Electronic Properties of n-Type Carbon Nanotubes Prepared by CF$_4$ Plasma Fluorination and Amino Functionalization

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Single-walled carbon nanotubes (SWNTs) have been fluorinated by CF$_4$ plasma exposure and further functionalized with 1,2-diaminoethane. The degree of amino functionalization is dependent on the degree of initial fluorination rather than oxygen or carbon defects. Reaction at both ends of 1,2-diaminoethane was observed to increase with fluorine content. Back-gated SWNT devices have shown p-type semiconducting behavior for CF$_4$-functionalized SWNTs and n-type semiconducting behavior for amino-functionalized SWNTs. The degree of n-type behavior increases with the amount of nitrogen attached to the SWNTs.

Single-walled carbon nanotubes (SWNTs) are promising materials for the next generation of electronic devices due to their unique electrical properties. It is well known that SWNTs can behave as metallic conductors or semiconductors, depending upon their chirality.[1] The inherent behavior of SWNT field effect transistors is p-type,[2] limiting their uses for logic applications. Electron-donating amine-containing substituents have been exploited by several groups to make n-type SWNT devices. The use of polyethylene imine (PEI) was developed by Dai et al.[3] to provide permanently n-type doped SWNT devices; this was expanded to produce soluble n-type SWNTs from a starting material of SWNT(COCl)$_n$.[4] Butylamine,[5,6] 3′-(aminopropyl)-triethoxysilane (APTES), proplyamine,[5] and hydrazine[7] have also been used to alter the electrical behavior of SWNTs.

Here, 1,2-diaminoethane has been used to dope plasma fluorinated SWNTs with electron-donating groups for the development of n-type SWNT field effect transistors (SWNT-FETs). The plasma fluorination process was developed previously within the group in 2003 by exposing SWNTs to a CF$_4$ plasma within a standard reactive ion etch (RIE) system as discussed elsewhere.[8,9] CF$_4$ plasma functionalization of SWNTs has also been carried out by Valentini et al. in 2005, who further functionalized the SWNTs with butylamine.[6] Stevens et al. developed a functionalization method with *N*-alkylidene amine groups as a tool for the potential binding of SWNTs to biomolecules and polymers.[10] The fluorination process used here differs from both Stevens et al. and Valentini et al. in that we exploit the advantages of short exposure times and low bias voltages in the CF$_4$ plasma to preserve SWNT structural integrity. Stevens et al. used fluorinated SWNTs subjected to long gas exposure times at 150 °C, in the manner described by the Rice University group,[11] to reach CF$_2$ stoichiometry.

Valentini et al. used high bias voltages (200 V) at room temperature, and their devices show limited n-doping. 1,2-Diaminoethane was used here in contrast to alkylamines or diamines with longer alkyl spacers for two reasons. First, the extra amino group should increase the degree of electron donation to the nanotube. Second, by using shorter spacers electron transport through the molecule from the second amino group may be facilitated. As discussed elsewhere, CF$_4$ plasma exposure leads to the attachment of both semi-ionic and covalent fluorine to the SWNT sidewalls.[8,9] The C−F bond is more charge-separated in semi-ionic fluorine than covalent fluorine, giving 1,2-diaminoethane the potential to bond with either the semi-ionic or covalent fraction: this may also provide insight into the reaction mechanism.

Single-walled carbon nanotubes purchased from CNI (HiPCO SWNTs) were fluorinated in a CF$_4$ plasma at a 40 sccm flow rate for periods of 10, 20, 40, and 60 s at the low bias end of the reactor (30 V D.C. bias). The fluorinated SWNTs were functionalized with 1,2-diaminoethane following a method similar to Stevens et al.[10] Plasma-fluorinated SWNTs were added to 1,2-diaminoethane (5 cm^3) and sonicated briefly (5 min) to aid dispersion. The plasma exposed CNTs were observed to disperse very readily in comparison to pristine CNTs. A catalytic quantity of pyridine (5 drops) was added and the suspension was stirred under argon at reflux (116 °C) for 6 h. The reaction vessel was allowed to cool to room temperature and filtered on a 0.2 μm micropore filter to leave a black nanotube residue that was washed twice with ethanol. X-ray photoelectron spectroscopy (XPS, VG Scientific Sigma Probe) using a monochromatic (Al(Kα) = 1486.6 eV) source was used to characterize the functionalized products. The C 1s, N 1s, O 1s, and F 1s peaks were deconvoluted using XPS Peak software (freeware, written by R. Kwok). Atomic ratios were determined by taking a linear background and using Al Wagner coefficients. Raman spectroscopy (LabRam 300, 633 nm HeNe laser) was used to probe the structural integrity of the SWNTs. A back-

