Carbon nanotubes network ambipolar field effect transistors with $10^8$ on/off ratio

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Due to their unique 1-dimensional structure, single walled carbon nanotubes (SWNTs) possess outstanding near ballistic transport properties that makes them one of the leading candidates to replace silicon in the fabrication of high-speed and low-voltage field-effect transistors (FET). In fact, SWNTs on the contrary of graphene, have a substantial bandgap and display semiconducting properties. SWNTs can be classified as intrinsic semiconductors, which allow full control of the state (on and off) of the FETs by applying a gate voltage. Interestingly, these transistors are equally able to accumulate electrons and holes, thus allowing the fabrication of FETs that can change polarity depending on the applied gate voltage (ambipolar).

Complementary metal-oxide-semiconductor (CMOS) devices are fundamental components of integrated circuits. In the standard configuration a n- and a p-type field effect transistors are used to obtain different functions. CMOS-like devices instead of using two separate transistors, the use of a single fabricated using two ambipolar FET would allow the
reduction of the number of elements in fabrication steps, thus lowering the effort necessary for the fabrication of logic circuits.\textsuperscript{[1]} Besides the CMOS-like devices high on/off ratio is required by many different FET applications, including the one used as driving electronics for displays (on/off >10\textsuperscript{7}) and resistance based memories (>10\textsuperscript{8}).\textsuperscript{[2]}

However, achieving the required high on/off ratio and mobility necessary for this applications with SWNTs CMOS with ambipolar FET is still a great challenge. In principle, state-of-the-art single-strand SWNT FETs can meet most of these requirements: high mobility, and high on/off ratio.\textsuperscript{[3,4]} However, their fabrication procedure is not suitable for large scale production, and does not show the high reproducibility required for high throughput device fabrication.\textsuperscript{[4]} An alternative strategy is to use solution-processed SWNTs networks, which so far have not demonstrated their full potential due to the random distribution of nanotubes of different species in the transistor channel.

The alignment of SWNTs in the transistor channel can significantly improve the device performance.\textsuperscript{[5]} Several efforts to align SWNTs have been made utilizing techniques such as Langmuir-Schaefer deposition,\textsuperscript{[6]} chemical self-assembly,\textsuperscript{[7]} and dielectrophoresis (DEP).\textsuperscript{[8]} In general, aligned SWCNT networks demonstrated higher charge carrier mobility compared to random networks. However, the state-of-the-art on/off ratio for FETs made using these methods still remains low (10\textsuperscript{5}), which hampers practical applications (vide supra). One of the causes is the low purity of the semiconducting SWNT solutions. Exposure to oxygen and water has also a detrimental effect on the off current and transforms the transistors in p-type.\textsuperscript{[9]}

Among the many techniques\textsuperscript{[10-12]} developed in the past several years to select semiconducting single-walled carbon nanotubes (sSWNT) from a mixture, one of the most interesting is the polymer-assisted separation method due to its high effectiveness and scalability.\textsuperscript{[13]} Recently, we reported highly enriched selection of small diameter semiconducting nanotubes using polyfluorene derivative (PF8).\textsuperscript{[14-16]} Later on, we
demonstrated that nanotubes with various diameters, including large diameter ones (~1.5 nm), can be selected by exploiting polyfluorene derivatives bearing side chains of different lengths.\cite{17} Nevertheless, polyfluorenes are not the only conjugated polymers able to select sSWNTs. Recently, it was demonstrated that also poly(3-dodecylthiophene-2,5-diyl) is very efficient in sorting semiconducting carbon nanotubes.\cite{18}

Here we report the fabrication of high-performance FETs showing a record $10^8$ on/off ratio in a simple device geometry with bottom contact and bottom gate with channel length of 10 µm. The devices were obtained with semi-aligned polymer wrapped SWNT networks deposited on SiO$_2$ dielectric by blade coating from solutions using different types of polymers, namely, poly-9,9-di-n-dodecyl-fluorenyl-2,7-diyl (PF12) and poly(3-dodecylthiophene-2,5-diyl) (P3DDT). The blade coating technique (Figure 1a) allows the alignment of SWNTs in the transistor channel and determines an enhancement of the device parameters to record values. Interestingly, several device parameters appear to be influenced by the nature of the polymer used for the selection of the semiconducting tubes. We rationalize this effect in terms of the relative position of the energy levels of the polymer and the SWNTs.

