

Full and Modulated Chemical Gating of Individual Carbon Nanotubes by Organic Amine Compounds

Jing Kong and Hongjie Dai*

Department of Chemistry, Stanford University, Roth Way, Stanford, California 94305

Received: December 31, 2000; In Final Form: February 26, 2001

The adsorption of several types of alkylamine molecules on individual semiconducting and metallic single-walled carbon nanotubes is investigated by electrical transport measurements. The electrical conductance of semiconducting nanotubes changes drastically upon adsorption of butylamine and 3'-(aminopropyl)-triethoxysilane in the vapor phase. The amine groups in the molecules are electron donating and responsible for charge transfer to the semiconducting nanotubes, and thus, the observed electrical conductance change. Molecular adsorption on metallic single-walled nanotubes causes no significant change in the electrical conductance of the nanotube samples, consistent with earlier finding that the electrical properties of metallic nanotubes are relatively insensitive to molecular adsorption. Adsorption of the amine compounds on partial lengths of semiconducting nanotubes causes modulated chemical gating and intramolecular wire junctions that exhibits pronounced rectifying diode behavior. The physisorbed amine molecules desorb from nanotubes typically in 12 h, restoring the nonrectifying characteristics of the samples. Cross-linking of the hetero-functional 3'-(aminopropyl)triethoxysilane molecules on partially exposed nanotubes via siloxane bridges leads to permanent intranotube rectifiers.

Molecular adsorption effects to the electrical properties of single walled carbon nanotubes (SWNTs) are of fundamental interest and importance to potential nanotube molecular electronics and sensors.^{1–3} Because a SWNT has every atom on its surface, surface effects could be critical to the manifestation of its physical properties. It is known that semiconducting SWNTs are extremely sensitive to electrical gating, exhibiting orders of magnitude conductance change under various electrostatic gate voltages.^{2,4–6} Drastic electrical property changes of semiconducting nanotubes due to charge transfer caused by adsorbed molecules have also been observed and are referred to as chemical gating effects.² Charge transfer between nanotubes and adsorbed oxidizing (e.g., NO₂, O₂) or electron donating molecules (e.g., NH₃) can increase or decrease hole carriers in semiconducting nanotubes, thus significantly affecting the electrical conductance of the nanotubes.^{2,3} On the basis of this observation, several groups have suggested the application of nanotubes as miniature chemical sensors.^{2,3} Metallic SWNTs on the other hand, are relatively insensitive to molecular adsorption and chemical gating, since charge transfer does not significantly affect the charge density at the Fermi level.²

Electrical measurements of individual SWNTs with potassium atoms adsorbed on the nanotubes surfaces have been carried out.^{7–10} The electron donating power of potassium is dramatically greater than small molecules. Potassium doping can convert as-grown semiconducting SWNTs from p-type to n-type.^{8–10} The electrical conductance of individual metallic SWNTs, however, is not affected significantly by potassium adsorption, similar to the case of small molecule adsorption on metallic nanotubes. Recently, we have devised a strategy to adsorb potassium atoms on part of the length of a semiconducting SWNT. This approach, referred to as modulated chemical doping, creates a doping profile along the length of a single-nanotube by design, and leads to intramolecular wire pn junctions exhibiting negative differential conductance similar to conventional Esaki diodes.¹⁰

Although weaker than common dopants for carbon materials including potassium, the chemical gating effects of small molecules to semiconducting SWNTs are far from negligible. This letter presents an investigation of the adsorption of small amine-containing organic molecules on nanotubes, and modulated chemical gating of individual semiconducting SWNTs by these molecules. The electron donating power of the adsorbed –NH₂ groups is found to be sufficient to cause significant change in the electrical conductance of nanotubes. Partially exposed nanotubes develop on-tube junctions and become electrical rectifying diodes. Molecular desorption from nanotubes can be prevented by polymerizing hetero-functional molecules adsorbed on nanotubes in the gas phase. This leads to nanotube-organic hybrid electronic devices.