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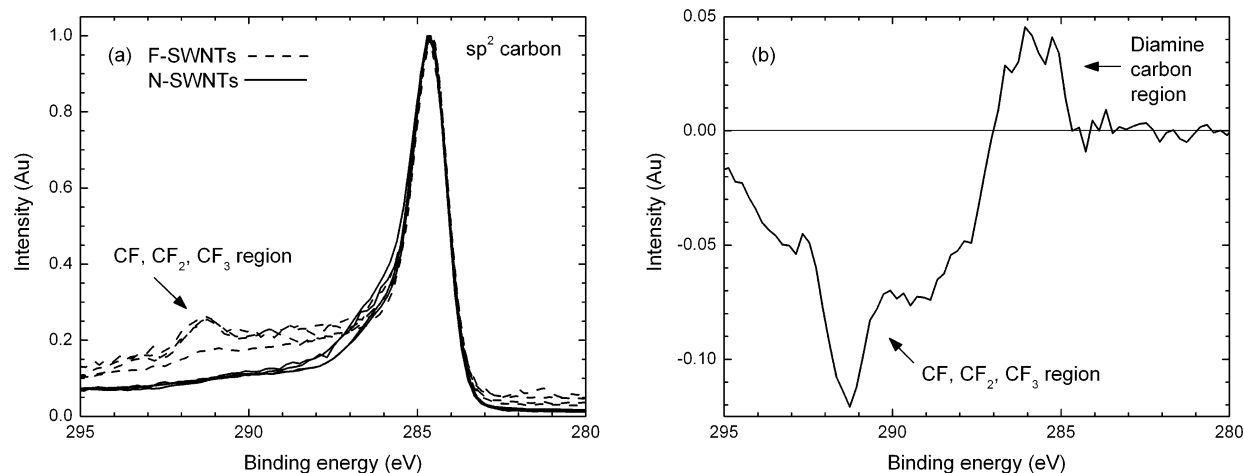‡ School of Chemistry.

Figure 1. (a) C 1s peaks for the F-SWNTs (dashed lines) and N-SWNTs (solid lines). (b) Averaged C 1s difference spectrum for N-SWNTs minus F-SWNTs.

TABLE 1: Stoichiometry of the Functionalized SWNTs as Determined by XPS

CF$_4$ plasma conditions		Stoichiometry			
CF$_4$ exposure time	DC Bias	F-SWNTs	O/C	N-SWNTs	O/C
10 s	20 V	C F$_{0.30}$	0.222	C N$_{0.065}$ F$_{0.015}$	0.12
20 s	30 V	C F$_{0.51}$	0.262	C N$_{0.068}$ F$_{0.014}$	0.11
40 s	30 V	C F$_{0.63}$	0.104	C N$_{0.077}$ F$_{0.019}$	0.10
60 s	30 V	C F$_{0.55}$	0.130	C N$_{0.059}$ F$_{0.013}$	0.089

gated silicon substrate with a 50 nm thermal SiO$_2$ layer was used, onto which Ti/Au 5/25 nm source and drain electrodes were fabricated by e-beam lithography. The electrode spacing was 500 nm for all device characteristics probed. The functionalized carbon nanotubes were then dispersed in 1,2-dichloroethane before being spin coated onto electrode structures. The SWNT suspensions were highly dispersed in an attempt to achieve smaller bundles of SWNTs bridging the electrodes, although some large bundles of SWNTs were observed by electron microscopy. The current−voltage (I−V) characteristics were probed using an HP4156B probe analyzer.

