

Semiconductor-enriched single wall carbon nanotube networks applied to field effect transistors

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Substantial progress on field effect transistors (FETs) consisting of semiconducting single wall carbon nanotubes (s-SWNTs) without detectable traces of metallic nanotubes and impurities is reported. Nearly perfect removal of metallic nanotubes is confirmed by optical absorption, Raman measurements, and electrical measurements. This outstanding result was made possible in particular by ultracentrifugation (150 000 g) of solutions prepared from SWNT powders using polyfluorene as an extracting agent in toluene. Such s-SWNTs processable solutions were applied to realize FET, embodying randomly or preferentially oriented nanotube networks prepared by spin coating or dielectrophoresis. Devices exhibit stable *p*-type semiconductor behavior in air with very promising characteristics. The on-off current ratio is 10^5 , the on-current level is around $10 \mu\text{A}$, and the estimated hole mobility is larger than $2 \text{ cm}^2/\text{V s}$. © 2008 American Institute of Physics. [DOI: 10.1063/1.2939560]

Semiconductor materials for field effect transistors (FETs) and thin-film transistors (TFTs) are highly demanded.¹ In particular, semiconducting single wall carbon nanotubes (s-SWNTs) are very promising, because individual s-SWNTs are known to exhibit high on-off current ratio, high electron/hole mobilities, to carry high current density and to operate at high frequencies.²⁻⁴ Several groups have demonstrated excellent transfer characteristics using individual s-SWNTs, but generally poor ones using ensembles (networks and thin films) of SWNTs due to traces of metallic nanotubes (m-SWNTs) and impurities (catalytic and amorphous particles).⁵⁻¹⁰ Therefore, efficient methods to selectively synthesize s-SWNTs or to selectively extract s-SWNTs from as-grown nanotubes are still in great need.

In recent years, several approaches to extract s-SWNTs from nanotube powders have been explored using for instance chemical functionalization, DNA, polymers wrapping, and density gradient ultracentrifugation techniques.^{5,7,11-13} The latter efficiently separates s-SWNTs and m-SWNTs, but traces of surfactant and density gradient materials may limit the performances of the FET. Very recently, two groups have reported on the selective extraction of near-armchair s-SWNTs from nanotube powders using polyfluorene as an extracting agent.^{14,15} According to Nish *et al.*,¹⁴ the sample shows no detectable traces of m-SWNTs. However, it was based only on optical spectroscopy, and neither the electrical properties nor the fabrication of FET devices were addressed.

In this letter, we report on the electronic properties of FETs consisting of semiconductor-enriched SWNTs without detectable traces of m-SWNTs and impurities. This unprecedented achievement is made possible by ultracentrifugation (150 000 g), sonication, and filtration of solutions prepared from SWNT powders using polyfluorene as an extracting agent in toluene. Evidence for the removal of m-SWNTs is provided by optical absorption, Raman measurements, and electrical measurements (see Fig. 1). We shall demonstrate

that such s-SWNTs realize high-performance FET devices.

The s-SWNTs solutions were prepared as follows. First, SWNTs powders (as-prepared HiPco, Carbon Nanotechnologies Inc.), Poly-9,9-di-n-octyl-fluorenyl-2,7-diyl (PFO) (Sigma-Aldrich) and toluene were mixed in the following ratio SWNT (5 mg): PFO (5 mg): toluene (30 ml) and ho-