Electrical devices of individual SWNTs were obtained by chemical vapor deposition growth of SWNTs on catalytically patterned SiO₂ substrates followed by metal contacting of the nanotubes using microfabrication techniques.^{11,12} On a typical 1 × 1 cm² SiO₂ substrate, the growth and integration approach yields about 10 two-terminal individual nanotube devices (Figure 1 a). We identified the metallic or semiconducting nature of SWNTs in the devices by measuring their room temperature electrical conductance under various gate-voltages applied to the underlying heavily doped Si substrate (Figure 1). A semiconducting SWNT was identified when the conductance of its device exhibits large variations with gate-voltage.^{2,4–6} A metallic SWNT is identified when its conductance exhibits little change under various gate-voltages. The SWNT was either exposed along their length for full molecular adsorption (Figure 1b) or partially covered by poly(methyl methacrylate) (PMMA) for modulated chemical gating (Figure 1c). In the latter case, only the exposed part of the nanotube allowed for molecular adsorption. The PMMA covered tube length is blocked from molecules.¹⁰

Butylamine (CH₃(CH₂)₃NH₂, 99.5%), 3'-(aminopropyl)triethoxysilane (APTES, NH₂(CH₂)₃Si(OEt)₃, 99%) and propyl-

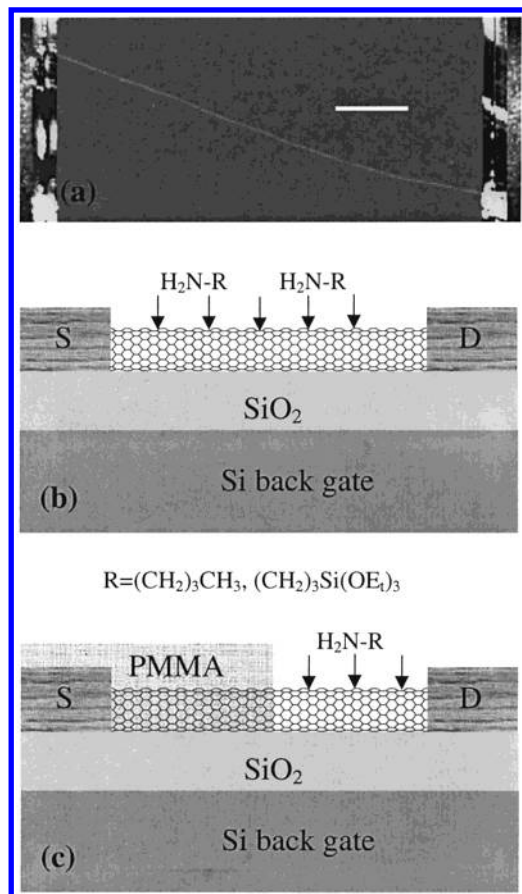


Figure 1. (a) Tapping mode atomic force microscope image of a SWNT device. The nanotube is contacted by two Ti/Au electrodes (regions at the two ends of the image). Scale bar: 500 nm. (b) Scheme for molecular adsorption on the full length of a SWNT and electrical measurements. The SiO₂ layer is 500 nm thick. (c) Scheme for molecular adsorption on the partial length of a SWNT. The nanotube segment without PMMA coverage is exposed for adsorption.

amine (CH₃(CH₂)₂NH₂, 99%) were purchased from Aldrich Chemicals. Propyltriethoxysilane (CH₃(CH₂)₂Si(OEt)₃, 99%) was obtained from Gelest Inc. These chemicals are liquids at room temperature.

Adsorption of the organic molecules on SWNT devices was carried out under ambient conditions by exposing the sample to the vapor of the molecules. This was done by simply placing the sample at the opening of a vial containing a chemical, with the sample facing the interior of the vial. Typically, the sample was exposed to the molecules for 1 min. The electrical characteristics (e.g., current vs voltage curves under various gate-voltages) of the SWNT devices were recorded before and after exposure to the molecules.

Cross-linking APTES molecules on nanotube device samples was carried out using a method similar to gas-phase silylation.¹³ A drop of APTES was placed next to a sample in a bottle. The bottle was sealed and then heated in an oven at 100 °C for 24 h. SWNTs grown directly on a grid by chemical vapor deposition¹⁴ was also placed inside the bottle and used for transmission electron microscopy (TEM) imaging of nanotubes after the cross-linking reaction.

