transistors (CNTFET), in terms of understanding both their scaling and performance limits [1]. However, the Schottky barriers (**SB**) formed between the CNT and the source/drain metal contacts lead to contacts-dominated switching, resulting in low drive current, undesirable subthreshold characteristics, and strong ambipolar conduction when the transistor is scaled down vertically [2], all unacceptable in logic applications. Here we report on chemical doping schemes utilizing molecules and a charge transfer mechanism to obtain self-aligned, stable and unipolar CNTFETs to meet the performance challenges. We demonstrate an ability to change carrier injection properties; and to improve device performance in both **ON**- and **OFF**- transistor states. In particular, oxidizing and redox-active molecules are introduced to modify the work-function of the source and drain electrodes of CNTFETs and, correspondingly, of their **SB**s. We demonstrate successful ambipolar-to-unipolar conversion and p-to-n polarity switching of CNTFETs.

II. CHARGE TRANSFERRED DOPING

A. p-doping

We have utilized triethyloxonium hexachloroantimonate (**OA**) $(C_2H_5)_3O^+SbCl_6^-$ to dope both the channel and the contacts of a CNTFET. **OA** is a one-electron oxidant whose interaction with CNT leads to hole injection in the tube. CNTFETs were fabricated using laser ablation CNTs, pladium source and drain electrodes separated by 300 nm on top of 10 nm SiO_2, and a Si back-gate. Doping was carried out by immersing the devices in a 1mg/mL solution of **OA** in dichlorobenzene.
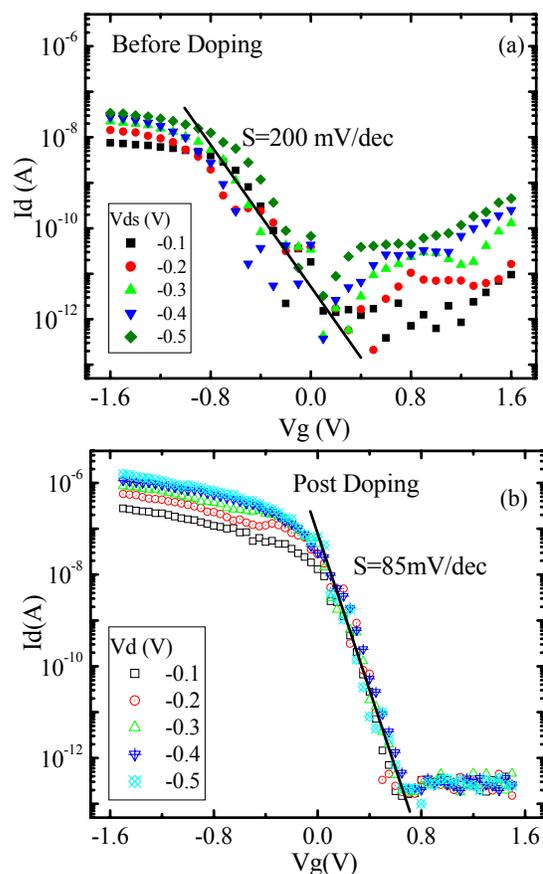

Fig. 1 Transfer characteristics of a CNTFET before (a) and after (b) **OA** doping under various V_{ds} (-0.1 to -0.5V @ -0.1V step).

Typical transfer characteristics before and after doping (Fig. 1a and 1b, respectively) shows the V_{th} for hole conduction increased from -0.8V to 0.05V; the I_{on}, at constant overdrive, increased by about two orders of magnitude; the subthreshold swing $S=dV_g/d(logI_d)$ decreased from 200mV/dec to 85mV/dec; the minority carrier (electron current) injection at the drain successfully suppressed after doping and the transistor characteristics transformed from ambipolar to unipolar. Further study of selective doping of CNTFETs in the channel of the transistors and at the vicinity of the contacts indicated that doping in the channel contributed to increase of carrier density in the bulk of the tube, while doping at the contacts resulted in the modification of the work-function of the source and drain electrodes and, correspondingly, of their **SB**s. The modification of work-function involves the adsorption of the $SbCl_6^-$ counter ions, which, with the induced image charge in the source/drain metal, produce an outward-directed dipole that increases local work-function. This increase favors hole injection at one electrode, while suppressing electron injection at the other. The important role of the **SB**s can be seen in Fig. 1 which shows the improvement of the **ON**- and **OFF**- state characteristics of a CNTFET upon doping with **OA**.