To select the semiconducting species from the starting mixture of nanotubes produced by high-pressure CO conversion (HiPCO), we utilized two different polymer backbones PF12 and P3DDT (Figure 1b), which have both alkyl side chains with 12 carbon atoms. The preparation of the solution includes two major steps, sonication and ultracentrifugation.\cite{14,17} Through sonication, we are able to de-bundle and disperse nanotubes in the organic solvent polymer solution. By ultracentrifugation, contaminants, bundles and undispersed metallic species are removed. In this way, a rather diluted dispersion of sSWNTs ($\approx$6.5 µg/ml for PF12-wrapped and $\approx$54 µg/ml for P3DDT-wrapped) containing a large amount of excess polymer is obtained. Therefore, to obtain higher concentration of SWNTs and to reduce the amount of excess polymer, a further enrichment step is necessary. The enrichment, as we have
reported previously, requires a precipitation of the sSWNTs selected as supernatant, a washing step to eliminate the excess polymer and a re-dispersion.$^{[17]}$

The absorption spectra of PF12-wrapped HiPCO (PF12-SWNT) and P3DDT-wrapped HiPCO (P3DDT-SWNT) solutions before and after the enrichment are shown in Figure 1c and Figure 1d, respectively. We can clearly observe the reduction of the polymer peaks below 400 nm (PF12) and 600 nm (P3DDT) in the spectra of the enriched solution obtained with both polymers. At the same time, the intensity of the peaks corresponding to sSWNT increases in the range between 1000 nm and 1500 nm. From the absorption of the solution and using cross sections for absorption reported in literature,$^{[19]}$ the enrichment process is estimated to give rise to concentrations of sSWNTs $\approx 23\mu g/ml$ for PF12-SWNTs and $\approx 210\mu g/ml$ for dispersions made with P3DDT.

The ink obtained in this way can be used with every solution processing technique. In this work we compare the blade coating method (Figure 1a) with simple drop casting technique, which we have previously exploited successfully for device fabrication.$^{[14]}$

Blade coating is a very attractive technique for large volume and large area device fabrication, being highly scalable and reproducible. In terms of technical challenges, deposition by blade coating of the sSWNTs ink is by far easier and faster than DEP and Langmuir-Schaefer assembly. Moreover, in blade coating, SWCNTs are being aligned during the deposition process.

Two batches of SWNT FETs were fabricated from PF12-SWNT and P3DDT-SWNT enriched solutions by using both drop casting and blade coating. The drop casting samples are fabricated following the same procedure as previously reported for small diameter nanotubes wrapped with PF8.$^{[14]}$

Figure 2a shows the atomic force microscopy (AFM) image of carbon nanotubes randomly distributed in the channel for drop casted films, while Figure 2b shows the SWNT network deposited by blade coating. Blade coating results in a partial alignment of the
nanotubes along the direction of the blade movement. An alignment ratio of up to 52% is obtained by this method. This value is obtained by counting the number of tubes aligned within ± 30° of the preferred orientation obtained analysing the AFM pictures of the transistor channel. Due to the high aspect ratio of the nanotubes, we expect in this semi-aligned sample to have a higher number of connections between the source-drain electrodes and the nanotubes, thus increasing the maximum current of the transistor in the on-state and obtaining a higher charge carrier mobility.

$I_D-V_G$ transfer characteristics of the random and semi-aligned PF12-SWNT network FETs are reported in Figure 2c and Figure 2d, respectively. The random-network FET fabricated with PF12-SWNT shows an on/off ratio of only $10^4$ for the hole current. The sample deposited by blade coating displays an on/off ratio as high as $3 \times 10^6$ at $V_D= -5$ V (Figure 2d). The observed increase of the on/off ratio is due to the enhancement of the on current. The on-current in the semi-aligned network increases from 30 µA to 0.2 mA and the hole mobility improves from $9.00 \times 10^{-3}$ cm²/V·s to 2.17 cm²/V·s. Such a drastic improvement in the on/off ratio and carrier mobility arises from the reduction of the number of nanotube-nanotube cross junction in the transistor channel when going from random to aligned network. Cross junctions are known to be one of the main reasons causing carrier trapping and mobility losses, especially because the polymer wrapped around the nanotubes can act as an additional barrier (or trap) for charge transport through the network.

Figure 2e and figure 2f show the comparison between the transfer characteristics in the linear regime of P3DDT-SWNT FETs fabricated by drop casting and blade coating, respectively. In the supplementary information are reported the transfer characteristics measured at saturation (+/- 25V) and the gate current of the devices. The devices fabricated with P3DDT-SWNT are strongly dominated by hole transport. Moreover, the transfer characteristics of both the drop casted and semi-aligned tubes display a considerable shift (20V) of the threshold towards negative gate voltages. Similarly to what has been obtained
with PF12-SWNT FETs, the aligned P3DDT-SWNT nanotube devices demonstrated higher on/off ratio, up to $7 \times 10^7$, compared with $4 \times 10^5$ in the random network device. The FETs fabricated with semi-aligned P3DDT-SWNTs also exhibit higher mobility ($3.71 \text{ cm}^2/\text{V} \cdot \text{s}$) than the random network ($0.03 \text{ cm}^2/\text{V} \cdot \text{s}$). It is important to underline that the hole on/off ratio of $7 \times 10^7$ is the highest ever reported for any solution-processed SWNT network FETs and for any solution processed semiconductor, especially on SiO$_2$ dielectric.

