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High Performance Ambipolar Field-Effect Transistor of Random Network Carbon Nanotubes

Satria Zulkarnaen Bisri,* Jia Gao, Vladimir Derenskyi, Widiyanta Gomulya, Igor Iezhokin, Pavlo Gordiichuk, Andreas Herrmann, and Maria Antonietta Loi*κ

Field-effect transistors (FETs) based on semiconducting single-walled carbon nanotubes (sSWNTs) are one of the most promising building blocks for the generation of superfast electronic devices. Among the proposed nanocarbon based materials, with very high carrier mobilities, sSWNTs are the only true semiconductor. Their band gap (∼0.7 eV) is, in fact, compatible with the integration in logic circuits, since it allows FETs based on sSWNTs to be turned off.

However, the fabrication of sSWNT FETs remains a great challenge. Until now, High performance ambipolar devices combining a high carrier mobility and a high on/off ratio were only achieved with sSWNTs grown by chemical vapor deposition (CVD) on a rigid substrate at high temperatures (∼900 K). Furthermore, those devices were fabricated by serially patterning the electrode by electron beam lithography on the selected sSWNT (single strand or network). These processes are expensive, low throughput, energy demanding, and currently unsuitable for the demands of large area and flexible device integration.

The ability to disperse SWNTs in water and organic solvents makes solution-based processes more attractive for the fabrication of sSWNT based devices. The related solution-based techniques, i.e., drop-cast, self-assembly (evaporative, Langmuir–Blodgett, DNA-assisted), and inkjet printing, allow large area device preparation at room temperature that are well suited for device integration. Nevertheless, many challenges remain to achieve a comparable performance with those obtained with the “ideal” sSWNT FET, fabricated by the aforementioned CVD method. In general, the devices produced by solution-based methods are characterized by low carrier mobilities because of the sparse coverage of the SWNTs on the FET channel and the random orientation of the nanotube network. Although some improved carrier mobilities were reported by increasing the nanotube density or by aligning the SWNTs on films, these devices have shown low on/off ratios due to the remaining metallic tubes content. The reduction of the on/off ratio compromised the merit of sSWNT over other competing nanocarbon FETs, especially when considering the short channel length. Therefore, purifying and sorting sSWNTs from any remaining metallic SWNTs is of paramount importance.

Several recent reports showed that conjugated polymers (e.g., poly-9,9-di-n-octyl-fluorenyl-2,7-diyl (PFO)) can be effectively used to prepare sSWNT dispersions since their extensive π-conjugated structure can interact strongly with the nanotube. However, fabricating high performance devices from the sSWNT dispersions still remains a challenge. It turned out that removal of the polymers is essential to achieve good device performance. Izard et al. reported the separation of dispersed HiPCO SWNTs from excess PFO by extensive washing. The resulting FETs, in which the SWNTs were oriented by dielectrophoresis, showed a relatively good performance but without any ambipolar behavior. In any case, the washing, filtration and iterated rinsing with copious amounts of solvents makes the process laborious and costly.

In this article, we demonstrate a scalable and efficient method for the preparation of high purity sSWNT dispersions, in which the excess polymer can be removed effectively. High performance solution-processed ambipolar sSWNT-FETs are obtained showing electron mobilities around 3 cm²/V·s in randomly oriented sSWNT network FETs, with on/off ratios of 10⁶. Remarkably, this value is even obtained in transistors with very short channel length (5 μm). Moreover, we discuss the influence of the post-treatment on the transport properties of the FETs, and we compare the device performance with the other nanotube network FETs.

To prepare the sSWNT dispersion, we performed strong sonication of the SWNT/polymer solution followed by ultracentrifugation. We used CoMoCAT SWNTs because of narrower chirality distribution, in comparison with HiPCO SWNTs. Poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) (Mₕ = 58 200 g/mol by GPC) was used as the dispersant. PFO solution in toluene has been proven to be one of the most effective methods for sorting semiconducting SWNTs due to the unique interaction between the polymer chains and semiconducting carbon nanotubes. Dry nanotubes were added to 10 mL of polymer solution in a weight ratio (SWNT/polymer) of 1:3. The mixture was ultrasonicated for 2 h in a high-power water-bath sonicator to produce the as-dispersed solution. After sonication, the crude dispersion was ultracentrifuged at 40 000 rpm (190 000 g) for 1 h. The supernatant (50%) was collected and transferred into new centrifuge tube for a second round of centrifugation.