Devices of as-grown semiconducting SWNTs exhibited p-type characteristics with hole-conduction, as reported previously.^{2,6} Upon butylamine adsorption, semiconducting SWNTs showed drastically reduced conductance as seen from current vs bias voltage (*I* vs *V*) curves (Figure 2a) under the same gate-voltage

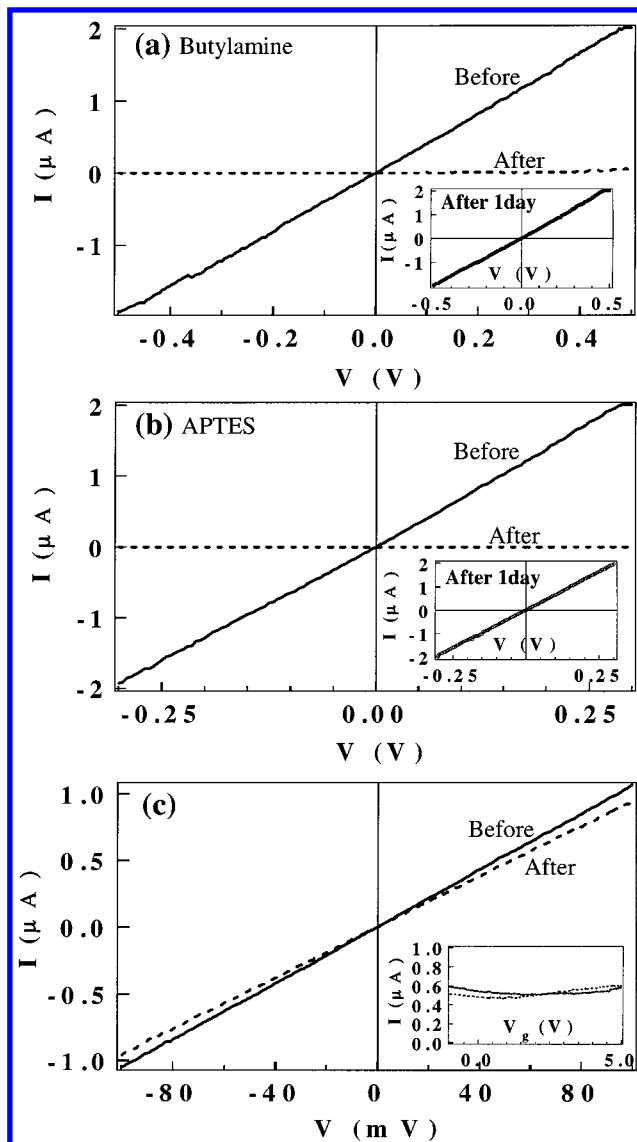


Figure 2. (a) *I*-*V* curve recorded for a semiconducting SWNT device before and after the exposure to butylamine vapor. Inset: *I*-*V* curve recorded 1 day after butylamine adsorption. (b) *I*-*V* curve recorded for a semiconducting SWNT device before and after exposure to APTES vapor. Inset: *I*-*V* curve recorded 1 day after APTES adsorption. (c) *I*-*V* curves recorded with a metallic SWNT before and after exposure to the butylamine vapor. Inset: *I*-*V_g* curves recorded before (solid curve) and after (dashed curve) butylamine adsorption, showing insensitivity of metallic tubes to electrical and chemical gating.

(*V_g*) recorded before and after adsorption. Similar effect was observed in the case of adsorption of APTES molecules on semiconducting SWNT sample (Figure 2b). As control experiments, we exposed samples of as-grown SWNTs to propyltriethoxysilane, and observed no obvious change in their *I*-*V* characteristics after adsorption of propyltriethoxysilane (data not shown). These results showed that the amine groups on butylamine and APTES are responsible for chemical gating of nanotubes. Electron donation by the amine groups of the adsorbed molecules reduces hole-carriers in p-type SWNTs and therefore decreases the conductance of the samples.