Figure 3 depicts the full characterization of the FETs fabricated with the P3DDT- and PF12-wrapped SWNTs aligned network (See Supplementary Information for hysteresis and gate leakage current). From the output characteristics shown in Figure 3c and Figure 3d, it is evident that the devices fabricated with P3DDT wrapped SWNTs have much lower electron contribution than the devices fabricated with PF12 wrapped SWNT. An estimation of the electron current difference between the two samples can be obtained from the transfer characteristics measured at $V_D=+5\text{V}$ (Figure 3a, b). About 1 order of magnitude difference in current can be seen between P3DDT-SWNTs and PF12-SWNTs. For a given gate voltage, PF12–based FET shows rather symmetric electron and hole contribution, while in the case of P3DDT we observe dominantly p-type characteristics.

As mentioned previously the threshold voltage of the devices fabricated with PF12-SWNTs and P3DDT-SWNTs show a difference of about 10V. Since the solution preparation and device fabrication are identical for both polymer-wrapped SWNT samples, we can attribute the differences observed in the device characteristics to the nature of the nanotube-polymer interaction or to the properties of the polymers themselves.

In order to clarify the origin of the device polarity different ratio between the electron and hole current variation and of the difference in the threshold voltage shift, we compare the transport characteristics of FETs fabricated from SWNTs enriched solutions and those fabricated from pristine (without enrichment) solutions produced with both polymers. Dashed and solid lines in Figure 4a show the $I_D-V_G$ transfer characteristics of
FETs prepared using pristine and enriched PF12-SWNT solutions, respectively. Both devices exhibit ambipolar behavior, with maximum hole mobility of 2.17 cm$^2$/V·s and maximum electron mobility of 0.86 cm$^2$/V·s measured for enriched solutions. The on/off ratio for hole accumulation increases from $5 \times 10^4$, in FETs fabricated from pristine solutions, to $3 \times 10^6$ in devices made with the enriched solution. Figure 4b shows a detail of the devices transfer characteristics from which the threshold voltage values are extracted. The threshold voltage for hole accumulation is found to be $-17.5$ V (dashed line) for the device fabricated with the pristine solution and $-7.5$ V (solid line) for the one fabricated with the enriched dispersion. This difference can be explained by the excess polymer in the pristine solution that might act as a barrier hindering the transport between tubes, but also might function as a trap decreasing the amount of carriers in the transistor channel. Consequently, the removal of the excess polymer in the enrichment process improves the hole accumulation and shifts the threshold of about 10 V towards $V_G=0$.

Figure 4c shows the $I_D$-$V_G$ transfer characteristics of FETs fabricated from P3DDT-SWNT solution with and without enrichment treatment. The highest hole mobility values are 0.42 cm$^2$/V·s for non-enriched and 3.71 cm$^2$/V·s for enriched solutions, respectively. Removing the excess of polymer, in the case of P3DDT-SWNT, gives rise to higher on/off ratio which reaches values of $7 \times 10^7$. The off current decreases from $\approx 100$ pA to $\approx 10$ pA in devices fabricated with enriched dispersion, while the on-current increases slightly, 0.5 mA (pristine) and 0.7 mA (enriched). In contrast to our findings for PF12-SWNT-based devices, we observe only very small threshold voltage difference between devices fabricated with the pristine P3DDT-SWNT ($-20.5$ V) and enriched solutions ($-18.5$ V). Moreover, while the enrichment of PF12-SWNT solution resulted in an improvement of the device ambipolarity, this is not the case for P3DDT-SWNT.

Polymer chains wrapped around the carbon nanotubes could have in principle a beneficial role in particular when using SiO$_2$ as gate dielectric, screening charges from
trapping sites in the dielectric. However, an excess of polymer between the SWNTs suppresses the charge transport between the tubes due to the high energetic barrier between the nanotube network.\textsuperscript{[14]}

Both polymers, P3DDT and PF12, exhibit a bandgap wider than that of HiPCO sSWNTs. As a consequence, charge carrier transport can be hindered by the barrier between the energy levels of sSWNT and polymer. In the case of polythiophene, the difference between the HOMO and LUMO levels of the polymer and (6,5) sSWNT is approximately 0.3 eV and 0.5 eV, respectively. Polyfluorene has a wider bandgap thus forming a higher energy barrier (about 1 eV) for electron and hole transport through the polymer. Further investigations are under way to validate the above model.