B. Self-aligned Chemical Doping

When one increases the doping concentration, a p-CNTFET can be converted to an almost metallic tube. In this case, the **SB**s 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 FET.
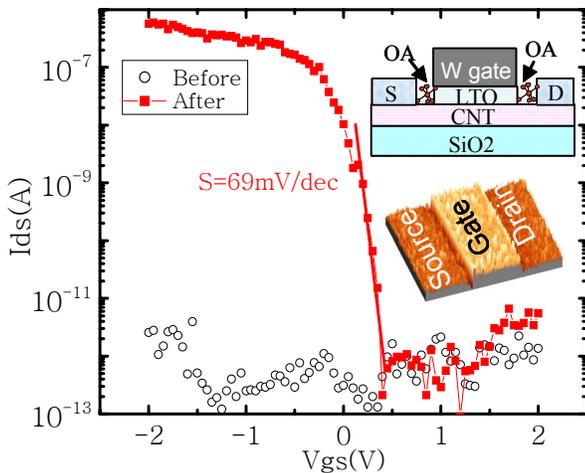

Fig. 2 Transfer characteristics of a W-top-gated CNTFET before and after **OA**-doping at V_{ds}= -0.5V. S is 69mV/dec post doping. The inset shows a schematics and a SEM picture of the device.

Fig. 2 shows a top-gated device with self-aligned 'extension-like' **OA** doping, realized by covering part of the channel of the CNT with oxide and an e-beam patterned tungsten (W) gate, leaving both the source/drain metals and the channel area close to the contacts un-gated and accessible for dopants (insets of Fig. 2). Before doping, the transistor was completely off due to the large **SB**s and lack of carriers in the un-gated regions; after doping, **OA** molecules modified the **SB**s at the contacts and increased carrier density on the un-gated section of the tube. The transistor was turned on as a p-FET 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. This is the first realization of a self-aligned top-gated CNTFET utilizing novel chemical doping [3].

C. n-Doping

To realize stable n-doping of CNTs, we introduced amine-containing hydrazine and observed similar device performance improvement in the doped CNTFETs. Fabricated samples were doped in a 3 M solution of hydrazine (N_2H_4) in acetonitrile. We show in Fig. 3 the successful conversion of a p-CNTFET to n-type after doping, where we improved I_{on} by 3 orders of magnitude; suppressed the minority carrier (hole current) injection; and obtained the sharpest S (87 mV/dec) among n-doped devices.
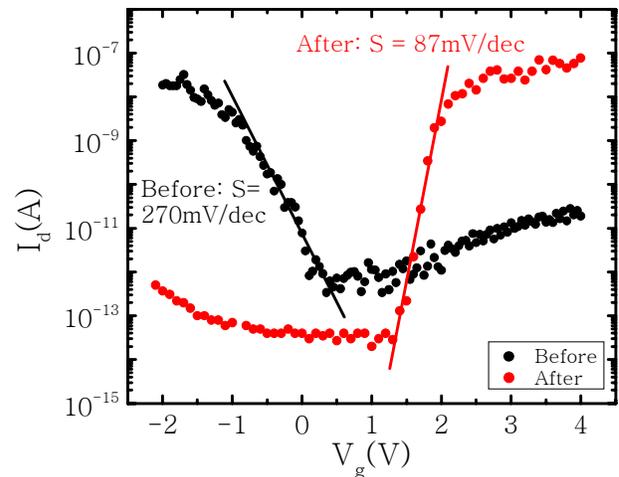

Fig. 3 Transfer characteristics of a CNTFET before and after hydrazine-doping at V_{ds}=0.5V. S improved from the original 270 to 87 mV/dec after doping.