XPS analysis showed that both the initial fluorination and the subsequent substitution reactions were successful, with the carbon (C 1s) region highlighting the difference between the fluorinated and amino-functionalized nanotubes (Figure 1). For clarity we will use the terms F-SWNTs to refer to the CF$_4$ plasma fluorinated SWNTs and N-SWNTs to denote the amino-functionalized SWNTs. The F-SWNTs exhibit three peaks at 289, 291, and 293 eV, which can be attributed to carbon 1s electrons in CF, CF$_2$, and CF$_3$ respectively.[12] The peak at 286 eV in the N-SWNTs arises from the diamine carbon atoms (Figure 1b).[13]

The fluorine (F 1s) region of the F-SWNT XPS spectra (see Supporting Information) was also studied: two peaks, attributed to semi-ionic and covalent fluorine, were observed, with the majority of fluorine detected covalently bound to carbon. At higher plasma exposure times the semi-ionic/covalent fluorine ratio increased slightly (in contrast to previous results at the high-bias end of the reactor[8]). The nitrogen (N 1s) XPS region (not shown here) deconvoluted to two peaks, at ∼399.5 eV and ∼400.5 eV, which can be attributed to NH$_2$ and NH, respectively.[13,14]

Atomic ratios of carbon, nitrogen, oxygen, and fluorine are shown in Table 1. Uncertainties in the XPS results are negligible. However, fluctuations in the stoichiometries could result from the manual handling of the samples between various stages of processing, even though attempts have been made to minimize

the errors introduced. The degree of fluorination, in general, appears to increase with plasma duration and voltage. However, it is clear that the 60 s sample shows a decrease in F/C relative to the 40 s sample. The plasma functionalization process is complex, and the mechanism for fluorine attachment to nanotubes has been studied previously.[8,9] The low F/C results at 60 s may be attributed to the nonlinearity of the plasma process, an effect also seen by others using CF$_4$ plasma to functionalize SWNTs.[15] As discussed previously, the plasma process exposes the SWNTs to ion bombardment.[8,9] The flux of ions reaching the SWNT sample surface should not vary considerably over time, after equilibrating during the first few seconds of bias voltage application. Functionalization via fluorination therefore requires a tradeoff between defect creation and production of sufficient concentrations of radicals capable of bonding to sites on the SWNTs. The atomic nitrogen to carbon (N/C) ratios of the N-SWNTs follow a similar trend to the atomic fluorine to carbon (F/C) ratios of the F-SWNTs (Figure 2). From the atomic oxygen to carbon (O/C) ratios (Table 1) it appears that not all the defect sites may be ascribed to fluorine (oxygen is a common defect in the SWNT structure). However, the similarity in trend between the F-SWNT F/C ratio and the N-SWNT N/C ratio implies that the amino functionalization is dependent on the initial fluorine content, rather than reacting with oxygen or at defect sites.

The most striking observation from Table 1 and Figure 2 is that the degree of functionalization in the N-SWNTs is considerably less than the F-SWNTs, an effect is also observed by both Stevens et al. and Valentini et al.,[6,10] raising the question: what happens to the majority of the fluorine during the amino functionalization reaction? The simplest explanation might be that some of the fluorine is only adsorbed onto the nanotubes rather than being chemically attached. Within the CF$_4$ plasma we expect the creation of radicals and molecular CF$_2$ and F$_2$, as well as charged ions, that could all be contributing to the extra fluorine observed. The adsorption of fluorine in the functionalization processes used by other groups[6,10] may also be the cause of their apparent incomplete removal of fluorine and failure to transfer all fluorine dopants to nitrogen: an explanation supported by Raman analysis. If all the fluorine detected by XPS were covalently attached to the SWNTs, the Raman spectra would show strong D-bands and a reduction in the radial breathing modes (RBMs). In particular, such an effect would be evident at 40 s plasma exposure where the C$_2$F limiting stoichiometry is apparently exceeded: this would imply struc-
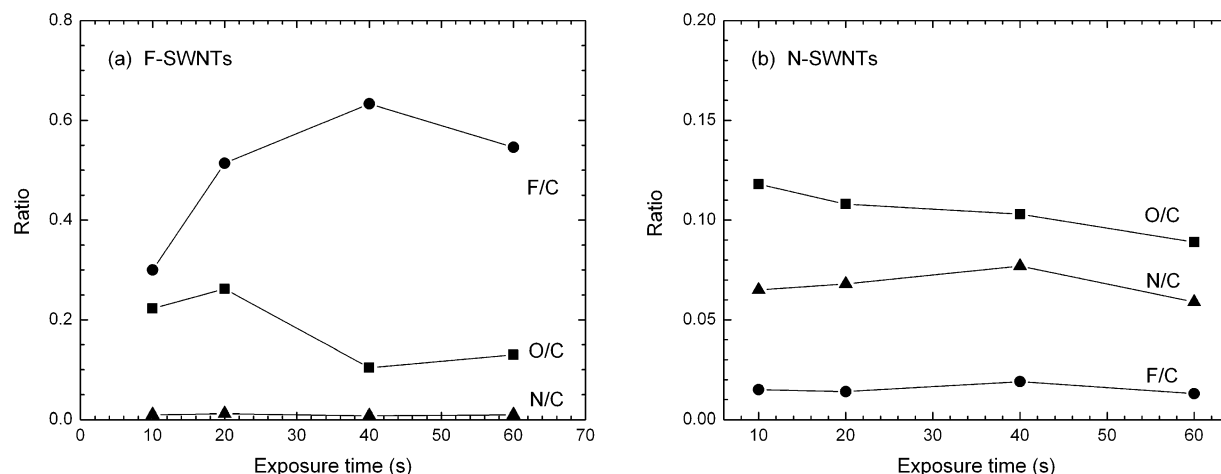
Figure 2. (a) F/C, O/C, and N/C ratios of the F-SWNTs. (b) F/C, O/C, and N/C ratios of the N-SWNTs.