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order to enrich sSWNTs and to remove the excess polymer. The solution was then ultracentrifuged at 55 000 rpm (367 000g) for 5 h. Over 90% of the dispersed SWNTs precipitated at the bottom of the centrifuge tube, accumulating into a little but visible black “mat”. The “mat” was carefully collected, washed three times with 2–3 mL of fresh toluene, and further subjected to a short sonication step in 2 mL toluene (20 min, 15 W), yielding the semiconductor-enriched SWNT dispersion with almost no background intensity, that indicates the minimum one after enrichment are shown in Figure 1a. The absorption spectra of the as-dispersed sSWNTs and the one after enrichment are shown in Figure 1a. The absorption spectrum of the as-dispersed SWNTs (solid red line) shows much higher absorbance intensity (O.D. = 0.4, sSWNT (7,5)) than that of the as-dispersed one (O.D. = 0.15). By taking into account the absorption cross section \( \alpha(E_{11}) = 1 \times 10^{-18} \) atom for dispersed carbon nanotubes,\(^{[14]} \) we estimated the sSWNTs concentration to be around 3.1 \( \mu \)g/mL for the as-dispersed solution and 7.8 \( \mu \)g/mL for the enriched one. No optical transitions from metallic SWNT in the spectral range of 420–600 nm were observed. The absorbance below the 400 nm spectral range (\( \lambda_{\text{max}} = 380 \) nm) was also significantly lowered from a saturated value to be as low as O.D. \( = 0.44 \), which corresponds to the estimated concentration of PFO between 2.92 and 7.00 \( \mu \)g/mL (see the Supporting Information). This indicates that the method we applied is highly efficient in removing excess PFO polymer from the dispersion. It should be noted that, to our knowledge, the value of the residual absorbance of PFO in the sSWNT dispersion has never been reported,\(^{[11d,15]} \) despite its importance in determining the remaining excess polymer. We assumed that the remaining polymer chains in our enriched solution were only those that wrapped around the sSWNT surface.

Figure 1. a) Optical absorption spectra of the as-dispersed sSWNTs (dash curve) and the enriched sSWNTs (solid curve) in toluene solution. b) Atomic force microscopy (AFM) image of the sSWNT film sparsely deposited on mica by drop casting for nanotube length determination. c) AFM image of 10 layers of sSWNT deposited in the device channel. The surface appears as a dense, yet homogeneous random network.

In comparison to other recent efforts to remove the excess polymer from PFO dispersed sSWNTs, our method is the most cost efficient with minimal usage of solvents, and is yet effective. Vijayaraghavan et al.\(^{[15a]} \) reported the realization of carbon nanotube device arrays by using PFO/toluene dispersed HiPCO SWNTs with a rinsing process performed after film deposition. The electronic transport characteristics indicated that there was still a significant amount of remaining polymer. Bindl et al.\(^{[15b]} \) presented a method with multiple centrifugation steps to get rid of the excess polymer, analogous to our technique. Our procedure has the advantage of being much less time-consuming, due to shorter centrifugation times (less than 8 h, in comparison to \( > 24 \) h in the previously reported methods\(^{[11]} \)) as well as avoiding any iterative redispersion and repelletization. Moreover, our result showed less background indicating lower amounts of nanotube bundles.

Subsequently, sSWNT FETs were fabricated by simply drop-casting the sSWNT dispersion in toluene on pre-patterned bottom-gate/bottom-contact substrates. Prior to the drop-casting of the nanotubes, the \( \text{SiO}_2 \) surface was modified with a self-assembled monolayer of 3-aminopropyltriethoxysilane (APTES) to induce adhesion of sSWNTs.\(^{[11c]} \) The drop-casting of the sSWNT dispersion was performed on a hotplate at 70 °C, to minimize the coffee-stain effect. For each device, we used 10 droplets of sSWNT dispersion with 0.5 \( \mu \)L/droplet and 10 s interval between depositions. Figure 1c shows the atomic force microscopy image of the deposited sSWNT network in the device channel.

