

Controlled deposition of individual single-walled carbon nanotubes on chemically functionalized templates

Jie Liu, Michael J. Casavant, Michael Cox, D.A. Walters, P. Boul, Wei Lu, A.J. Rimberg, K.A. Smith, Daniel T. Colbert^{*}, Richard E. Smalley

Center for Nanoscale Science and Technology, Rice Quantum Institute, and Department of Chemistry and Physics, Rice University, 6100 S. main Street, Houston, TX 77005, USA

Received 18 January 1999

Abstract

Carbon nanotubes offer great promise as molecular wires because they exhibit high electrical conductivity and chemical stability. However, constructing nanotube-based electronic devices requires a controlled means of assembling the tubes. We report procedures both for producing individual short SWNT segments and for their reliable deposition on chemically functionalized nanolithographic templates. Using this method, we have positioned individual nanotubes at specific locations and orientations in such a way that the nanotubes contact metal electrodes. This discovery is potentially very important for fabrication of simple electrical circuits with nanotubes, and provides a new tool for study of electron transport in nanotubes. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Single-walled carbon nanotubes have been the subject of intensive investigation for their unique electronic properties and potential application in molecular electronic devices [1–9]. Recent studies showed that a single carbon nanotube could be made into a tiny electronic switch [10] and even a room-temperature transistor [11]. In addition, theoretical calculations show that, unlike normal metallic wires in which conduction electrons become localized as the diameter of the wire reaches the nanometer scale, metallic nanotubes possess exceptional ballistic transport properties and long electron mean free paths [12], making nanotubes ideal candidates for

molecular-scale wires. Heretofore there has been no controlled and reliable technique for fabrication of carbon-nanotube-based devices, and nanotube devices have been made by either randomly depositing nanotubes on a electrode array or by pushing a nanotube onto electrodes with a probe microscope (AFM or STM) tip. Neither technique promises to make large numbers of nanotube devices in a reliable way. Recently, Burghard et al. reported controlled adsorption of multiwalled carbon nanotubes on chemically modified electrode arrays [13,14]. However, the degree of control illustrated in the report was still not sufficiently reliable for nanotube device fabrication and characterization. In this Letter, we report a new technology that enables reliable deposition of individual single-walled carbon nanotubes on chemically-functionalized nanolithographic patterns.

^{*} Corresponding author. E-mail: colbert@cnst.rice.edu

This new approach represents an important advance in manipulation of individual single-walled carbon nanotubes and offers promise in making structures and electronic circuits with nanotubes in pre-designed patterns.

2. Experimental

Nanotube material used in this study is prepared using the pulsed laser vaporization method [15,16] and purified by refluxing in 2.6 M HNO_3 [17]. A stable suspension of SWNT in DMF was prepared by sonicating purified SWNT material in N,N-dimethylformamide (Sigma-Aldrich, Milwaukee, WI) in a bath sonicator (Model 08849-00, Cole-parmer, Vernon Hills, IL) at a concentration of ~ 0.1 mg/ml for 15 h. This produces a suspension of nanotube segments with a mean length of ~ 1 μm as determined by AFM examination of dried deposits of the suspension. (We achieved similar results with other similar amide solvents such as NMP (N-methyl-pyrrolidinone).) A self-assembled monolayer with $-\text{CH}_3$ termination was prepared by chemical vapor deposition on oxidized Si samples cut from n-type Si (100) wafers. The samples were first cleaned in (10:1) HF solution and exposed to short-wave UV light in air for 20 min to oxidize the surfaces before being heated with 1 ml hexamethyldisilazane (Sigma-Aldrich, Milwaukee, WI) to 150°C for 5 h in a sealed glass container (200 ml). Then the samples were rinsed with chloroform and *iso*-propanol. After the treatment, sample surfaces became hydrophobic due to complete coverage with a trimethylsilyl (TMS) monolayer. The samples were then subjected to AFM lithography [18,19] or standard e-beam lithography [20,21] to expose patterns on TMS SAM layers. In both cases, the TMS SAM was removed and the SiO_2 underneath was exposed. Typical linewidth of the patterns is between 10–50 nm¹. A second SAM layer was prepared subsequently on the exposed SiO_2 pattern by soaking the samples in 1 mM solu-

tion of 3-aminopropyltriethoxysilane (Sigma-Aldrich) in chloroform for 30 min. The samples were rinsed in chloroform and *iso*-propanol again and blown dry with nitrogen.

Individual single-walled nanotubes were deposited on the chemically patterned surfaces by soaking the Si samples in nanotube solution for 10 min. The samples were rinsed with methanol immediately after being taken out of the SWNT/DMF solution and blown dry with nitrogen. Samples were then characterized with an AFM (Nanoscope III, Digital Instruments, Santa Barbara, CA) in tapping mode to characterize the prepared nanostructures.