tural damage of the SWNTs.[16] As it is, strong RBMs are observed in all samples along with high G-band and low D-band intensities (D/G ratios typically 0.3, see Supporting Information), implying the SWNTs are structurally intact.[17] It is of interest that the D-bands are slightly smaller after reaction with 1,2-diaminoethane, suggesting that some of the fluorine may have been removed without being replaced: the resulting positive charge on the SWNT carbon would be readily delocalized to provide stability.

As we have discussed above, CF_4 plasma fluorination produces a combination of semi-ionic and covalent fluorine attached to the SWNTs. After amino functionalization reaction both semi-ionic and covalent fluorine XPS peaks were observed on both the 10 and 20 s plasma-exposed samples. However, the N-SWNTs also show a lower semi-ionic/covalent fluorine ratio than the F-SWNTs. The 40 and 60 s plasma-exposed samples both show only covalent fluorine after amino functionalization. At first glance this would suggest that semi-ionic fluorine is preferentially substituted by 1,2-diaminoethane; this might happen because the semi-ionic C—F bond is more charge-separated, and therefore more reactive. It is also possible that some F is only adsorbed onto the SWNTs, not having formed a semi-ionic/covalent bond with the SWNTs, as will be discussed below. Due to the unknown contribution of adsorbed fluorine, it is not possible to accurately determine the semi-ionic/covalent ratio of chemically bonded fluorine on the F-SWNTs. Therefore, the F-SWNT and N-SWNT semi-ionic/covalent fluorine ratios cannot be compared, and the apparent reduction in the ratio may be misleading. It is expected that the reasonably severe conditions of the amino-functionalization reaction will result in the removal of adsorbed fluorine and perhaps some of the more weakly bonded fluorine: this is confirmed by the reduction of the D-band after amino functionalization. Further experiments were carried out whereby samples of F-SWNTs were sonicated in excess ethanol for 5 min. Figure 3 shows the F/C ratio before and after the sonication. A reduction in F/C is observed post sonication: this is consistent with the removal of adsorbed or weakly bound fluorine. The graph also indicates clearly that the remaining F/C ratio increases monotonically at longer reactor times. The resulting stoichiometry is consistent with the post-amino-functionalization results shown in Table 1. We conclude that adsorbed or weakly bound fluorine is removed during the amino-functionalization process. Further work is required to determine the amino functionalization reaction mechanism after fluorination in a SF_6 plasma, which is known to produce predominantly covalent F 1s peaks
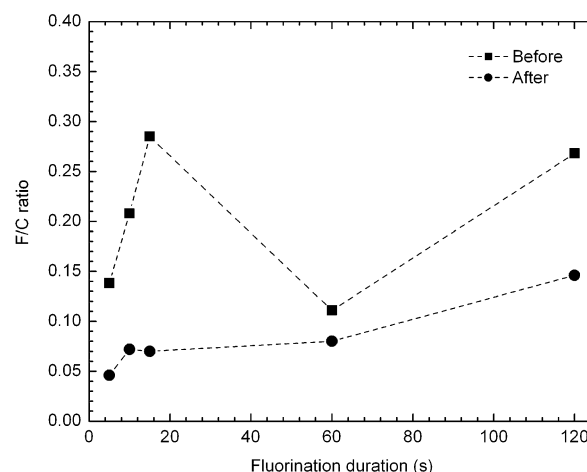

