HAL
open science

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

Nicolas Izard, Saïd Kazaoui, Kenji Hata, Toshiya Okazaki, Takeshi Saito, Sumio Iijima, Nobutsugu Minami

To cite this version:

Nicolas Izard, Saïd Kazaoui, Kenji Hata, Toshiya Okazaki, Takeshi Saito, et al.. Semiconductor-enriched single wall carbon nanotube networks applied to field effect transistors. Applied Physics Letters, 2008, 92, pp.243112. 10.1063/1.2939560 . hal-00444351

HAL Id: hal-00444351

https://hal.science/hal-00444351

Submitted on 6 Jan 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

N. Izard, S. Kazaoui*, K. Hata, T. Okazaki, T. Saito, S. Iijima, and N. Minami
National Institute of Advanced Industrial Science and Technology (AIST)
1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565 Japan

Substantial progress are reported on field effect transistors (FET) consisting of semiconducting single wall carbon nanotubes (s-SWNTs) without detectable traces of metallic nanotubes and impurities. This outstanding result was made possible in particular by ultracentrifugation (250,000g) of solutions composed of SWNT powders with polyfluorene as 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 a 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 μA and the estimated hole mobility is larger than 2 cm^2/vs. The present results are demonstrated by optical absorption, Raman and electrical measurements.

PACS numbers:

Novel semiconductors materials for field effect transistor FET and thin-film transistors TFT 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 mobility, to carry high current density and to operate at high frequencies.[2,3,4,5] Several groups have demonstrated excellent transfer characteristics using individual s-SWNTs,[2,3,4,5] but generally poor ones using ensemble (network and thin film) of SWNTs due to traces of metallic nanotubes (m-SWNTs) and impurities (catalytic and amorphous particles).[6,7,8] Therefore, very efficient methods to selectively synthesis s-SWNTs or to selectively extract s-SWNTs from as-grown nanotubes are still required.

In recent years, several approaches to extract s-SWNTs from nanotube powders were explored using for instance chemical functionalization,[9,10,11] DNA and polymers wrapping,[12,13] and density gradient ultra-centrifugation techniques.[6] The latter efficiently separates s-SWNTs and m-SWNTs, but traces of surfactant and density gradient materials 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 extracting agent.[14,15] According to Nish *et al.*,[14] the sample shows no detectable traces of m-SWNTs based only on optical spectroscopy. However, neither the electrical properties nor the fabrication of FET devices were addressed.

In this letter, we report on the electronic properties of FET consisting of *semiconducting-enriched single wall carbon nanotubes, without detectable traces of metallic nanotubes and impurities*, with in our detection limits. This unprecedented achievement is made possible by ultracentrifugation (250,000g), sonication and filtration of solutions composed of SWNT powders with polyfluorene as extracting agent in toluene. Evidences are gathered by optical absorption, Raman and electrical measurements (see Fig.1). We shall demonstrate that such s-SWNTs realize high-performances FET devices compare to networks/thin films of SWNTs and solution processable polymers/organic materials.[1,6,16]

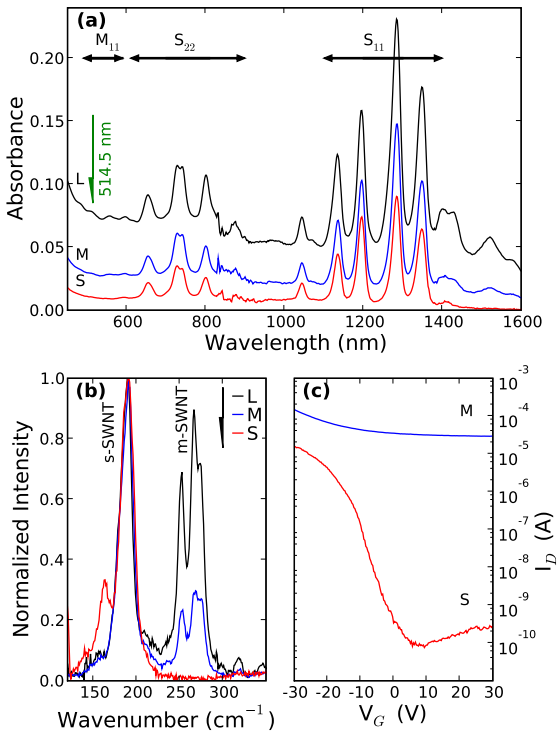

FIG. 1: (Color online): (a) shows the optical absorption spectra and (b) the Raman spectra at 514.5 nm of L, M and S samples . (c) displays the transfer characteristic, I_D vs V_G for V_{DS}=-14V of FET devices made of sample M and S.