The adsorption of the amine molecules on SWNTs is strong physisorption and weak chemisorption in nature. Desorption occurs as signaled by the full recovery of the *I*-*V* characteristics of the nanotube samples after typical $\Delta t \approx 12$ h of nanotube exposure to the molecules (Figure 2a,b, insets). Using the transition state theory,¹⁵ $1/\Delta t = f \times \exp(-E_b/K_B T)$, where $f \approx$

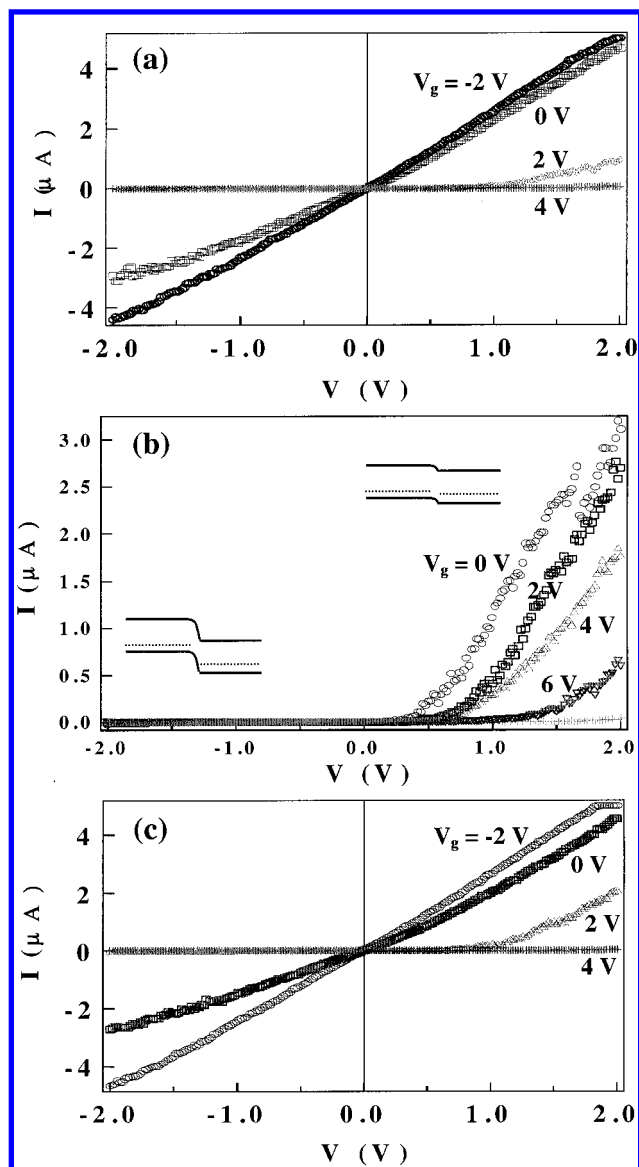


Figure 3. (a) I–V characteristic of a SWNT partially covered with PMMA before exposure to APTES vapor under various gate-voltages. (b) Highly rectifying I–V curves recorded after APTES adsorption. Inset: schematic diagrams showing the intra-tube p/p(–) junction under forward (right diagram) and reverse biases (left diagram). (c) I–V characteristics measured 1 day after exposure to APTES resemble these in (a), signaling that molecules have desorbed from the nanotube.

$10^{13}/\text{s}$ is the typical molecular vibration frequency, we estimate that the binding energy between the molecules and SWNTs is $E_b \approx 1 \text{ eV} = 23 \text{ kcal/mol}$.

The electrical characteristics of metallic SWNTs remain unchanged after exposure to the amine molecules (Figure 2c). This is consistent with previous results that the conductance of metallic nanotubes is insensitive to adsorbed chemical species including potassium, NO_2 and NH_3 ,² relative to semiconducting tubes. This is because that the electronic density of states of metallic SWNTs is nearly a constant over a large energy scale ($\sim 2 \text{ eV}$).¹⁶ Small shift of the Fermi level due to charge transfer does not significantly affect the carrier density in metallic nanotubes.