The FET measurements were performed in a nitrogen-filled glovebox at room temperature in the dark and the devices were never exposed to air or moisture during and after the fabrication process. Figure 2a shows the \( I_{DS}-V_{DS} \) output characteristics of the FET with 20 \( \mu \)m channel length and 10 mm channel width. Ambipolar characteristics of the device are observed with obvious saturation behavior in both hole and electron accumulation regimes. The \( I_{DS} \) for p-channel operations shows a nearly linear increase in the \( V_{GS} \) range of 0 to –2 V. This suggests that ohmic contacts for hole injection can be achieved between the Au electrodes and the sSWNT network. On the other hand, the devices only exhibit weak nonlinear Schottky behavior for electron injection. The transfer characteristics shown in Figure 2b indicate an “on/off” ratio as high as 10\(^6\) and 10\(^5\) for electrons and holes, respectively. The off current is of the order of 10\(^{-1}\) nA at a source drain bias, \( V_{DS} = -5 \) V, and the respective “on” current can reach 26 mA. The values of the on/off ratio are the
The parallel plate model can overestimate the capacitance of the carbon nanotube networks, thus underestimate the value of the extracted carrier mobilities. There is a more rigorous approach to calculate the capacitance for the mobility extraction, which considers the percolation of the sSWNT network.\textsuperscript{[11a,16]}

This is expressed by the formula

\[
C = C_q^{-1} + \frac{1}{2\pi \varepsilon_0} \ln \left[ \frac{\pi \sinh(2\pi t_{ox}/\varnothing)}{R} \right]^{-1} \varnothing^{-1} \quad (2)
\]

where \( C_q \) is the quantum capacitance of carbon nanotubes, \( C_q = e^2 g = 2.3 \), \( g \) is the electron density of states in the nanotube,\textsuperscript{[17]} \( \varnothing^{-1} \) is the density and \( R \) is the radius of the nanotube, respectively. In an infinite 2-dimensional nanotube percolation network, we can have \( L(\pi N_c)^{1/3} = 4.236 \) as the relationship between the percolation threshold \( (N_c)^{1/3} \) and the nanotube length \( L \). From the AFM image of sparsely deposited sSWNT (Figure 1b), we determined the average length of our nanotube as 659 nm. Therefore, the percolation threshold of our film was \( 13/\mu m^2 \). Meanwhile, we calculated the density of the nanotube on a sSWNT FET channel approximating \( 90/\mu m^2 \) from the AFM image of the device channel (Figure 1c). Therefore, the fabricated nanotube networks in our devices are above the percolation threshold. This also justifies the use of the parallel plate capacitance to extract the values of charge carrier mobility, since the capacitance of the network model approaches the one of the parallel plate model in this limit.

Nevertheless, we also calculated the capacitance using \textit{Equation 2} with \( \varnothing^{-1} \) of \( 10/\mu m^2 \). From the absorption spectrum shown in Figure 1a, the primary dispersed nanotube is \((7,5)\) with a diameter \( (2 \times 10^{-10} /m) \). The mobility values for both hole and electron remain almost constant (within the same order) with the increase of the channel length. This indicates the existence of bulk mobility in these devices. The presence of metallic nanotubes and percolation effects usually cause severe length dependent mobility in network sSWNT FETs, where the mobility value increases by channel length.\textsuperscript{[18]} In contrast, our results show that there is no dependency, implying the absence of metallic species in our nanotube films. Moreover, the on/off ratios remain constant with \( 10^6 \) for electron and \( 10^5 \) for holes, even for the bottom-contact devices with very short channel length (5 \( /m \)). To the best of our knowledge, very high on/off ratio in random network nanotube devices with a short channel length are unprecedented so far. The results of the length dependent electronic transport unambiguously confirm the high purity of the sSWNT dispersion being free of metallic tubes and only containing minimal amounts of residual polymer. The results are also in good agreement with the optical measurements (see the Supporting Information, Figure S4).

highest reported for ambipolar FETs of a sSWNT network. Both the nearly ohmic characteristics as well as the very high on/off ratios indicate the very high quality of the sSWNT dispersion and minimal influence of the residual polymer chains in the film.