3. Results and discussion

The as-grown nanotube material prepared by the laser vaporization method contains nanotubes up to several hundred micrometers long that are joined by van der Waals forces to form ‘ropes’ of 10–1000 individual nanotubes. These nanotube ropes are not suitable for making nanoelectronic devices since they may be made of nanotubes with different electronic

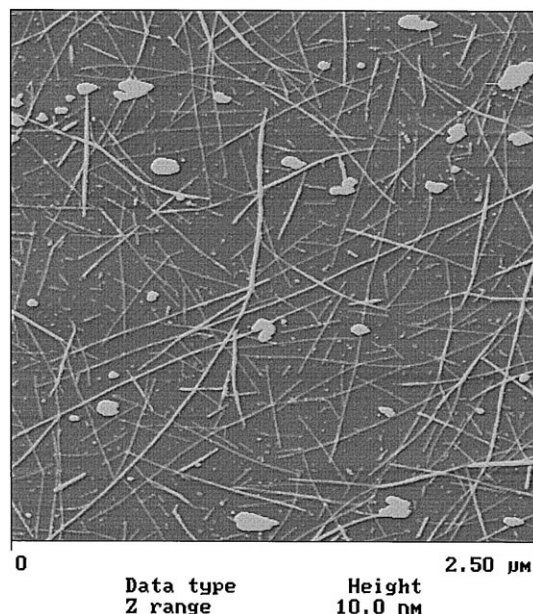


Fig. 1. Tapping mode AFM image of single-walled carbon nanotubes on mica surface. The sample was prepared by drying SWNT suspension in DMF.

¹ The linewidth was measured in the tapping mode AFM phase image. The lines were clearly visible in AFM phase images since the interaction between the destroyed SAM and AFM tip is different from unmodified SAM.

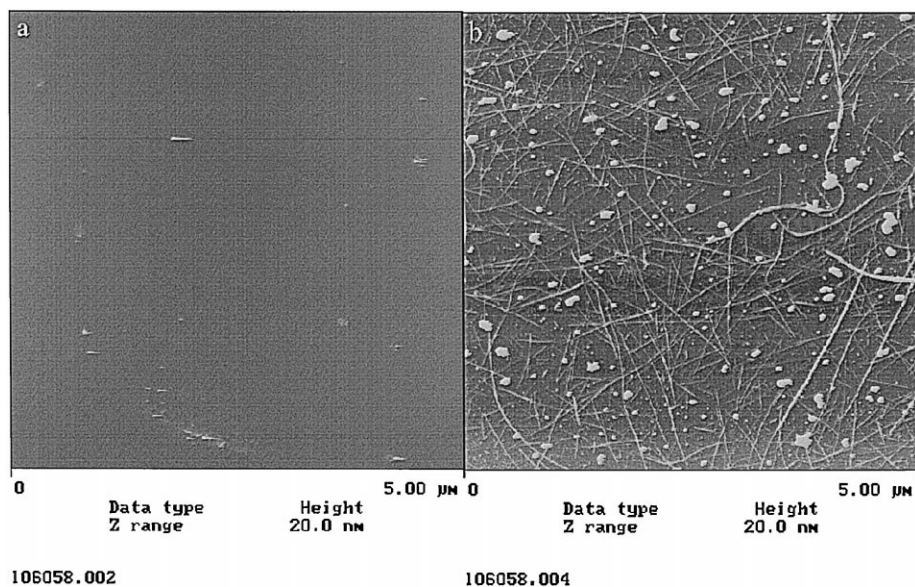


Fig. 2. Tapping mode AFM images of: (a) $-\text{CH}_3$ functionalized SiO_2 surface and (b) $-\text{NH}_2$ functionalized surfaces after soaking in SWNT/DMF suspension for 10 min and rinsing with methanol.

properties. Recently, we have [17] shown that we can purify raw carbon nanotubes, cut them into short lengths and suspend them in aqueous solution with the help of surfactant. However, even the cut tubes in stable aqueous suspensions are in the form of bundles, which contain up to dozens of individual nanotubes.

We have made two advances in technology that enable assembly and characterization of nanotubes in nanoelectronic devices. First, we have developed means of suspending *individual* nanotubes in solution as described above. Fig. 1 shows an AFM image of nanotubes sonicated in DMF and dried on a mica surface. Measurements of nanotube height indicated that the DMF contains primarily individual nanotubes. Such suspensions are also very stable and can be stored at room temperature for several months without precipitation. This discovery represents a significant step in development of carbon nanotube based nanotechnology since we now have individual nanotubes suspended in solvent. This provides the opportunity for manipulation of individual nanotubes into nanostructures and nanodevices by chemical means.