We have exploited the chemical gating effects of organic amines to obtain intramolecular junctions by partial exposure of semiconducting SWNTs to the molecules. The I–V characteristics of semiconducting SWNTs partially covered by PMMA are symmetrical under most gate-voltages (Figure 3a) prior to

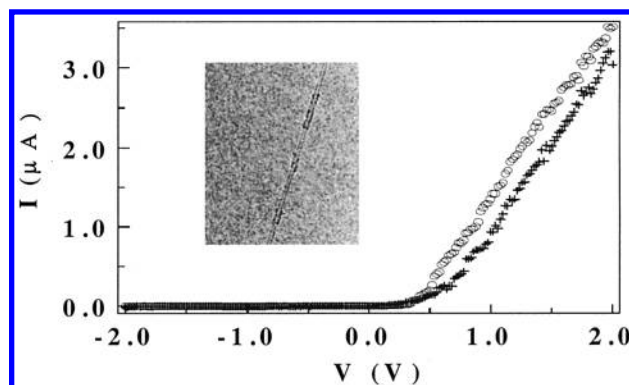


Figure 4. SWNT diode with APTES molecules cross-linked on the partial length of a nanotube. The two rectifying I–V curves were recorded several days apart 3 weeks after the cross-link reaction under the same gate voltage $V_g = -12 \text{ V}$. Inset: A TEM image showing the cross-linked APTES coating on the nanotube surface.

molecular adsorption. After adsorption of butylamine or APTES on part of the lengths of SWNTs, the devices exhibit pronounced rectifying behavior (Figure 3b). In the exposed part of the nanotube, the adsorbed molecules cause a shift of the Fermi level toward the conduction band by electron donation, leading to a p/p(–) junction in the nanotube. The rectifying mechanism is similar to that of a conventional pn junction.¹⁷ Current flows as forward bias lowers the potential barrier across the junction and is diminished under reverse bias as the potential barrier across the junction increases (Figure 3b insets). The intratube diodes formed by vapor phase amine adsorption on modulated SWNT devices revert to the mostly symmetrical I–V characteristics and become nonrectifying (Figure 3c) upon full desorption of the physisorbed molecules in 12–24 h.

Permanent intra-SWNT rectifying diodes are obtained by cross-linking APTES on nanotubes and thus irreversibly anchoring amine groups on nanotubes. The cross-link reaction takes place at 100°C in air where water molecules are present. The APTES molecules adsorb onto SWNTs in the vapor phase. At the elevated temperature, the ethoxy groups are hydrolyzed and polymerization of APTES molecules occurs via the formation of $-\text{O}-\text{Si}-\text{O}-$ siloxane bonds. Such reactions with modulated semiconducting SWNT devices lead to permanent intra-tube rectifier. Rectifying I–V characteristics of the devices persist under ambient conditions weeks after the reactions (Figure 4). The I–V curves measured under a given gate-voltage are stable with only small drifts as a function of time (Figure 4). Notably, it is known that $-\text{NH}_2$ groups can react with CO_2 in air to form carbamate (NH^+CO_2^-) after extended period of time (e.g., days). In our case, SWNTs modulation gated by the cross-linked APTES exhibit no significant change in the rectifying I–V characteristics in air for long times. This points to negligible effect of ambient CO_2 molecules to the electrical properties of the SWNT-amine diodes. A likely reason could be that the amine groups are mostly associated with the SWNTs and thus inaccessible for the carbamate reaction.

We have characterized the structures of SWNTs with cross-linked APTES on the sidewalls by TEM. Whereas the as-grown SWNTs are nearly molecularly clean with no amorphous materials observed on the sidewalls, the nanotubes that have undergone the cross-link reactions show thin amorphous coating (Figure 4 inset). The coating does not appear very homogeneous. Nevertheless, the TEM data prove that condensed polymeric materials are irreversibly anchored onto the sidewalls of SWNTs.

SWNT diodes have been obtained previously by intra-tube hetero-junctions containing topological defects,¹⁸ and by nano-

tube crosses formed by metal-semiconducting SWNTs.¹⁹ Schottky junctions are invoked to explain the rectifying behaviors. It is unclear how to obtain such devices in a controlled fashion. The modulated chemical gating approach presented here is straightforward and can reliably yield intratube junctions exhibiting excellent rectifying characteristics. The rectifiers have been reproduced with five different SWNT samples. The modulated gating by organic amine compounds differ from that by potassium reported earlier.¹⁰ Potassium atoms are highly electron donating, capable of converting p-type SWNT to n-type and forming degenerately doped intratube p/n junctions that exhibit negative differential conductance.¹⁰ Electron donation from organic amine compounds only reduces the p-type characteristics of nanotubes and leads to the formation of p/p(−) rectifying junctions.