The values of charge carrier mobilities were calculated from the \( I_D-V_G \) transfer curve at the linear regime \( (V_{DS} = \pm 5 \text{ V}) \) by using the following formula

\[
\mu = \frac{L_C}{W_C V_{DS} C} \frac{\partial I_D}{\partial V_G} \quad (1)
\]

where \( L_C \) and \( W_C \) are the channel length and width, respectively, defined by the pattern of the electrodes. \( C \) is the capacitance, in which we use the parallel plate model, \( C = \varepsilon e_{SiO_2}/t_{ox} = 15 \text{ nF/cm}^2 \) with \( \varepsilon \) is the dielectric constant and \( t_{ox} \) is the thickness of the SiO\(_2\). By applying the previous formula, we obtained mobility values of 0.08 cm\(^2\)/V·s and 2.86 cm\(^2\)/V·s for holes and electrons, respectively. To the best of our knowledge, these values, particularly the electron mobility, are among the highest reported for ambipolar devices made with solution processed bottom-gated random network sSWNT devices.

Figure 2. a) \( I_D-V_G \) output characteristics of the sSWNT FET showing a clear ambipolar transport characteristic. b) p-Channel (left) and n-channel (right) \( I_D-V_G \) transfer characteristics of the corresponding device from which the on/off ratio was extracted.
In the past years, many authors have pointed out that the exposure of sSWNTs to oxygen and water moisture can induce hole doping and electron trapping. To study this effect in regard to random network enriched sSWNT FETs, we compared devices that were stored for a prolonged time in a N₂ glovebox atmosphere with devices that were exposed to air for a short period. We performed this comparison also due to the fact that the performance benchmark for sSWNT FETs is always provided for hole transport characteristics after oxygen exposure. This can be due to short time exposure during transfer of the device, or because the device measurements are performed in air. To remove the PFO from the film, in order to avoid any influence of residual polymer during the oxygen exposure experiment, the sSWNT devices were baked inside two different vacuum ovens (400 °C, 4 h, P < 10⁻¹ mbar). For the air-exposed samples, we used an oven outside the glovebox, with a total air (18 °C, R_H ≈ 80%) exposure time of 30 min. For the samples without air exposure we used a vacuum oven connected to the glove box. The final device measurements were performed inside a N₂-filled glovebox for both set of samples.

Figure 3. a) Channel length dependence of the hole mobility and corresponding on/off ratio. b) Channel length dependence of the electron mobility and the corresponding on/off ratio.

Figure 4. a) Comparison of the p-channel I/D⁻¹/₂-V_G transfer characteristics of the sSWNT device before and after oxygen exposure, showing a reduction of V_Th for hole accumulation. The transfer curve for the pristine device was multiplied by 6 to accommodate both plots. b) Comparison of the n-channel transfer characteristics before and after oxygen exposure for showing an increasing of 23 V of the V_Th. The transfer curve for the oxygen-exposed device was multiplied by 100. c) Channel length dependence of the hole mobility and the corresponding on/off ratio after the device was exposed to the air.

after air exposure, respectively. The ambipolar characteristics are still present also for the device that was exposed to the air for relatively short time (30 min). Nevertheless, the threshold
voltage for electron accumulation increases by 23 V and the electron mobility decreases to $2.52 \times 10^{-3}$ from 2.86 cm$^2$/V·s. The threshold voltage ($V_{th}$) for hole accumulation is only decreased by 4 V. Our results are consistent with the ones reported by Aguirre et al. which demonstrated that the oxygen/water redox couple could electrochemically induce electron transfer from sSWNTs and suppress electron conduction. This contributes to the deep electron traps that shift the $V_{th}$ for electrons. The removal of the oxygen/water redox couple cannot be done by simply storing the device inside the glove box or under vacuum. On the other hand, the $V_{th}$ shift of holes occurred due to the oxygen doping of the nanotube that concurrently affects the value of the $V_{th}$ shift of electrons. Therefore, we estimate that the number of trapped electrons by the oxygen/water redox couple is $1.8 \times 10^{13}$/cm$^2$ from the residual $V_{th}$ shift of 19 V. It is important to note that the devices that were annealed in a vacuum oven connected to the glovebox did not undergo any changes in their amphoteric characteristics. The linear parallel-plate-model mobility for holes increases to 2.66 cm$^2$/V·s (compared with the original value prior to air exposure of 0.08 cm$^2$/V·s) in the devices that were exposed to air. Moreover, the value of hole on/off ratio after air exposure increased to $10^6$, due to the increase of the "on" current. From Figure 4c, one can see that the on/off ratio and the value of hole mobility remain almost constant for all measured devices with different channel lengths even after air exposure. This demonstrates both the absence of metallic tubes and the bulk nature of hole transport in the annealed devices, and that oxygen exposure only changes the polarity of the transistor to favor more hole dominant transport.