To place our results into the context of the state-of-the-art of carbon-nanotube-network electronics, we compared the performance of our devices with those reported by other authors.\textsuperscript{[5,6,18,20-28]} Figure 5 summarizes all SWNT network FETs fabricated on SiO\textsubscript{2}/Si gates worldwide. The devices based on PF12-SWNT solution with semi-aligned networks are superior regarding the effective mobility and on/off ratio, for both electrons and holes, in relation to PF8-SWNT FETs that were previously reported by our group.\textsuperscript{[14]} Certainly PF12 wrapping provides HiPCO solution with much higher nanotube concentrations than PF8,\textsuperscript{[17]} but also the alignment of the nanotubes significantly contributes to the high mobility and high on/off ratio. The achieved on/off ratio values are comparable with results obtained in single-strand SWNT ambipolar FET.\textsuperscript{[3]}

The hole branch of P3DDT-SWNT FET demonstrates record average on/off ratio of $7 \times 10^7$ with channel lengths shorter than 10 $\mu$m. This value is the highest ever reported for both solution-processed and CVD-grown SWNT FETs and for any solution processable materials.

The achievement of very high on/off ratio in these devices derives from different factors: i) the precise control of the polymer wrapping mechanism, which guarantee samples of high purity in terms of semiconducting species; ii) the high concentration of the
semitrated tubes in the starting solution and the reduction of the polymer content achieved with the enrichment procedure; iii) the alignment of the SWNTs through the blade coating technique.

In conclusion, we reported the fabrication of FETs with semi-aligned polymer wrapped carbon nanotube networks with effective carrier mobilities ranging from 0.42 cm²/V·s to 3.71 cm²/V·s and record on/off ratio of 10⁸. Interestingly, the wrapping polymer is found not only to influence the SWNT dispersion in terms of quantity of semiconducting tubes but also to tune the FET performance. While PF12-wrapped network shows almost symmetric ambipolar characteristics, samples fabricated with P3DDT-wrapped-SWNT show much lower electron current. The polymer concentration reduction through the enrichment process is found to be an important factor in modifying the transport characteristics of the PF12-SWNT-FETs, especially by influencing the electron threshold voltage. The effectiveness and scalability of the nanotube network deposition and alignment as well as the ability to control ambipolarity by polymer wrapping are expected to broaden the SWNT-FET application in both high performance and large-area electronics. The high on/off ratio obtained for these devices is compatible with high-speed and low leakage CMOS fabrication the highest demand applications for field effect transistors.

Experimental Section

Preparation and characterization of the semiconducting SWNT dispersion: The polymers, P3DDT (Mₙ = 43800, Mₚ = 47500) and PF12 (Mₙ = 162000, Mₚ = 373000), were solubilized in toluene, with concentration 3 mg per 10 ml of solvent. Subsequently, 3 mg single-walled HiPCO (High Pressure Carbon Monoxide) carbon nanotubes (Unidym) were added. The solution was then sonicated with an Ultrasonic Liquid Processor (Sonicator 3000) for 2 hours at 69 W and 16°C. Two-step centrifugation was performed to remove bundles, carbon contaminants, and metallic nanotubes, as well as to enrich the SWNT solution. During the
First ultracentrifugation with a Beckman Coulter (Optima XE-90; rotor: SW55Ti), (1 h, 40,000 rpm, 190,000 g), the high density components precipitated forming a pellet at the bottom of the centrifugation tube, while the low density components, containing individualized sSWNTs wrapped by polymer, stayed in the upper part as supernatant. The second step (5 h, 55,000 rpm, 367,000 g) was used in order to enrich SWNTs and to remove excess polymer.[14] Here, individualized sSWNTs are precipitated to form a pellet. Finally, the pellet is re-dispersed in 2 mL of toluene.

The purity of the nanotube solution was examined by absorption spectroscopy using UV/Vis/NIR spectrophotometer (Shimadzu UV 3600). The spectra of the HiPCO nanotube solution were recorded in the range between 300 nm and 1600 nm. From the absorption measurements the concentration of the sSWNTs in different samples was estimated using the calculated cross section for absorption of carbon.[19]

Fabrication of carbon nanotube transistors: Nanotubes were deposited on a highly doped silicon wafer with 230 nm thick SiO₂ dielectric. The source and drain electrodes were defined by a bilayer of ITO (10 nm) and Au (30 nm), forming transistor channel of 10 µm length and 10 mm width.