In conclusion, full and partial chemical gating effects of organic molecules to SWNTs are studied in the Letter. The fact that amines are electron donating when coupled to other molecules or surfaces is known. With SWNT “molecules”, such effect can be probed by electrical measurements. The molecular interactions with nanotubes are strong physisorption in nature. Theoretical work elucidating the detailed picture of the interactions is currently lacking and called for. Modulated gating of individual SWNTs by organic amines lead to intramolecular rectifying diodes. These results continue to demonstrate that single-walled carbon nanotubes are ideal nanomaterials for chemistry and physics basic studies and have significant potential for building functional devices.

Acknowledgment. We thank Jien Cao for help with the electrical measurements, Dr. Y. Zhang and Dunwei Wang for their TEM work, and Robert Chen for help in the APTES cross-link reaction. This work is supported by NSF, SRC/Motorola,

a Packard Fellowship, a Terman Fellowship, and a Camille and Henry Dreyfus New Faculty Award.

References and Notes

- (1) Dai, H. *Phys. World* **2000**, 13, 43–47.
- (2) Kong, J.; Franklin, N.; Zhou, C.; Chapline, M.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, 287, 622–625.
- (3) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science* **2000**, 287, 1801–1804.
- (4) Tans, S.; Verschueren, A.; Dekker, C. *Nature* **1998**, 393, 49–52.
- (5) Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, P. *Appl. Phys. Lett.* **1998**, 73, 2447–2449.
- (6) Zhou, C.; Kong, J.; Dai, H. *Appl. Phys. Lett.* **1999**, 76, 1597.
- (7) Lee, R. S.; Kim, H. J.; Fischer, J. E.; Lefebvre, J.; Radosavljevi, M.; Hone, J.; Johnson, A. T. *Phys. Rev. B* **2000**, 61, 4526–4529.
- (8) Bockrath, M.; Hone, J.; Zettl, A.; McEuen, P. L.; Rinzler, A. G.; Smalley, R. E. *Phys. Rev. B* **2000**, 61, R10 606–R10 608.
- (9) Kong, J.; Zhou, C.; Yenilmez, E.; Dai, H. *Appl. Phys. Lett.* **2000**, 77, 3977.
- (10) Zhou, C.; Kong, J.; Yenilmez, E.; Dai, H. *Science* **2000**, 290, 1552.
- (11) Kong, J.; Soh, H.; Cassell, A.; Quate, C. F.; Dai, H. *Nature* **1998**, 395, 878.
- (12) Soh, H.; Quate, C.; Morpurgo, A.; Marcus, C.; Kong, J.; Dai, H. *Appl. Phys. Lett.* **1999**, 75, 627–629.
- (13) Wikstrom, P.; Mandenius, C. F.; Larsson, P. O. *J. Chromatogr.* **1988**, 455, 105.
- (14) Zhang, Y.; Franklin, N.; Chen, R.; Dai, H. *Chem. Phys. Lett.* **2000**, 331, 35–41.
- (15) Adamson, A. *Physical Chemistry of Surfaces*; John Wiley & Sons: New York, 1990.
- (16) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996.
- (17) Streetman, B. G. *Solid-State Electronic Devices*; Prentice Hall: Englewood Cliffs, New Jersey, 1995.
- (18) Yao, Z.; Postma, H. W. C.; Balents, L.; Dekker, C. *Nature* **1999**, 402, 273–276.
- (19) Fuhrer, M. S.; Nygård, J.; Shih, L.; Forero, M.; Yoon, Y.-G.; Mazzoni, M. S. C.; Joon, H.; Choi, J. I.; Louie, S. G.; Zettl, A.; McEuen, P. L. *Science* **2000**, 288, 494–497.