Figure 5 shows the comparison of the performance of our ambipolar FETs with the other reported nanotube network devices fabricated on SiO$_2$/Si gates. The plot allows comparison of the values of hole mobility and on/off ratios, since most of the previous examples reported these two values, but the devices rarely showed ambipolar transport characteristics. From Figure 5, it is clear that our sSWNT FETs showed excellent performance combining high on/off ratios and high values of hole mobility, among the highest for short channel, random-network, solution-processed nanotube films. Moreover, the on/off ratio for the electron transport is the highest ever reported for solution processed sSWNTs FETs.

In terms of hole mobilities, the values we obtained are still lower than those of CVD-grown nanotube networks and some of the solution dispersed nanotubes, but those were achieved with alignment processes during the deposition. Nevertheless, the on/off ratios presented herein are far better than for those devices. For the CVD-grown sSWNTs, the on/off ratios are usually in the range of $10^{-1}$ to $10^{-2}$, because of the high portion of metallic tubes. A similar reason undervalues the high on/off ratio reported by Sun et al., which occurs only for very long channel devices. The high mobility demonstrated by Miyata et al. is due to the alignment process during deposition, in addition to the length sorting of the nanotubes. The higher on/off ratios obtained in our experiments indicate the successful enrichment process obtained using PFO. From this comparison, it becomes obvious that both our enrichment and purification techniques for sSWNTs are the most efficient ways to produce high performance solution processable SWNTs devices. The utilization of this nanotube ink in combination with optimized device fabrication processes (e.g., nanotube alignment, length sorting, advanced gating, passivation, ink-jet printing, etc.) will be the subject for future research.

In conclusion, we reported a fast, scalable, efficient, and cost-effective method to obtain enriched sSWNT solutions from CoMoCAT nanotubes. In particular we developed an effective technique to remove excess conjugated polymer, which acts as a selective dispersing agent. By employing this sSWNT dispersion, we successfully realized ambipolar FET fabrication and operation of networks of sSWNT with a record value of electron mobility (3 cm$^2$/V·s). The hole mobility of the devices also reached high values after exposure of the devices to air. The very high values of the on/off ratios for hole and electron accumulation showed that the deposited sSWNT films have no metallic content, placing these devices amongst the best ever obtained with a solution-processed random-network sSWNT configuration. The purity of the resulting nanotube ink as well as the fast and efficient method to obtain it will make the scaling up of the fabrication of high performance sSWNT FETs more feasible, in a close competition with the other nanocarbon technologies (e.g., graphene).

**Experimental Section**

CoMoCAT SWNTs and poly(9,9-di-n-octyfluorenyl-2,7-diyl) (PFO) ($M_w$ = 58 200 g/mol by GPC) were obtained from Southwest Nanotech and Sigma-Aldrich, respectively. The solution of sSWNT and polymer was...
ultrasonicated (in Misonic 3000 water bath sonicator) at 90 W power. We used a Beckman Coulter (Optima XE-90, SW 55 Ti) ultracentrifuge for both processes to disperse the nanotube and to remove the excess polymer. The absorption spectra of the dispersion were recorded using a UV-vis-NIR spectrophotometer (Perkin-Elmer, Lambda 900) with a 1-cm-thick cuvette.

A thermally grown SiO2 layer (230 nm thickness), on heavily doped Si wafer, served as the gate dielectric for the FETs. The source and drain electrodes consisted of 30 nm Au on top of a 10 nm Ti adhesive layer, which were patterned to form a interdigitated channel. All substrates were cleaned by standard procedures for cleaning SiO2 surface, involving quick immersion in basic piranha solution (mixture of 30% NH4OH solution and 30% H2O2), followed by sonication in acetone and isopropanol. The substrates were then treated with a vacuum UV-plasma cleaner to remove residual organic contaminants from the surface. To functionalize the SiO2 surface with self-assembled monolayer of 3-aminopropylthiethoxysilane (APTES, Sigma Aldrich), the substrates were immersed in a solution of APTES (6 µL) in isopropanol (20 mL) for 1 h and then rinsed with isopropanol (5 mL). After dropcasting the sSWNT dispersion, the substrates were heated at 150 °C for 2 h. The electronic transport characteristics of the sSWNT FETs were measured using an Agilent E5270B semiconductor parameter analyzer. All steps for the device fabrication were performed inside a dry nitrogen filled glovebox.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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