Growth of Single-Walled Carbon Nanotubes from Microcontact-Printed Catalyst Patterns on Thin Si_3N_4 Membranes**

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Single-walled carbon nanotubes have been grown by chemical vapor deposition from methane and hydrogen on catalyst patterns prepared by microcontact printing on 20 nm thick silicon nitride substrates. A higher yield of single-walled carbon nanotubes was obtained by the simple expedient of introducing hydrogen during deposition. Based on atomic force microscopy and transmission electron microscopy measurements, we found that high-quality single-walled carbon nanotubes with a broad diameter distribution were obtained.

1. Introduction

Carbon nanotubes are hollow cylindrical molecular systems that can be conceptually constructed by rolling up a graphene sheet. The single-walled nanotubes obtained in this way may be semiconducting or metallic, depending on the helicity and diameter of the nanowire. Recent experiments have demonstrated nanotube-based electronic devices, such as single-electron transistors and quantum wires[1,2] at low temperature and room-temperature field-effect transistors.[3,4] Therefore, carbon nanotubes seem to be a very promising material for nanoelectronics.

Developing controlled synthesis methods to obtain ordered carbon nanotube architectures is a crucial step toward nanotube-based devices.[5] Recently, single-walled and multiwalled carbon nanotubes have been fabricated by chemical vapor deposition (CVD) with CH_4 and C_2H_2, respectively, on catalyst patterns defined by standard lithographic techniques.[6–8] Free-standing single-walled carbon nanotubes (SWCNTs) between silicon towers were grown from catalysts prepared by printing with a flat poly(dimethylsiloxane) (PDMS) stamp;[9] however, carbon nanotubes on flat substrates are more suitable for nanoelectronics. Compared to the standard electron-beam lithographic and photolithographic patterning techniques used in these experiments, soft lithography[10–12] is suitable for patterning large areas (>1 cm^2) in one single process step. One method of soft lithography is microcontact printing, which has been used to pattern flat substrates for the growth of multiwalled carbon nanotubes.[13]

Here we report on the *single*-walled carbon nanotube fabrication on microcontact-printed catalyst patterns that are deposited on electron-transparent, ultrathin silicon nitride membrane substrates. The SWCNT catalyst[5] was transferred to the substrate using a microcontact-printing process. Tubes were grown by CVD of methane and we introduced H_2 to activate the catalyst and to obtain a higher yield of carbon nanotubes. By choosing the 20 nm ultrathin Si_3N_4 substrates, high resolution transmission electron microscopy (HRTEM) can be used to investigate the as-grown nanotube arrangement. In addition, atomic force microscopy (AFM) and electrical transport measurements can easily be performed on the same nanotube on a *flat* substrate.

2. Results and Discussion

For the first step of microcontact printing, the PDMS stamps and ultrathin silicon nitride membrane substrates were hydrophilized by an O_2 plasma in order to increase the conformal contact between the stamp, the substrate surface, and ethanol-soluble catalysts. Stamps and substrates were stored under water. After the stamp and substrate had been blown dry with argon gas, the stamp was inked and dried again, then the catalyst was printed on the substrate by conformal contact. Subsequently, the substrate was annealed in air at 500 °C for 10 h. During this annealing, the block copolymer decomposed, resulting in a porous structure of the catalysts,[14,15] as confirmed by our scanning electron microscopy (SEM) images. Then the substrate was placed in a tube furnace, which was heated to 950 °C in an argon atmosphere. Hydrogen was introduced with a flow rate of 500 sccm (standard cubic centimeters per minute) together with 500 sccm Ar. After 30 min argon gas was replaced by CH_4 gas with a flow rate of 500 sccm. Another 30 min later hydrogen and methane were switched off and the substrate allowed to cool in an argon atmosphere to room temperature. Figure 1A shows the AFM image of the micropattern of porous catalyst islands obtained after heat treatment at 500 °C, the height of one catalyst island being 200 nm. The optical image of the same sample after nanotube growth (Fig. 1B) demonstrates that the printed pattern is maintained after carbon nanotube growth. We found that the ultrathin silicon ni-