D. Polarity Switching

Using redox chemistry, it is possible to manipulate charge transfer and switch between the *p*- and *n*- polarities of a CNTFET in addition to straightforward doping. By accessing different oxidation states of polyaniline (PANI)

and controlling its charge donating/accepting ability, we can effectively switch a *p*-CNTFET to *n*- type and *vice versa* [4]. PANI has three distinct oxidation states: the electron-accepting oxidized state, the electron-donating reduced state, and the partially oxidized and partially reduced state (**P**). In Fig. 4, we show that an originally undoped CNTFET (shown by the black curve) was converted from *p*- to *n*- type (red curve) after we decorated the device with the reduced PANI form by heating the **P** form in N-methylpyrrolidinone (NMP) at 160°C for 2 h in N_2. This *p* to *n* conversion after doping is consistent with the hydrazine doping result where the electron lone pair in the amine group donates electrons to CNTFETs and, in addition, modifies the metal-tube interface band line-up. By immersing the same device in a 1% solution of tetrachloro-1,4-benzoquinone (TCBQ) in 4:1 acetonitrile/dimethylacetamide at 80°C for 30 min, we form the oxidized form of PANI. The transfer characteristic after the oxidation process is shown by the blue curve in Fig. 4, where the CNTFET was successfully converted from *n*- back to *p*-type. Therefore, by modifying the oxidation state of PANI from the reduced state to the oxidized state, we have demonstrated a polarity switching of a CNTFET from *p*- to *n*- then back to *p*-type.
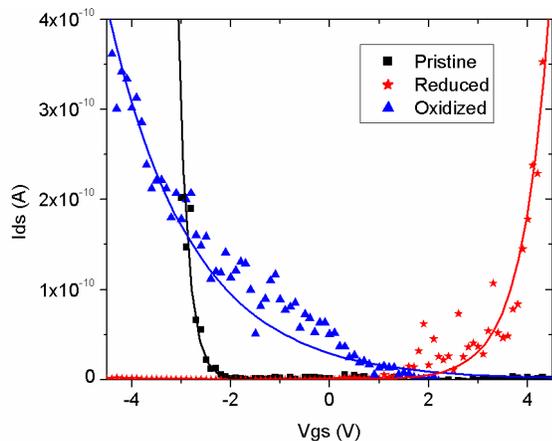

Fig. 4 Transfer characteristics of a CNTFET after reduced PANI doping at V_{ds} = 0.5V, which converted the CNTFET from *p*-type to *n*-type and back to *p*-type after oxidized PANI doping of the same nanotube transistor. The solid lines are meant as guides to the eyes.

III. ELECTROLUMINESCENCE

Using ambipolar CNTFETs with appropriate biasing we can inject electrons and holes simultaneously from the source and drain of the nanotube. CNTs being direct band gap 1D semiconducting material, it allows us to observe radiative e-h recombination from individual nanotube channels in their 3-terminal transistor configuration [5].

A. Hot Carrier Electroluminescence

Fig. 5 shows electroluminescence spectra from two individual CNTFETs with different channel lengths [6]. The long channel device (L≥5µm) gives narrow, symmetric peak, while the short channel (~300nm) device gives broad, asymmetric spectrum. This distribution is determined by the carrier transit time in the CNT and the phonon scattering rates. In long CNTs, electroluminescence involves relaxed carriers since the transit time of around 60ps is long compared to both the optical phonon scattering times of 20fs and the acoustical phonon scattering rate of 400fs. In short CNTs, however, the carrier transit time of 600fs does not permit the thermalization of the injected carrier distribution below the energy of the optical phonons (~180meV). Thus we have shown that the emission line-shapes reflect the carrier energy distribution in the channel of the CNTFET.
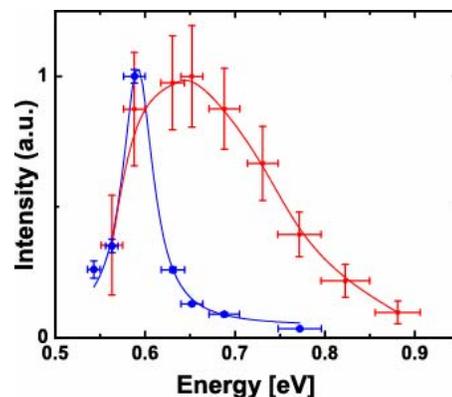

Fig. 5 Electroluminescence spectra from two single-nanotube CNTFETs. The narrow width spectrum arises from a long nanotube (>5µm), while the broad emission is obtained with a short (~300nm) nanotube.