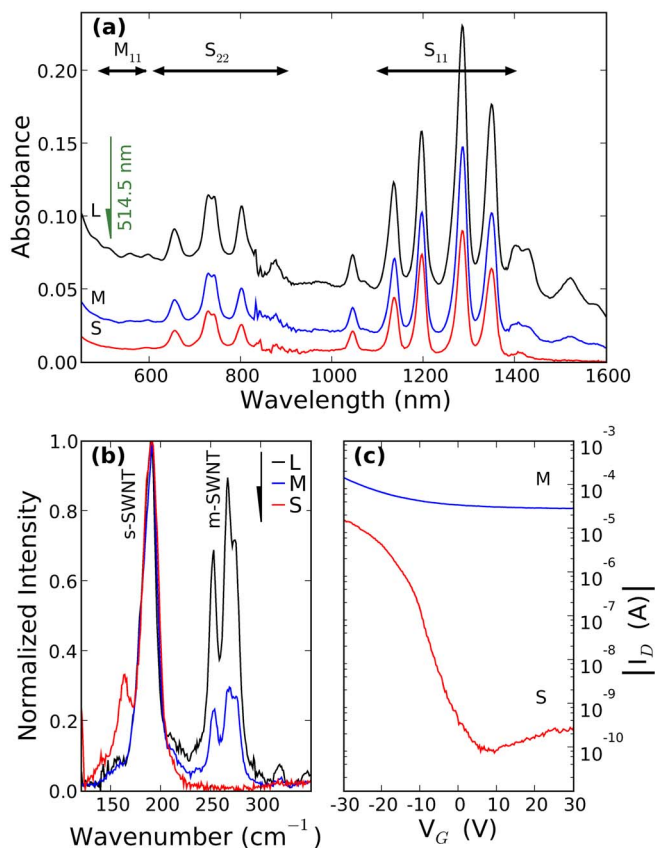


FIG. 1. (Color online) (a) shows the optical absorption spectra and (b) the Raman spectra at 514.5 nm of L, M, and S samples. The centrifugation conditions are improved in the following sequence: L, M, and S. (c) displays I_D vs V_G for $V_{DS} = -14 \text{ V}$ of FET devices made from samples M and S.

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mogenized by sonication (for 1 h using a water-bath sonicator and 5 min using a tip sonicator). Then, this mixture was centrifugated for 5–60 min using either a desktop centrifuge (angle rotor type, 10 000 g) or an ultracentrifuge (swing rotor type, 150 000 g). Next, the upper 80% of the supernatant solution was collected. To recover only SWNTs while washing out PFO, the supernatant solution was filtered through a 0.1 μm Teflon filter and rinsed with toluene several times (until the characteristic optical absorption band of PFO at 385 nm completely disappears from the filtrate). Finally, this filter was soaked in an organic solvent [such as toluene or N-methyl-2-pyrrolidone (NMP)] and subjected to mild sonication, yielding semiconductor-enriched SWNT solutions with minimal PFO residue. We shall focus on three types of SWNTs solutions centrifugated at 10 000 g for 15 min (labeled L), 150 000 g for 30 min (labeled M), and 150 000 g for 60 min (labeled S), with all the other processing parameters identical. These samples were characterized by optical absorption, Raman, and electrical measurements. To exclude residues of polymers and solvents, FET devices were annealed at 300–400 $^{\circ}\text{C}$ for 1 h in vacuum or nitrogen. Note that transmission electron microscopy reveals a significant amount of catalytic particles in sample L but no detectable traces in samples M and S.

Figure 1(a) displays the optical absorption spectra of L, M, and S samples in toluene. Sharp peaks in the ranges of 1100–1400 and 600–900 nm, labeled S_{11} and S_{22} , correspond to the first and the second optical transitions in s-SWNTs, respectively. Less resolved peaks in the range of 500–600 nm, labeled M_{11} , are assigned to optical transitions from m-SWNTs. The intensity of these features as well as the absorption background decrease in the following sequence: L, M, and S. Remarkably, the optical absorption spectrum of sample S is dominated by S_{11} and S_{22} features (s-SWNTs) without detectable traces of M_{11} peaks (m-SWNTs). To ascertain this result, the Raman spectra were recorded at 514.5 nm, which resonantly probes m-SWNTs. We observed that the radial breathing mode around 270 cm^{-1} (m-SWNTs) normalized to the mode around 190 cm^{-1} (s-SWNTs) decreases from L to M, and eventually vanishes in sample S [Fig. 1(b)]. We further corroborated these results by electrical measurements.

The electrical properties were investigated in the field effect configuration. A few droplets of SWNTs solutions were spin coated on a Si/SiO₂ wafer, with prepatterned drain and source electrodes (Cr/Au) and Si as a back gate electrode. Figure 1(c) presents drain current I_D versus gate bias V_G with drain-source bias $V_{DS} = -14$ V. Sample S presents a sizable gate bias dependence characteristic of *p*-type semiconductor behavior, whereas sample M exhibits a weaker gate effect and higher conductivity typical of metallic behavior. Similar results were observed at least on ten devices made from sample S and three devices from sample M, as will be later explained. The electrical measurements unambiguously prove that sample S essentially consists of s-SWNTs, whereas sample M (and to a greater extent L, not shown) contain s-SWNTs, m-SWNTs, and probably impurities.