Two techniques, drop casting[14] and blade coating, were used for nanotube deposition. Schematic description of the equipment (Zehntner ZAA 2300 Automatic film applicator coater) used for SWNT deposition is shown on Figure 1a. The setup consists of a heating plate, and an aluminum blade, which can move with variable speed above the plate. The distance between the blade and the substrate can be adjusted with two micrometric screws. Silicon chips were placed on top of a hot glass and heated up to 55°C. 20 µl of SWNTs solutions were dropped on the chip, the excess solution was removed by the flat blade moving above the substrate. The process of deposition was repeated 10 times to increase the density.
of nanotube network. The substrate was subsequently annealed in nitrogen atmosphere at 140°C for 3 h to remove the residual organic solvent.

Characterization of the CNT transistor: Electrical measurements were performed using a probe station placed in the nitrogen-filled glovebox at room temperature under dark conditions. The probe station is connected to Agilent E5270B Semiconductor Parameter Analyzer with resolution of 10 fA. All devices are measured without being exposed to air, starting from the SWNT deposition process until the electrical characterization.

The mobility values were extracted from the linear regime of the \( I_D-V_G \) transfer characteristics at \( V_{DS}= \pm 5 \) V for both p- and n-channels. Since the density of the nanotube network (51/\( \mu \)m\(^2\)) in all devices was above the percolation limit (6/\( \mu \)m\(^2\)), the parallel plate model was used to calculate the capacitance of the gate dielectric. The quantum capacitance of the nanotube was not taken into account, so the total capacitance values were overestimated; thus the effective mobility values are underestimated. A statistic of the measured transistor effective mobility and on/off ratio obtained for different polymer wrapped SWNTs is reported in Figure S2 of the supplementary information.

The threshold voltages are extracted using a standard method as describe by Sze.\[29\]

Characterization of SWNT networks by AFM: The SWNT networks within the channel of the FETs were imaged by AFM in tapping mode. The scanning region was the channel area exhibiting a size of 20 \( \mu \)m\(^2\). The images were recorded with a MultiMode 8 Microscope and TESP probes (Bruker) with a spring constant \( k = 42 \) N\( \cdot \)m\(^{-1}\), resonance frequency \( f = 320–410 \) kHz and tip radius less than 10 nm. The scan rate and resolution of the measurements were selected to be 1 Hz and 1024 lines/sample, respectively. For each image a new probe was employed to avoid AFM tip broadening due to wear or contaminations from the conjugated polymer. The AFM images were analysed with NanoScopeAnalysis software.
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Figure 1. (a) Schematic illustration showing the blade coating process. (b) Chemical structures of poly-9,9-di-n-dodecyl-fluorenyl-2,7-diyl (PF12) and Poly(3-dodecylthiophene-2,5-diyl). (c) Absorption spectra of the pristine (dashed line) and enriched (solid line) P3DDT-wrapped HiPCO SWNT solution. (d) Absorption spectra of the pristine (dashed line) and enriched (solid line) PF12-wrapped HiPCO SWNT solution.
Figure 2. AFM image in tapping mode of the FET channel area showing (a) random SWNT network deposited by drop-casting and (b) semi-aligned SWNT network deposited by blade coating. The heights of the images are indicated with the color barcodes on the right. $I_D-V_G$ transfer characteristics of FETs measured at $V_D = -5 \ V$ corresponding to (c) Random PF12-SWNT network; (d) Semi-aligned PF12-SWNT network; (e) Random P3DDT-SWNT network; (f) Semi-aligned P3DDT-SWNT network.
Figure 3. $I_D-V_G$ transfer and $I_D-V_D$ output characteristics of FETs fabricated with P3DDT-wrapped sSWNT (a and c) and with PF12-wrapped sSWNT (b and d). Samples are fabricated by blade coating.
Figure 4. Comparison of $I_D-V_G$ transfer characteristics of the FETs fabricated by blade coating with (a) pristine and enriched PF12-wrapped-HiPCO sSWNT solution; (c) Pristine and enriched P3DDT-wrapped-HiPCO sSWNT solution. Comparison of the threshold voltage for pristine (dashed line) and enriched (solid line) solutions of sSWNTs wrapped by (b) PF12 polymer; and (d) P3DDT polymer.
Figure 5. Performance map of SWNTs FET fabricated with CVD and solution-based processes. The FETs with aligned and random SWNTs networks fabricated from solution are depicted with red and black symbols, respectively. The devices are categorized also according to their channel length.