Figure 3. F/C ratios of the F-SWNTs before and after 5 min sonication in excess ethanol at various plasma exposure times.

in the XPS spectra,[9] in contrast to the semi-ionic and covalent mixture for CF_4 functionalized SWNTs.

1,2-Diaminoethane has the capacity to displace fluorine at both −NH_2 ends of the molecule, which we refer to as bifunctionalization. Due to the short length of the 1,2-diaminoethane molecule (5 Å) the extent of bifunctionalization will be dependent on the availability of nearby C—F bonds: a greater degree of bifunctionalization would be expected for nanotubes with more fluorine substituents. The degree of bifunctionalization can be obtained from the N 1s region of the XPS spectra. The secondary amines (NH) at 400.5 eV are a product of the reaction of 1,2-diaminoethane with the F-SWNTs, while the primary amines (NH_2) at 399.5 eV arise from dangling amino groups. Therefore, the ratio of NH/NH_2 gives a measure of bifunctionalization. Figure 4a confirms the expected increase in the NH/NH_2 ratio with increasing fluorine content. For monofunctionalized SWNTs, one fluorine atom gives two nitrogen atoms (Scheme 1). For bifunctionalized SWNTs, two fluorine atoms are converted to two nitrogen atoms. Since bifunctionalization increases with increasing fluorine content, the relative nitrogen content ought to decrease: as observed (Figure 4b). We suggest intertube bifunctionalization is less likely than reaction with fluorine on the same nanotube because of the well-dispersed nature of the nanotube suspensions and the harsh amino functionalization reflux conditions. However, we note that for highly bundled nanotubes the intertube reaction may contribute since the distance between bundled nanotubes is minimal compared to the length of 1,2-diaminoethane.
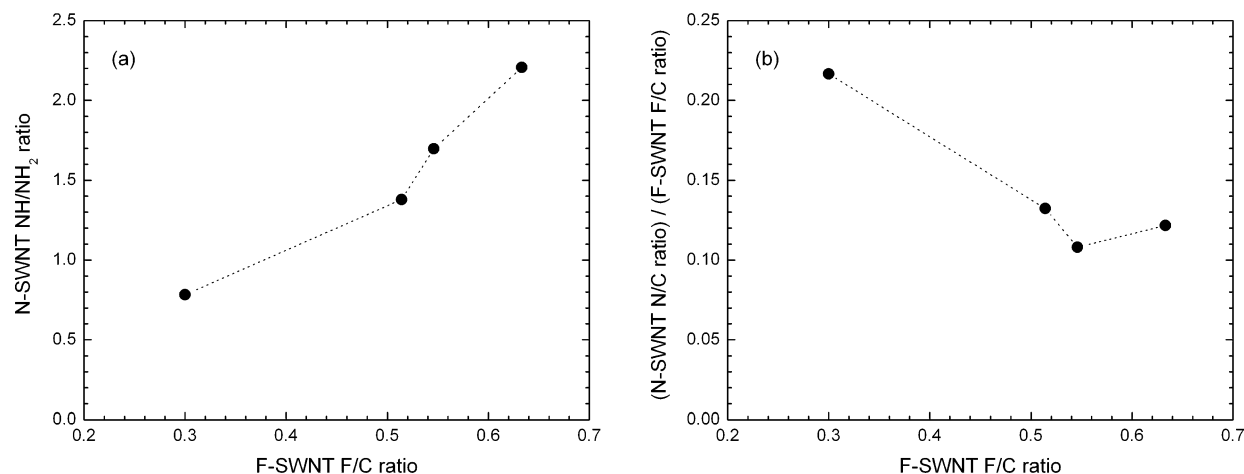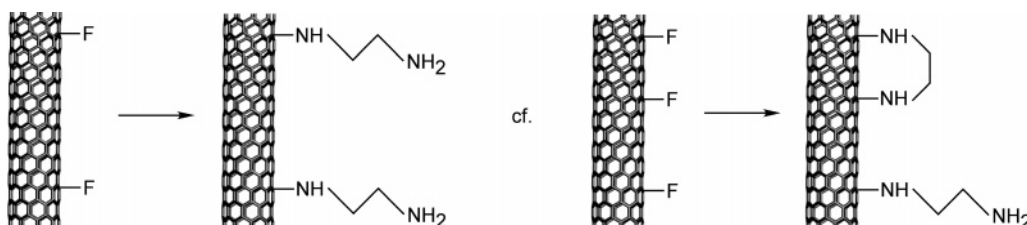
Letters