At this point, it is important to stress that the electrical, optical absorption, and Raman measurements provide strong evidence that sample S consist of s-SWNTs without detectable traces of m-SWNTs and impurities, within our detection limits. Ultracentrifugation (optimum conditions 150 000 g

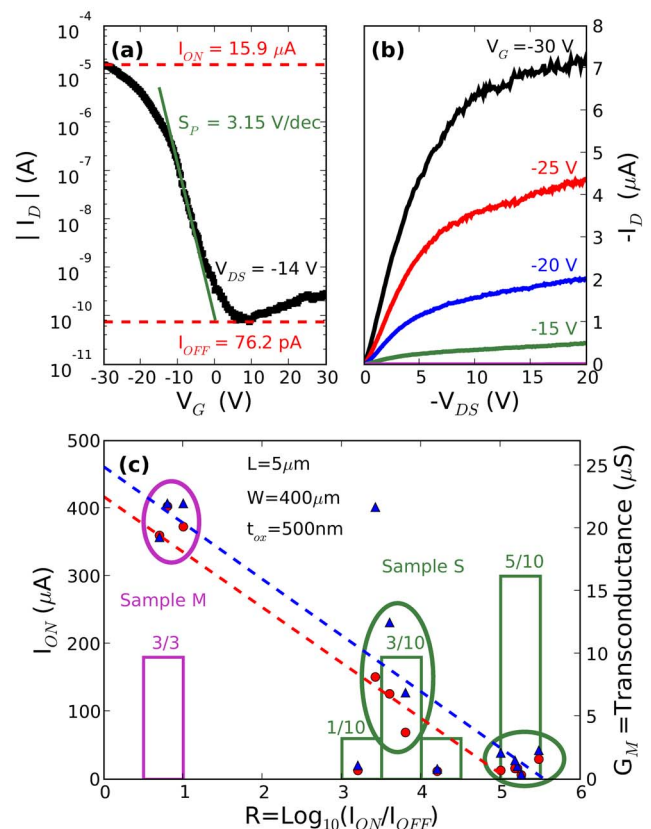


FIG. 2. (Color online) (a) and (b) display the transfer characteristic of an FET device made by spin coating. (c) presents the histogram, I_{on} (\circ , red) and transconductance (Δ , blue) vs $\log_{10}(I_{on}/I_{off})$ for samples S (ten devices) and M (three devices). Lines represent linear fit.

for 60 min) is the key technique that lead us to the selective extraction of s-SWNTs. Note that the centrifugation conditions (9 000 g, 3 min) described by Nish *et al.* are inadequate to remove traces of m-SWNTs.¹⁴ The selective extraction of s-SWNT and removal of m-SWNT might be described using the model already suggested for the extraction of near-armchair s-SWNT.^{14,16} The present achievement is extremely important for both basic and applied research.

Prototypical FET consisting of random network of SWNTs, fabricated by spin-coating sample S, exhibits very promising characteristics rarely observed simultaneously [Figs. 2(a) and 2(b)]. The on-off current ratio is around 10^5 , the on-current I_{on} is 15.9 μA , the transconductance G_m is 1.75 μS , the threshold slope S_p is 3.15 V/decade and $V_T = -26$ V at $V_{DS} = -14$ V [with $G_m = \delta I_D / \delta V_G$, $S_p = V_G / \log(I_D)$]. In addition, I_D versus V_{DS} curves exhibit a well defined linear and saturation regimes (with $\delta I_D / \delta V_{DS} = -0.2 \mu\text{A/V}$, $I_{sat} = -7.2 \mu\text{A}$). Similar results were observed on ten devices, which were recorded using the same device structure but not necessarily the same density of SWNTs. The histogram in Fig. 2(c) shows that five devices are in the range $R = 5 - 5.5$ and 3 are in the range $R = 3.5 - 4$ [with R defined as $R = \log_{10}(I_{on}/I_{off})$]. Admittedly, the characteristics of our devices are relatively scattered, but we believe that this technical challenge can be surmounted by improved processing.

Interestingly, Fig. 2(c) shows that I_{on} and G_m linearly decrease with increasing R (detail analysis will be provided elsewhere). In substance, devices only consisting of s-SWNTs show higher R but lower I_{on} and G_m , whereas de-