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

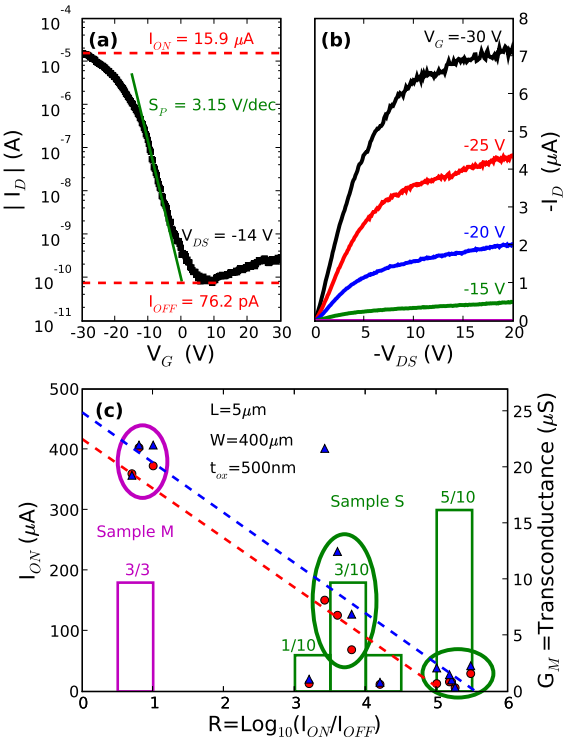

FIG. 2: (Color online): (a) and (b) display the transfer characteristic of an FET device made by spin-coating. (c) presents the histogram, I_{ON} $(-\bigcirc-)$ and Transconductance $(-\triangle-)$ versus $Log_{10}(I_{ON}/I_{OFF})$ for sample S and M. Lines represent the linear fit

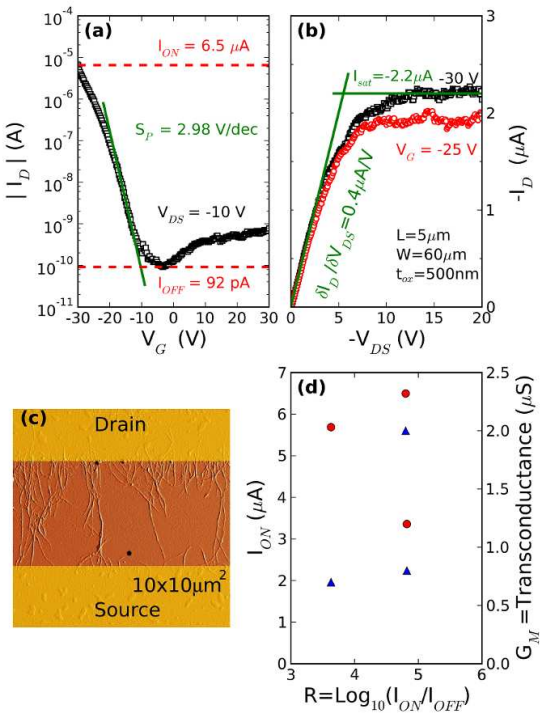

FIG. 3: (Color online): (a) and (b) show the transfer characteristic of an FET device made by electrophoresis. (c) displays the AFM image of a s-SWNTs network. (d) shows I_{ON} $(-\bigcirc-)$ and Transconductance $(-\triangle-)$ versus $Log_{10}(I_{ON}/I_{OFF})$.

and homogenized by sonication (1 hour using a water-bath and 5 minutes using a tip sonicators). Then, this mixture was centrifugated for 5∼120 minutes using either a desktop centrifuge (angle rotor type) or an ultra-centrifuge (swing rotor type). Next, the upper 80 % of the supernatant solution was collected. To recover only the SWNTs while washing out the PFO, the supernatant solution was filtered through 0.1 μm Teflon filter and rinsed with toluene several time (until the characteristic optical absorption band of PFO at 385nm completely disappears from the filtrate). Finally, this filter was soaked in organic solvent (such as Toluene or N-Methyl-2-pyrrolidone (NMP)) and subjected to mild sonication. We shall focus on three types of SWNTs processable solutions centrifugated at 10000 g for 15 min (labeled L), 250000 g for 30 min (labeled M) and 250000 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°C for 1 hour in vacuum or nitrogen. Note that the transmission electron microscopy (TEM) reveals significant amount of catalytic particles in sample L but no detectable traces in sample M and S.