J. Phys. Chem. B, Vol. 109, No. 47, 2005 **22099**

Figure 4. (a) N-SWNT ratio of secondary (NH) to primary (NH$_2$) amines plotted against the corresponding F-SWNT F/C ratio. (b) Plot illustrating the decrease in nitrogen content of N-SWNTs relative to the original fluorine content of F-SWNTs.

SCHEME 1:   Bifunctionalization at Increased Fluorine Contents

The primary goal of the amino-functionalization has been to produce n-type SWNT−FET devices. It is a common feature of carbon nanotube electronics that the unreliability of SWNT suspensions limits the reproducibility of device behavior.[18,19] Metallic conduction in SWNT devices is often thought to be caused by the dominating presence of metallic tubes in a semiconducting/metallic SWNT bundle. A technique known as "burnoff" is regularly used, whereby the application of a large current to a SWNT device can selectively destroy the metallic tubes.[18,19] Electrical characterization was carried out as follows. A source−drain voltage was applied from −5 V to +5 V at a spacing of 100 mV and, at each source−drain voltage, the gate voltage was altered from −5 V to +5 V at a spacing of 1 V. The variable order was then altered with the gate voltage swept at 100 mV spacing from −5 V to +5 V and, at each gate voltage, the source-drain voltage from −2.5 V to +2.5 V with 500 mV spacing. Devices that showed no gate voltage dependence were still metallic ("burnoff" was incomplete), and the source−drain voltage was reswept and then increased to −7.5 V to 7.5 V and higher until "burnoff" occurred, or in some cases complete breakdown of the devices.

Shown in Figure 5 is the drain current as a function of source−drain voltage (V_{ds}) and gate voltage (V_g) for the F-SWNTs (20 and 60 s exposed) and corresponding N-SWNTs. The F-SWNTs show no n-type effects and only p-type conduction. The N-SWNTs show decreased conduction as a function of both V_{ds} and V_g, in comparison to the F-SWNTs. Decreased conduction is the first stage of n-doping.[3,5,6,20] The N-SWNTs in Figure 5d also show a decrease in drain current compared to the p-type devices, as well as a slight increase in conductance at positive gate voltages. Each device is unique as a result of the distribution of tube diameters and bundling of the SWNTs between the electrodes. The conduction of both the F-SWNT and N-SWNT devices varies across each sample of functionalized SWNTs, which is likely to be due to statistical differences in the initial suspensions of the SWNTs changing the average

properties of each bundle. Shown in Figure 6 is a typical bundle of SWNTs bridging the electrodes. As seen in the figure, many SWNTs can form a single bundle, and it is difficult to know precisely how many SWNTs were laid between any given pair of electrodes.

The 20 s plasma exposed device post amino functionalization shows a strong metallic leakage path. However, there is still a field-dependent effect at positive V_g, indicative of n-type device behavior. Such n-type FET behavior can be attributed to the successful donation of electrons from the amino groups observed in the XPS spectra. n-Type doping by nitrogen-containing substituents has been observed by other groups[3−5,7,21] and attributed to electron donation.

Promisingly, the general trends for p-type and n-type behavior were seen across several devices on the same chip for F-SWNTs and N-SWNTs, respectively. Considering all four F-SWNT samples, as the fluorine content increased the F-SWNT devices became, on average, more metallic in behavior and likely to break down instead of burning off. The 10 s sample could easily be burnt off to show p-type semiconducting behavior, as is expected for SWNTs in air. At 40 s plasma exposure, the devices tended to break down rather than burn off, with little gate voltage dependent effects observed (the 40 s exposed sample showed the highest F/C ratio in Table 1, passing the structural breakdown stoichiometry). The n-type behavior is more pronounced for the 20 and 60 s plasma exposed N-SWNTs. The 40 s N-SWNT sample again produced devices that break down rather than displaying field-dependent characteristics. The atomic nitrogen to fluorine (N/F) ratio is highest for the 20 s device which shows n-type behavior with a metallic leakage path. The degree of bifunctionalization has also increased with increasing N/F ratio, further enhancing the n-type behavior of the devices.