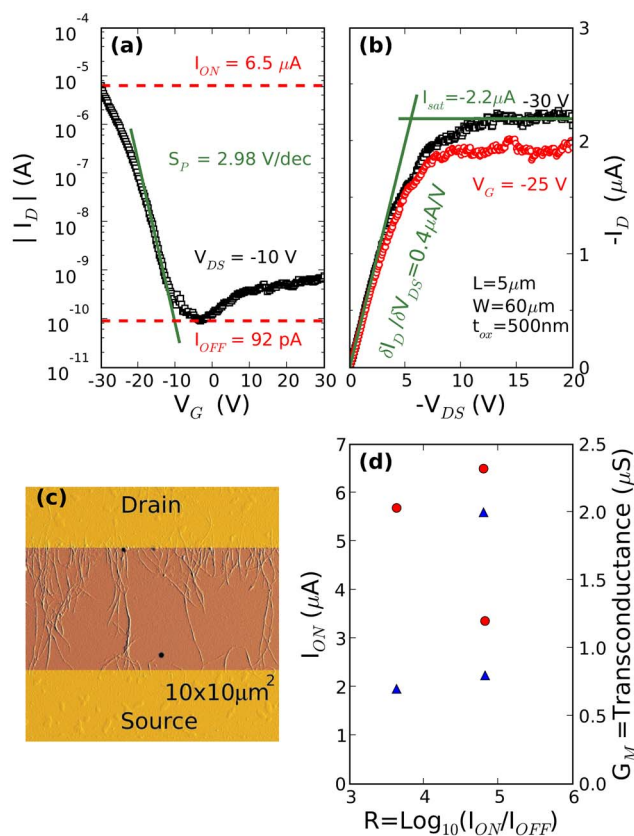


FIG. 3. (Color online) (a) and (b) show the transfer characteristic of an FET device made by dielectrophoresis. (c) displays the atomic force microscopy image of a SWNTs network. (d) shows I_{on} (○, red) and transconductance (△, blue) vs $\log_{10}(I_{on}/I_{off})$.

vices with higher fraction of m-SWNT show lower R but higher I_{on} and G_m . We anticipate that FET devices with desired transfer characteristics can be simply fabricated by tuning the centrifugation conditions, in other words by controlling the ratio semiconducting/metallic SWNTs.

To improve the performances of the FET devices, s-SWNTs in NMP (similar to sample S) were deposited on predefined location and orientation by dielectrophoresis (DEP).^{4,17} This technique leads to a relatively dense network of SWNTs oriented perpendicular to the electrodes, eventually bridging the electrodes with fewer nanotube-nanotube junctions than random network [Fig. 3(c)]. Here again, the device present relatively good characteristics: $R=4.8$, $I_{on}=6.5 \mu\text{A}$, $G_m=1.7 \mu\text{S}$, $S_p=2.98 \text{ V/decade}$ and $V_T=-26 \text{ V}$ at $V_{DS}=-10 \text{ V}$. Similar results were observed at least for three devices [two devices with $R=4.8$ and one device with $R=3.6$ as shown in Fig. 3(d)]. The estimated field effect hole mobility is larger than $2 \text{ cm}^2/\text{V s}$. The latter was calculated using established equations^{8,10,18} with the following parameters $G_m=1.7 \mu\text{S}$, $L=5 \mu\text{m}$ (source-drain gap), $W=60 \mu\text{m}$ (channel width), $t_{ox}=500 \text{ nm}$ (gate thickness) and $\epsilon=34.5 \text{ pF/m}$ (permittivity of silicon dioxide). If we divide I_{on} and G_m by W , then the performances of the FET made by DEP are exceeding those made by spin coating.

How do our technique and our FET characteristics compare with previous reports? The fabrication of FETs based on individual s-SWNTs is technically challenging, and methods involving selective breakdown of m-SWNT are difficult to control.^{6,8-10} In contrast, the deposition of already prepared s-SWNT solutions are compatible with printable FET and

TFT technologies. The performances of our devices are significantly improved compared to those made using SWNTs extracted by chromatography and by density gradient ultracentrifugation,^{5,7} better than the state-of-the-art solution processable polymers and organic molecules, but still lower than vacuum deposited pentacene and amorphous Si.¹

Further studies are in progress to improve I_{on} and G_m by choosing s-SWNT with larger diameter, increasing the density of s-SWNT, reducing t_{ox} and L , and replacing Au by Pd electrodes; and to suppress the hysteresis by performing surface treatment and encapsulation.

In conclusion, we have demonstrated the selective extraction of s-SWNTs, without detectable traces of m-SWNTs and impurities, from carbon nanotube powders using PFO as an extracting agent in toluene assisted in particular by ultracentrifugation (150 000 g). We anticipate that this method will lead to pure s-SWNTs produced in sizable quantities and formulated as a printable "ink." We have also demonstrated that s-SWNT processable solutions can realize high-performance p -type FETs with very promising characteristics: on-off current ratio around 10^5 , I_{on} around $10 \mu\text{A}$ and estimated hole mobility larger than $2 \text{ cm}^2/\text{V s}$. We believe that the present achievement paves the way for the future development of FET and TFT based on s-SWNT.

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