Polymer Functionalization for Air-Stable n-Type Carbon Nanotube Field-Effect Transistors

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Miniaturization by bottom-up approaches to length scales beyond the current semiconductor processing technology has generated tremendous research efforts in the areas of synthesis, characterization, and assembly of novel nanoscale materials such as quantum dots and wires.[1,2] Single-walled carbon nanotubes (SWNTs) are one-dimensional (1D) molecular wires ideally suited for elucidating basic phenomena in 1D and could play important roles in building miniaturized devices.[3] For instance, it has been shown that field effect transistors (FETs) can be constructed by using individual semiconducting SWNTs,[4] opening up the possibility of building more complex electronic architectures with molecular wire elements.

Widely known is that obtaining both p- and n-type materials and controlling their charge carrier densities are crucial to the current microelectronics. With SWNTs, an interesting phenomenon has been that tube-FETs under ambient conditions are always p-type with holes as the majority carriers. This has recently been revealed to be due to electron withdrawing by O_2 molecules adsorbed on SWNTs.[5] The ability to tune SWNTs into both n- and p-type should be important to their applications in molecular electronics. A classical approach to n-type electron-rich carbon materials is via charge-transfer doping with alkali metals.[6] Indeed, potassium doping has led to n-type SWNT FETs and enabled the derivation of more complex devices such as intra-tube p−n junctions with interesting electronic functions.[3b,7] However, alkali dopants suffer from immediate degradation upon exposure to air, making them undesirable for n-doping of SWNTs in practical device applications.

Recently, controlled exposure of SWNTs to inorganic (NH_3, NO_2)[5] and organic molecules (amines)[7] has revealed the extreme sensitivity of the electrical properties of semiconducting SWNTs to molecular species, and has suggested the possibility of building ultra-sensitive nanosensors. Such sensitivity also hints at a new method of tuning charge carriers in SWNTs by mere adsorption of molecules with suitable functional groups. Rather than a complete ionization of each donor or acceptor as in alkali or halogen doping, partial electron donating or accepting by adsorbed molecular functional groups could be exploited to vary charge carriers in SWNTs. After all, from a theoretical point of view, a doping fraction (number of charges per carbon atom) of $\sim 10^{-3}$–10^{-4} is sufficient to shift the Fermi level into the conduction band of a typical semiconducting SWNT, yielding a highly n-doped system.[3b,8]

In this Communication, we introduce a new concept of n-doping of carbon nanotubes by functionalization of SWNT sidewalls with polymers. Nanotube/polymer systems have received much attention recently for light emitting diodes[9] and solubilizing nanotubes.[10,11] Here, we show that functionalization of SWNTs by amine-rich polymers leads to the evolution of SWNTs from p-type to n-type. Thus, doping by functional groups of irreversibly adsorbed polymers on nanotubes presents a novel and simple means of changing the doping level of molecular wires. For the first time, we obtain n-type FETs based on individual nanotube wires that are stable in air without resorting to sealing the nanotubes in a vacuum or an inert environment.

Individual SWNT FETs were obtained by patterned chemical vapor deposition on SiO_2/Si substrates and a controlled integration step described earlier.[12,13] The sample was submerged in a 20 wt % solution of polyethylene imine (PEI, average molecular weight ~25 000, Aldrich chemicals) in methanol overnight, followed by thorough rinsing with methanol. This removed PEI nonspecifically adsorbed on the sample surface, leaving nearly a monolayer of PEI irreversibly adsorbed on SWNTs as described below.

Figure 1 shows the drastically altered electrical characteristics of a SWNT device after PEI adsorption recorded under ambient conditions. Prior to PEI adsorption, the as-made semiconducting SWNT exhibits p-type FET characteristics revealed by the decreasing conductance as a gate voltage (V_g) is stepped to more positive values (Figure 1a). The p-type behavior is also clear from the current vs gate ($I-V_g$) data (lower inset of Figure 1a), as positive V_g shifts the Fermi level away from the valence band into the band gap of the nanotube, thus depleting hole carriers in the system. The p-type behavior is due to adsorbed O_2 from the ambient and each O_2 molecule withdraws ~1/10 of an electron from the SWNT.[14] After PEI adsorption, the SWNT exhibits clear n-type FET characteristics. The conductance of the system increases when V_g is stepped to more positive values (Figure 1b). This is completely opposite to the behavior prior to PEI modification of the nanotube (Figure 1a).

The results above are highly reproducible with 10 independent SWNT FETs and lead to several important conclusions. First, PEI irreversibly adsorbs onto the sidewalls of SWNTs. Extensive rinsing of the sample cannot remove PEI completely from the nanotubes. This is consistent with a recent finding of irreversible polymer wrapping around SWNTs for solubilizing nanotubes in water.[10] Second, the adsorbed PEI is capable of and responsible for n-doping of SWNTs. Furthermore, n-doping by PEI can readily overcome p-doping effects of O_2, leading to stable n-type FET behavior in air. The highly efficient n-doping by PEI is explained by the electron-donating ability of amine groups in the polymer and the fact that PEI contains one of the highest densities of amine groups among all polymers. The electron donation resembles that by ammonia[5a] and alkyl-amines[7] adsorbed on SWNTs, causing hole-depletion in p-type SWNTs. The high density of electron donating amine functionalities in PEI brings about significant n-doping to a point where the adverse effect of p-doping by O_2 adsorption is overcome.