The devices made here are comparable to those observed in the literature under weakly functionalized conditions.[3−5,7,21] The observed decrease in the conduction with the amino functionalization is in agreement with the gate-dependent characteristics
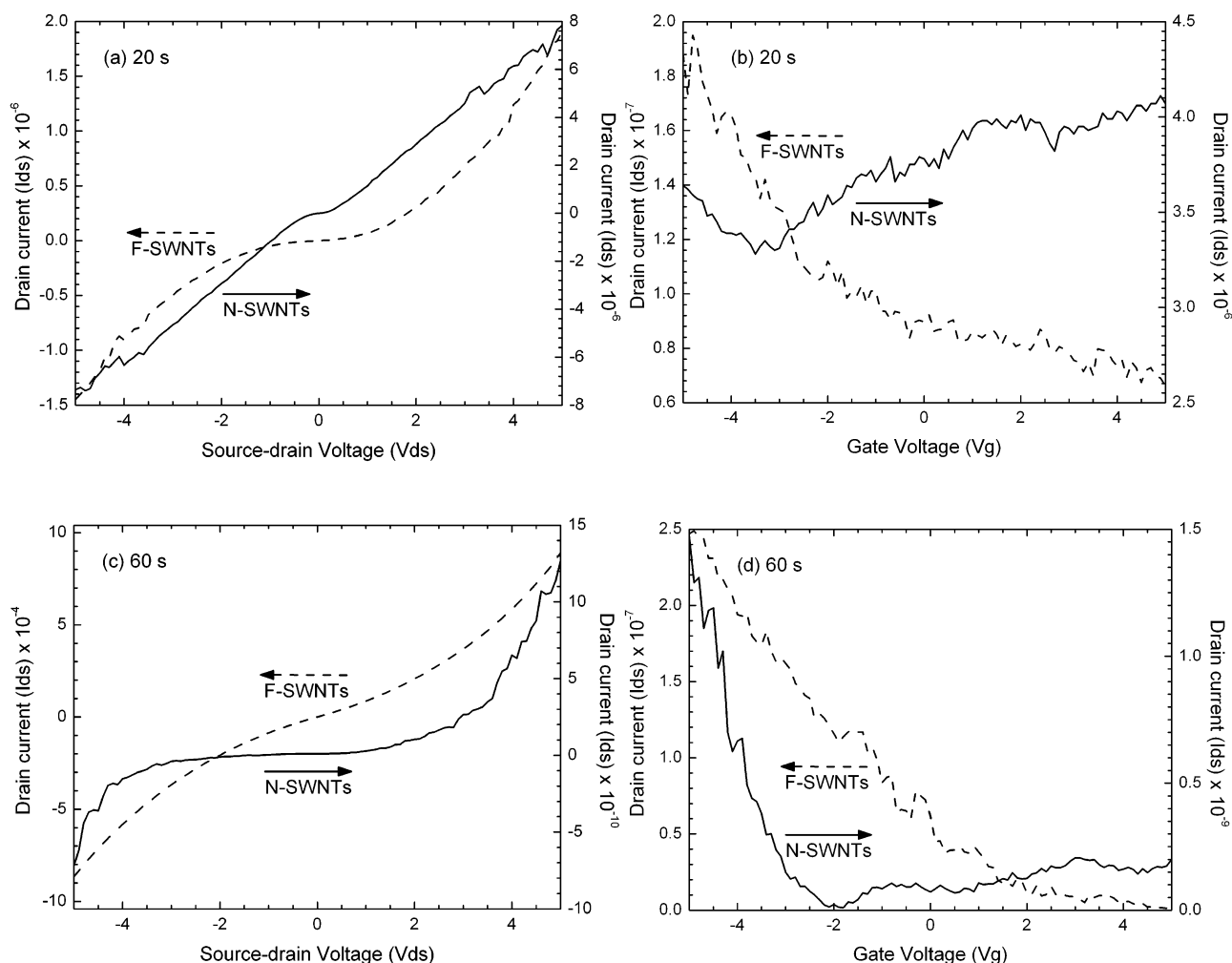
Figure 5. (a,c) Drain current vs source−drain voltage for F-SWNTs and N-SWNTs. (b,d) Drain current vs gate voltage for F-SWNTs and N-SWNTs.
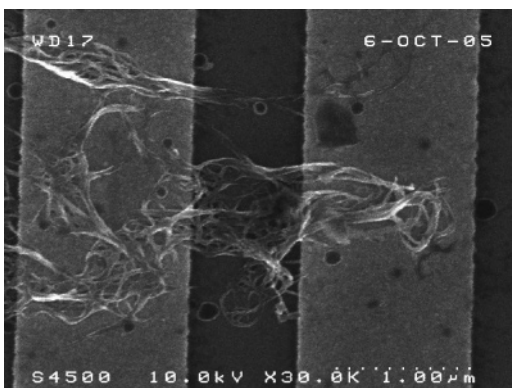