B. Spatially-resolved Electroluminescence

CNTFETs provide a novel form of molecular light source that requires neither external doping nor well defined space charge region as in conventional LEDs. We find that most of the electroluminescence is confined to a small segment of the carbon nanotube that can be controllably positioned by varying the gate voltage, unique to 1D devices. CNTFETs being three-terminal devices allow the modulation of not only the intensity of electroluminescence, but also the position along the length of the CNT from which the emission originates [7]. Fig. 6 shows an IR image of the source and drain electrodes bridged by a long CNT (not visible). Degenerately-doped

Si wafer was used as the back-gate. Superimposed on this image we show the emission spots from e-h recombination as the gate voltage is scanned at a constant drain current. We show that the recombination region can be moved over tens of microns in long CNTs by varying the gate potential. As we reduce the gate voltage (subsequently increasing the drain voltage to maintain constant current), the light near the drain first become stronger because more minority carriers (electrons) are injected with the increasing of the drain field, until before frame 2, the emitting spot that marks the ambipolar region in the device, leaves the drain contact region and moves into the nanotube channel. Between frames 2 and 3, the gate voltage moves the ambipolar region along the length of the tube. After the spot reaches the source contact (frame 4), the infrared emission is gradually diminished, as the hole current becomes the new minority carrier current and decreases.
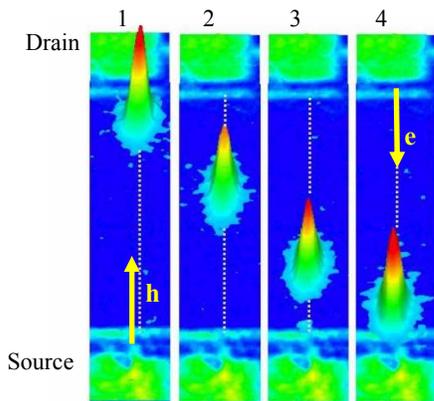

Fig. 6 Controlling the position of the e-h recombination along the channel of a 50μm-long CNTFET by varying the gate voltage under constant drain current conditions.

We quantify the spatial extent of the recombination region (i.e. the light source), by de-convoluting intensity profiles along and perpendicular to the direction of the CNT. A recombination length on the order of μm was obtained. Fig. 7a shows drain current as a function of drain bias at V_g = -5V. One notice that on the reverse sweep (blue curve), when the total drain current remained the same (V_d between -28V and -12V), the light intensity decays exponentially with the decrease of the drain field (Fig. 7b). Assuming proportionality between photon count and minority carrier current, the light emission is a measure of the **SB** transparency. The exponential decay of the light intensity is in agreement with the predicted exponential behavior of the leakage current in the off state of an ambipolar CNTFET [2].
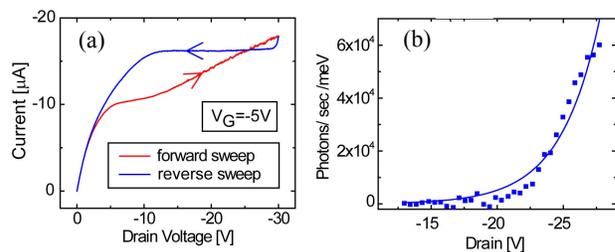

FIG. 7 (a) I_d-V_d scan at V_g=-5V. (b) IR intensity vs. drain voltage during the reverse sweep. The solid line is an exponential fit.

Such experiments provide new insights into the electronic processes in CNTs. They allow us to monitor carrier transport under varying bias conditions, determine the recombination lengths and recombination times, observe defects, etc.

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