Figure 1a displays the optical absorption spectra of L, M and S samples in toluene. Sharp peaks in the range 1100-1400 and 600-900 nm, labeled S_{11} and S_{22}, corresponds to the first and to the second optical transitions in s-SWNTs, respectively. Whereas, less resolved peaks in the range 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. It is worth noticing that 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 (RBM) around 270 cm^{-1} (m-SWNTs) normalized to the RBM mode around 190 cm^{-1} (s-SWNTs) decreases from L to M, and eventually vanishes in sample S (Fig. 1b). It is essential to corroborated those results by electrical measurements.

The electrical properties were investigated in field effect configuration. A few droplets of SWNTs solutions were spin-coated on Si/SiO_2 wafer, with pre-patterned drain and source electrodes (Cr/Au) and Si as a back gate electrode. Figure 1c present the drain current I_D versus gate bias V_G with drain-source bias V_{DS}=-14 V. The sample S presents a sizable gate bias dependence characteristic of a 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 10 devices made from sample S and 3 devices from sample M (see the histogram in Fig. 2c). The electrical measurements unambiguously prove that sample S essentially consists of s-SWNTs, whereas sample M (and to 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 250,000 g for 60 min) is the key technique that lead us to the selective extraction of s-SWNTs from nanotubes powders with PFO as extracting agent in toluene solution. 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 present achievement is extremely importance for both basic and applied research.

Next, prototypical FET consisting of random network of SWNTs were fabricated by spin-coating the sample S on Si/SiO_2 wafer with pre-patterned drain and source electrodes. Remarkably, such device exhibits very promising characteristics rarely observed simultaneously. The on-off current is around 10^5, the on-current is $I_{ON} = 15.9\mu$A, the transconductance is $G_m = 1.75\mu$S ($G_m = \delta I_D/\delta V_G$) and the threshold slop is S_p=3.15V/decade ($S_p = \delta V_{DS}/\delta Log(I_D)$). In addition, I_D vs V_{DS} exhibits a well defined linear regime ($\delta I_D/\delta V_{DS} = -0.2\mu$A/V) and a saturation regime ($I_{sat} = -7.2\mu$A). Similar results were observed on 10 devices, which were recorded using the same device structure but not necessarily the same density of SWNTs. The histogram in figure 2c shows that 5 devices are in the range R=5-5.5 and 3 are in the range R=3.5-4 (with R the on-off ratio 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 and reproducible FET can be fabricated.

Interestingly by plotting the data related to sample S and M, the figure 2c can be divided in 3 areas indicated with circles. On one side, high R is correlated to low I_{ON} and G_m, on the other side low R is correlated to high I_{ON} and G_m, and in between there is an intermediate situation. Remarkably, I_{ON} and G_m decreases linearly with increasing R. In substance, this result suggest that FET devices can be fabricated with desired transfer characteristics depending on the targeted application, by simply tuning the centrifugation conditions (in other words, the ratio semiconducting/metallic SWNTs) and the spin-coating conditions (density of SWNTs).

To improve the performances of the FET devices, s-SWNTs in NMP (similar to sample S) were deposited on pre-defined location and orientation by dielectrophoresis (DEP).[5,17] This technique leads to a relatively dense network of s-SWNTs oriented perpendicular to the electrodes eventually bridging the electrodes with a few nanotube-nanotube junctions (Fig. 3c). Here again, the device present relatively good characteristics: R=4.8, I_{ON}=6.5μA, G_m=1.7μS, and S_p=2.98V/decade. Similar results were observed at least for 3 devices (2 devices with R=4.8 and 1 device with R=3.6 as shown in figure 3c). The estimated field effect hole mobility is larger than μ=2 cm^2/vs. The latter was calculated using established equations[7,8,16] with the following parameters $L = 5$ μm (source-drain gap), $W = 60$ μm (channel width), t_{ox}= 500nm (gate thickness) and $\epsilon = 34.5$ pF/m (permittivity of silicon dioxide). If we normalize I_{ON} and G_m to the width of the electrode W, than the performances of the FET made by DEP are exceeding (by a factor 400 μm/60 μm) those made by spin-coating method.