Our second advance is the development of a reliable way to manipulate individual nanotubes. We

found that nanotubes in DMF suspension specifically adsorb onto amino-functionalized surfaces. Fig. 2

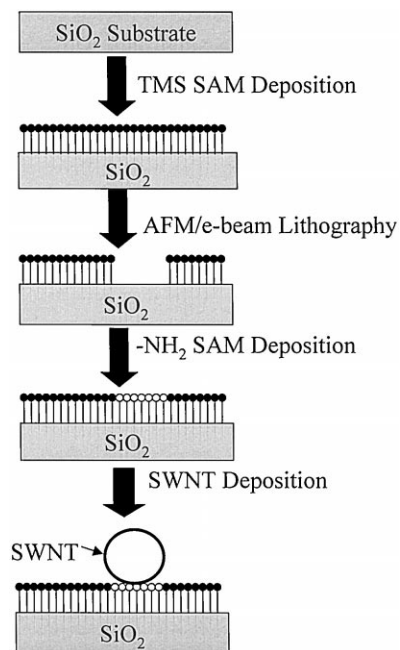


Fig. 3. Schematic diagram of controlled deposition of SWNT on chemically functionalized lithographic patterns.

shows AFM images of $-\text{CH}_3$ and $-\text{NH}_2$ functionalized SiO_2 surfaces that were soaked in SWNT/DMF suspension for 10 min and rinsed with methanol immediately after removed from the nanotube suspension. No SWNTs were observed on the $-\text{CH}_3$ functionalized surfaces, while a nearly complete coverage was observed on $-\text{NH}_2$ functionalized surfaces. This dramatic difference in adhesion of SWNTs to these functionalized surfaces suggests use of chemically functionalized nano-patterns on SiO_2 surfaces as means of positioning individual tubes. As shown in Fig. 3, our approach involves the steps described above. Conceptually, the steps are: (1) to prepare an oxidized Si surface so that nanotubes are not attracted to it (TMS SAM); (2) to destroy the TMS SAM in a specific pattern on the surface; (3) to prepare a second SAM with $-\text{NH}_2$ functionality on the exposed SiO_2 surface of the patterned area; and (4) to deposit nanotubes on the NH_2 -functionalized pattern. A typical result of this process is shown in Fig. 4, where the pattern prepared is in the form of the letter 'Q'. The observation that nanotubes bend in order to align well with the functionalized patterns

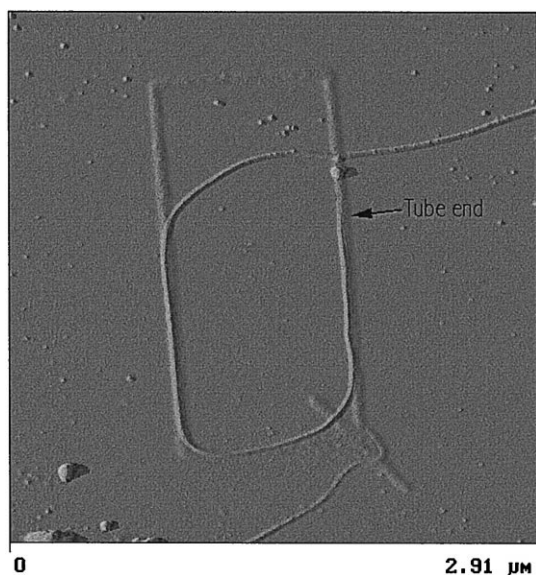


Fig. 4. Tapping mode AFM image of an individual SWNT aligning with chemically functionalized patterns on surface. Note the nanotube bends to align well with the pattern, which is an indication of strong interaction between the tube and $-\text{NH}_2$ on the surface.

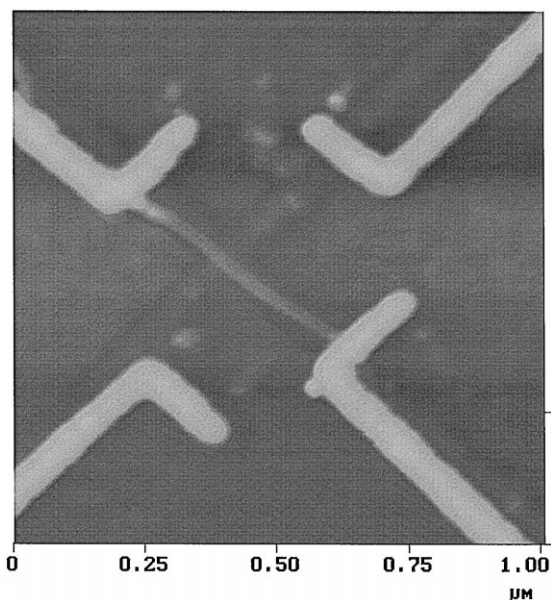


Fig. 5. Tapping mode AFM images of a device made of an individual SWNT connected to two Au electrodes.

shows that the interaction of the nanotube with $-\text{NH}_2$ groups on the surface is quite strong. One possible explanation for this strong interaction could be the Coulombic attraction between the positively charged $-\text{NH}_2$ groups on surface and negatively charged SWNTs in DMF suspension. Further research is currently underway on the nature of this strong interaction.