Figure 6. SEM images of bundles of SWNTs between electrodes for the CF$_4$ 60s plasma exposed sample.

shown by Valentini et al.,[6] although the gate-dependent effects are greater for both F-SWNT and N-SWNT devices produced here. In particular, this can be attributed to the thickness of the gate oxides used. Our gate oxide is 50 nm (although thick by comparison to state-of-the-art silicon-based devices), whereas the Valentini group used 250 nm thick thermal oxide, which would cause a smaller gate dependence over the ranges swept. Moreover, the plasma bias voltages used here were low at −30 V in comparison to the −200 V used by the Valentini method, thus we expect a reduction in plasma-induced defects.

The relationship between the dopants and the SWNTs will be somewhat complicated by the presence of atmospheric

oxygen. Since measurements were taken in air, with no annealing stage, the charge carriers on the SWNTs and the SWNT/electrode interface will be affected by the influence of atmospheric oxygen. Other groups have found a combination of chemical doping and contact annealing with thin (approx. 5 nm) gate oxides highly successful for producing SWNT n-type devices with excellent characteristics.[20] The noise observed on the drain current for our devices may indicate the creation of defect sites on the SWNTs. Also, when conduction takes place through a network of SWNTs, electrons and holes may have to overcome potential barriers from neighboring SWNTs and the functional groups. Finally, for the devices produced here the effect of the nanotube/electrode contacts will be important, particularly as the functionalization level is relatively low.[7] However, the change in observed n-type behavior with N/F ratios suggests that the behavior of the functionalized SWNT devices can be controlled.

In summary, substitution reactions of 1,2-diaminoethane onto CF$_4$ plasma-fluorinated SWNTs have been achieved. Our major finding is that the extent of functionalization is dependent on the initial fluorination of the SWNTs, which can be controlled in the initial plasma exposure stages. Further experiments are required to determine preferences for amino substitution at semi-ionic or covalent fluorine sites. Evidence of reaction at both ends of 1,2-diaminoethane (bifunctionalization) has been observed, where the ratio of primary to secondary amines has increased. Bifunctionalization has been shown to depend on the availability of nearby fluorine. Back-gated SWNT devices show

Letters

J. Phys. Chem. B, Vol. 109, No. 47, 2005 **22101**

altered gate dependence between p-type (F-SWNTs) and n-type (N-SWNTs), due to electron donation from the amino groups: the degree of doping can be largely controlled by the combined CF_4 plasma/amino-functionalization treatment. However, the statistical differences in the SWNT solution dispersed onto the electrode structures are a limiting factor to these results. It is proposed that further experiments and use of molecular stamping and self-assembly techniques developed in other work by the group will aid the uniformity of SWNTs in any given device.[22]

In conclusion, the plasma fluorination and amino-functionalization process developed is a useful and expedient first step to create n-type SWNT devices. Fluorine content can be controlled by CF_4 plasma exposure time and nitrogen content has been shown to depend on initial fluorine content.

Supporting Information Available: XPS spectra (fluorine region) of F-SWNTs. Raman spectra of pristine SWNTs, F-SWNTs, and N-SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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