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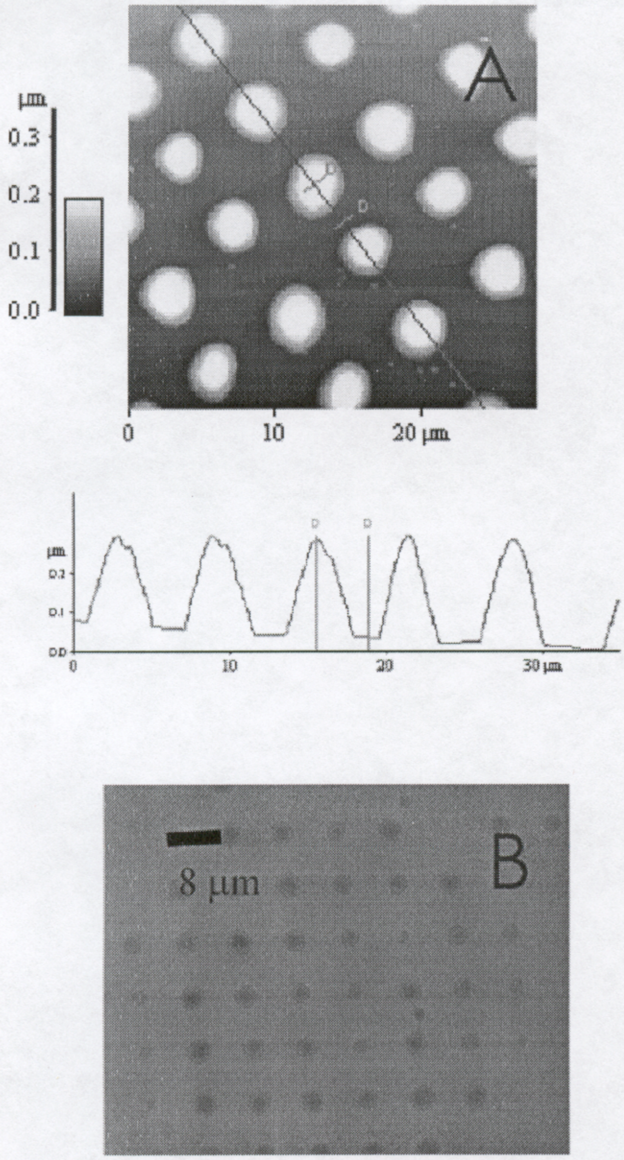

Fig. 1. Micrographs of patterns: A) AFM image before carbon nanotube growth; B) optical microscopy image after carbon nanotube growth. After carbon nanotube growth it is not easy for an AFM tip to approach for a large-area scan owing to the much rougher surface.

tride membrane substrates remain intact after both microcontact printing and carbon nanotube growth at 950 °C.

We tried to grow carbon nanotubes with pure CH_4 gas; however, the yield was found to be extremely low, typically less than one carbon nanotube per catalyst island. Processes to promote the growth yield of SWCNT involving a suitable concentration of benzene together with methane and supercritical drying have been reported.[16,17] We found that a simple treatment with H_2 can activate the catalyst during carbon nanotube growth to increase growth yield.

Figure 2 shows two typical AFM images of carbon nanotubes grown from catalyst islands. Due to the height of 200 nm of the catalyst island, some nanotubes are partially free standing.

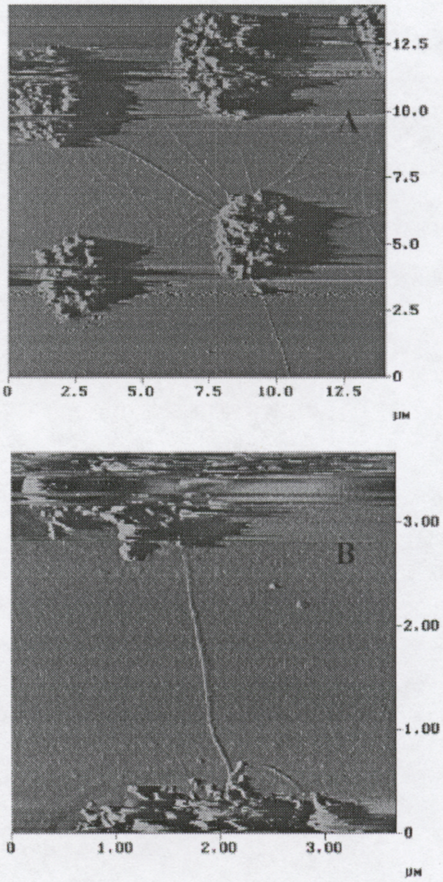

Fig. 2. AFM images, using an amplitude mode, of carbon nanotubes grown from catalyst islands: A) high area density of carbon nanotubes grown from catalyst islands; B) one free-standing carbon nanotube with a height of 5 nm.

Such tubes exhibit different apparent heights depending on the setpoint of the tapping mode of the atomic force microscope. The tube on the right in Figure 2B displays this type of behavior whereas the tube on the left in this figure is in contact with the membrane substrate.