How our technique and the performances of our FET compare with previous reports? Fabrication of FET based on individual s-SWNTs are technically challenging, and methods involving selective break-down of m-SWNT occasionally damage the entire device.[7,8] In contrast, deposition of already prepared s-SWNT processable solutions are compatible with FET and TFT technology. The performances of our device are comparable to those made using density gradient technique, larger than the state-of-the-art solution processable polymers and organic molecules, but lower than amorphous Si and vacuum deposited Pentacene.[1,16]

In conclusion, we have demonstrated the selective extract s-SWNTs, without detectable traces of m-SWNTs and impurities, from carbon nanotube powders using PFO as extracting agent in toluene assisted in particular by ultracentrifugation (250,000g). 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-SWNTs processable solutions can realize high-performances p-type FET with very promising characteristics: the on-off current ratio around 10^5, I_{ON} around 10 μA and the estimated hole mobility larger than 2 cm^2/vs. We believe that the present achievement pave the way to the future development of FET and TFT based on s-SWNT. Admittedly, further study and optimization of both the materials and the devices are still necessary to met the industrial requirements.

Acknowledgments

We thank all the members of the Nano-Carbon Team (AIST). N. Izard thanks the Japan Society for the Promotion of Science for financial support.

[1] J. Jang, Materials Today, **4**, 46 (2006).

[2] M. J. Biercuk, S. Ilani, C. M. Marcus, and P. L. McEuen,

"Carbon Nanotubes Advanced Topics in the Synthesis, Structure, Properties and Applications", J. Ado, G. Dresselhaus, M. S. Dresselhaus (Eds.), Topics in Applied Physics, Vol. 111, 455-493 (2008), (Springer-Verlag, Berlin Heidelberg 2008).

[3] Ph. Avouris and J. Chen, Materials Today **10**, 46 (2006).

[4] T. Durkop, B. M. Kim, and M. S. Fuhrer, J. Phys. Condens. Matter. **16**, R553 (2004).

[5] A. Le Louarn, F. Kapche, J.-M. Bethoux, H. Happy, G. Dambrine, V. Derycke, P. Chenevier, N. Izard, M. F. Goffman, J.-P. Bourgoin, Appl. Phys. Lett. **90**, 233108 (2007).

[6] M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp, M.C. Hersam, Nature Nanotech. **1**, 60 (2006).

[7] T. Fukao, S. Nakamura, H. Kataura and M. Shiraishi, Jpn. J. Appl. Phys. **45**, 6524 (2006).

[8] E.S. Snow, P.M. Campbell, M.G. Ancona, J.P. Novak, Appl. Phys. Lett. **86**, 033105 (2005).

[9] M.S. Strano, C.A. Dyke, M.L. Usrey, P.W. Barone, M.J. Allen, H.Shan, C.Kittrell, R.H. Hauge, J.M. Tour, R.E. Smalley, Science **301**, 1519 (2003).

[10] C. Menard-Moyon, N. Izard, E. Doris, C. Mioskowski, J. Am. Chem. Soc. **128**, 6552 (2006).

[11] Y. Maeda, S.. Kimura, M. Kanda, Y. Hirashima, T. Hasegawa, T. Wakahara, Y. Lian, T. Nakahodo, T. Tsuchiya, T. Akasaka, J. Lu, X. Zhang, Z. Gao, Y. Yu, S. Nagase, S. Kazaoui, N. Minami, T. Shimizu, H. Tokumoto, R. Saito, J. Am. Chem. Soc. **127**, 10287 (2005).

[12] M. Zheng, A. Jagota, M.S. Strano, A.P. Santos, P.Barone, S. Grace Chou, B.A. Diner, M.S. Dresselhaus, R.S. Mclean, G. Bibiana Onoa, G.G. Samsonidze, E.D. Semke, M. Usrey, and D.J. Walls, Science **302**, 1545 (2003).

[13] S. Kazaoui, N. Minami, B. Nalini, Y. Kim, N. Takada and Y. Hara, Appl. Phys. Lett.**87**, 211914 (2005).

[14] A. Nish, J-Y. Hwang, J. Doig, and R.J. Nicholas, Nature Nanotech. **2**, 640 (2007).

[15] F. Chen, B. Wang, Y. Chen, and L.-J. Li, Nano Lett. **7**, 3013 (2007).

[16] S. Scheinert and G. Paasch, Physics of organics semiconductors, W. Brtting (Edi.) (Wiley-VCH, Weinheim, 2005).

[17] A. Vijayaraghavan, S. Blatt, D. Weissenberger, M. Oron-Carl, F. Hennrich, D. Gerthsen, H. Hahn, R. Krupke, Nano Lett. **7**, 1556 (2007).

[18] T. Yasuda, K. Fujita, T. Tsutsui, Y. Geng, S. W. Culligan, and S. H. Chen, Chem. Phys. **17**, 264 (2005).