As a test of the effectiveness of this new method in working toward a viable molecular-level electronic technology, we selectively deposited a nanotube so that it connected two electrodes deposited on a silicon wafer. The electrodes were first put on the SiO_2 surface by standard e-beam lithography and we then used the process described above, preparing a 'bed' for the nanotube between the electrodes. Fig. 5 shows the result, which is simply a nanotube joining two of the four electrodes shown. The $-\text{NH}_2$ functionalized pattern is a straight line between the electrodes, and the stiff tube makes good contact with the gold electrodes. As shown, the nanotubes are only present in the desired place, while the rest of the surface is nearly free of tubes. This indicates a significant degree of control in deposition of individual nanotubes at specific sites on a surface. The

technique is fairly reliable. About 70% of the time, the NH_2 -functionalized lines are found to be covered with one or more individual nanotubes. However, more works need to be done to control the position of the tubes along the lines as well as the length of the tubes. Nevertheless, this degree of control is far superior other known methods for positioning nanotubes. Furthermore, initial measurement of the devices we made showed that the contact resistance between carbon nanotubes and Au electrodes is in the range of 0.5–2 M Ω – similar to the value previously reported for tubes in contact with gold electrodes [11].

In conclusion, we have demonstrated a new approach that permits precise control of the position of individual carbon nanotubes deposited on chemically functionalized nanolithographic patterns. This new method enables us to make simple nanostructures with carbon nanotubes, and to connect these to other structures. This discovery represents a major step toward experiments on the electron transport characteristics of carbon nanotubes, and ultimately toward fabrication of carbon-nanotube-based molecular electronic devices. Further development of the current process and combination with other lithographic methods such as soft lithography may enable us to fabricate a large number of devices simultaneously.

Acknowledgements

RES wishes to acknowledge support from the Robert A. Welch Foundation (grant # C-0689), and NASA (grant # 961204). AJR acknowledges support

from the Robert A. Welch Foundation (grant # C-1369) and the Alfred P. Sloan Foundation.

References

- [1] C.T. White, J.W. Mintmire, *Nature (London)* 394 (1998) 29.
- [2] J.W. Mintmire, B.I. Dunlap, C.T. White, *Phys. Rev. Lett.* 68 (1992) 631.
- [3] J.W. Mintmire, D.H. Robertson, C.T. White, *J. Phys. Chem. Solids* 54 (1993) 1835.
- [4] J.W. Mintmire, C.T. White, *Appl. Phys. A* 67 (1998) 65.
- [5] D.H. Robertson, D.W. Brenner, J.W. Mintmire, *Phys. Rev. B* 45 (1992) 12592.
- [6] H. Ajiki, T. Ando, *J. Phys. Soc. Jpn.* 62 (1993) 2470.
- [7] R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Phys. Rev. B: Condens. Matter* 50 (1994) 14698.
- [8] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, CA, 1996.
- [9] M.S. Dresselhaus, *Annu. Rev. Mater. Sci.* 27 (1997) 1.
- [10] P.G. Collins, A. Zettl, H. Bando, A. Thess, R.E. Smalley, *Science* 278 (1997) 100.
- [11] S.J. Tans, A.R.M. Verschueren, C. Dekker, *Nature (London)* 393 (1998) 49.
- [12] C.T. White, T.N. Todorov, *Nature (London)* 393 (1998) 240.
- [13] J. Muster, M. Burghard, S. Roth, G.S. Duesberg, E. Hernandez, A. Rubio, *J. Vac. Sci. Technol. B* 16 (1998) 2796.
- [14] M. Burghard, G.S. Duesberg, G. Philipp, J. Muster, S. Roth, *Adv. Mater.* 10 (1998) 584.
- [15] A. Thess et al., *Science* 273 (1996) 483.
- [16] A.G. Rinzler et al., *Appl. Phys. A* 67 (1998) 29.
- [17] J. Liu et al., *Science* 280 (1998) 1253.
- [18] H. Sugimuri, N. Nakagiri, *J. Vac. Sci. Technol. B* 15 (1997) 1394.
- [19] H. Dai, N. Franklin, J. Han, *Appl. Phys. Lett.* 73 (1998) 1508.
- [20] C.S. Whelan, M.J. Lercel, H.G. Craighead, K. Seshadri, D.L. Allara, *Appl. Phys. Lett.* 69 (1996) 4245.
- [21] E.T. Ada et al., *J. Vac. Sci. Technol. B* 13 (1995) 2189.