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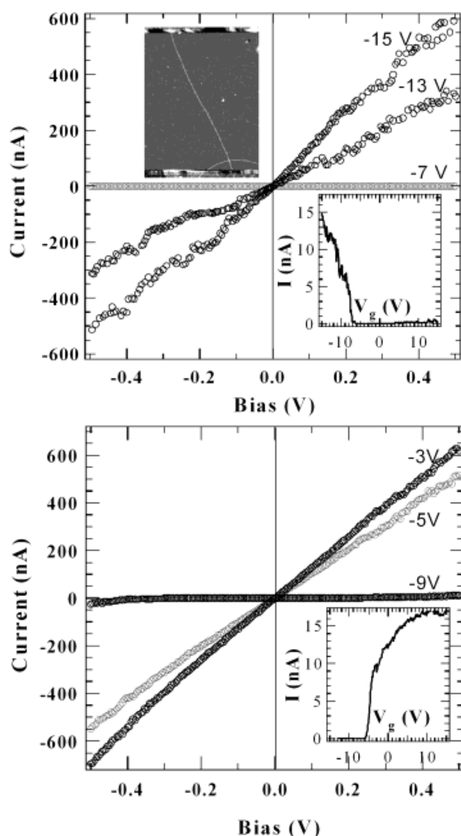

Figure 1. Current versus voltage characteristic of SWNTs before (a) and after (b) PEI functionalization. The lower right insets are the corresponding current versus gate voltage plots measured at 10 mV bias. The upper left inset in part a is an AFM image (2 × 3 μm) of the actual SWNT device.

We have estimated the doping-fraction by PEI using the FET characteristics of the n-type SWNTs. From the V_g at which electron depletion occurs and the capacitance of the gate estimated following ref 15 the doping fraction is calculated to be $\sim 5 \times 10^{-3}$ for the sample in Figure 1b. The doping fractions range from 1×10^{-3} to 6×10^{-3} for 10 independent samples, significantly high to shift the Fermi level into the conduction band of a SWNT. Noteworthy is that transmission electron microscopy studies reveal roughly a monolayer of amorphous PEI coating on the SWNTs after dip-coating and thorough rinsing with solvents. The thin layer of PEI, albeit not uniform at the molecular scale, is responsible for the observed drastic n-doping effect.

Importantly, the PEI functionalized nanotubes exhibit excellent n-type FET characteristics. The conductance of the n-type SWNTs is typically comparable to that of p-type SWNTs (insets of Figure 1a,b). Further, electron mobility in the n-FETs is high. For the sample shown in Figure 1b, the transconductance, dI/dV_g, is 4×10^{-9} A/V in the linear $I-V_g$ regime. Under a source-drain bias voltage of 10 mV, we estimate the electron mobility μ_e to be $\sim 6 \times 10^2$ cm^2/V•s.[15] The highest electron mobility measured in our samples is $\sim 8 \times 10^3$ cm^2/V•s, higher than that of heavily doped n-Si[16] and p-type tube FETs[15] obtained previously. These results strongly suggest that PEI functionalization of SWNTs represents a novel chemical doping approach to high-performance n-type molecular-wire FETs.

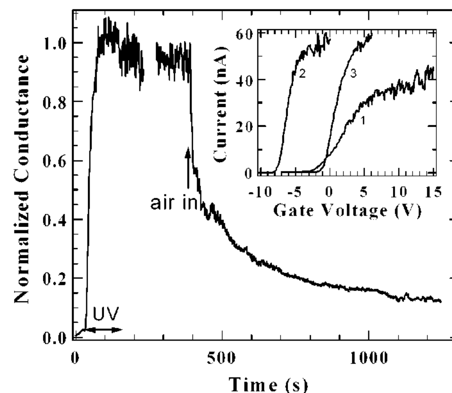

Figure 2. Normalized conductance without an applied gate voltage as PEI-coated SWNT is exposed to UV (maximum intensity at 254 nm) and when air is allowed back in. The corresponding $I-V_g$ plots of the SWNT device as prepared (curve 1), UV-exposed under Ar (curve 2), and reexposed to air (curve 3) are shown in the inset.

It is shown recently that exposure of SWNTs to ultraviolet (UV) light can lead to efficient molecular photodesorption from SWNTs.[17] We find that photodesorption of O_2 from PEI-coated SWNTs renders nanotube FETs to higher n-doping levels. Figure 2 shows that the conductance of a PEI coated nanotube n-FET increases upon UV illumination. This is due to an increase in electron density upon photoremoval of O_2 adsorbed on the nanotube prior to PEI functionalization. The increased n-doping is also clearly observed in the evolution of $I-V_g$ characteristics of the sample (inset of Figure 2). The doping fraction increases from $\sim 2 \times 10^{-3}$ (curve 1) to $\sim 6 \times 10^{-3}$ (curve 2) with an increase in electron mobility from $\sim 1 \times 10^3$ to $\sim 4 \times 10^3$ cm^2/V•s upon photoremoval of O_2. When reexposed to O_2, the conductance and $I-V_g$ of the sample exhibit incomplete recovery, indicating readsorption of O_2 onto the PEI-coated SWNTs but to a lesser degree, presumably due to blocking effects of PEI. The nanotube exhibits excellent n-FET characteristics that remain stable under ambient conditions.

We have demonstrated a new scheme for n-doping carbon nanotubes by polymer functionalization. Unlike the classical alkali metal approach, doping by functional groups leads to air-stable n-type SWNT FETs. Such devices are expected to facilitate the development of miniature electronics based on nanotube molecular wires. With the abundance of organic molecules and polymers and a wide range of electron-donating and -withdrawing functional groups attached to them, functionalized nanotubes could play an important role in shaping nanoelectronics.

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