The main advantage of the use of the ultrathin Si_3N_4 membranes as substrates is their electron transparency, which enables a characterization of the as-grown nanotube arrangement by TEM. Typical TEM images are presented in Figures 3A and 3B. Figure 3A shows a low magnification phase contrast overview picture in which a great number of tubes can be observed. Most of the tubes grow in loops around one catalyst island but some connect two islands. Zooming in on the tubes (Fig. 3B) reveals only single-walled nanotubes with different diameters and closed carbon nanotube ends without catalytic particles (not shown). Therefore we can assume the base-growth mechanism for our carbon nanotube growth. That is, during the CVD process, the catalyst particles responsible for nanotube nucleation and growth remain pinned on the support surfaces. The alternative, tip growth, involves a metal catalyst nanoparticle at a nanotube end that is carried away as the nanotube grows and is responsible for supplying carbon feedstock for the nanotube growth.[6,18–20]

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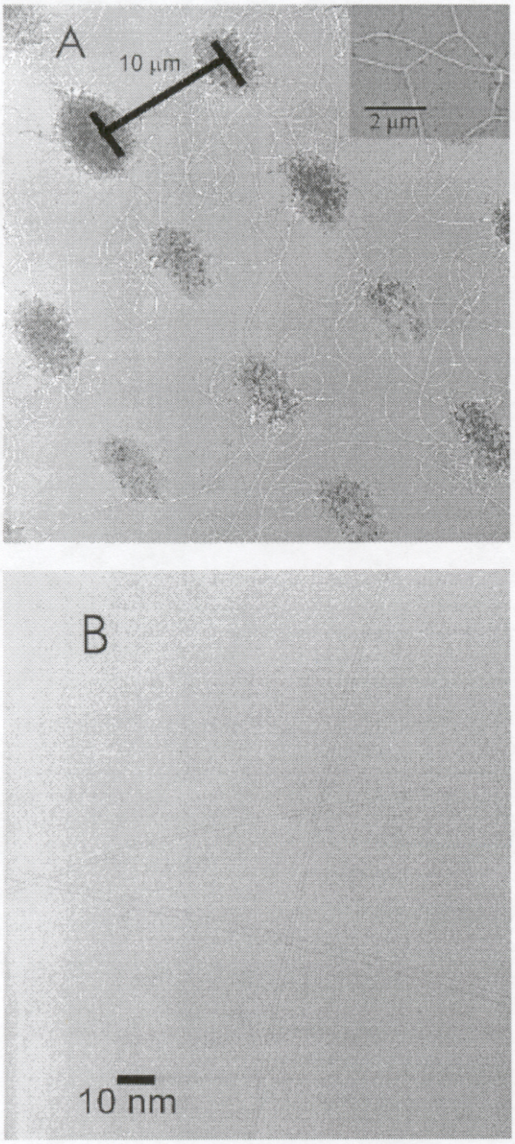

Fig. 3. TEM images of single-walled carbon nanotubes of an as-grown sample. The clean surface of carbon nanotubes can be observed. A) Low-resolution TEM image; Y-type entanglements are shown in the inset. B) HRTEM image of SWCNTs.

Based on AFM and TEM images we conclude that our carbon nanotubes are free of amorphous carbon coatings in as-grown samples. It has been reported that by limiting CVD synthesis to a short time (10 min) and using a relatively high flow rate (1000 sccm to 6500 sccm of methane), amorphous carbon coating could also be avoided.[6] In our case, however, hydrogen may play an important role in avoiding amorphous carbon coatings, because it was found that amorphous carbon can be etched away by hydrogen during diamond growth by CVD.[21] Entangled carbon nanotubes were observed in our samples; three Y-type entanglements are shown in the inset of Figure 3A.

The diameter distribution of the obtained SWCNTs was determined from the height profile of carbon nanotubes found in AFM measurements, which is shown in Figure 4. The diameter of the SWCNTs ranges from 0.5 nm to 5 nm, while HRTEM indicates a distribution from 0.8 nm to 7.6 nm. Both values are relatively broad compared with the reported[6,22,23] range of 1–3 nm for tubes prepared by CVD and of 1–5 nm for tubes synthesized by arc discharge. One possible reason for our broad range is that hydrogen may stabilize the lower and higher fullerenes capping the carbon nanotubes by terminating certain dangling bonds. Another possible reason is that the relatively high concentration of catalyst solution we used results in larger catalyst particles for SWCNT growth and consequently larger-diameter SWCNTs.

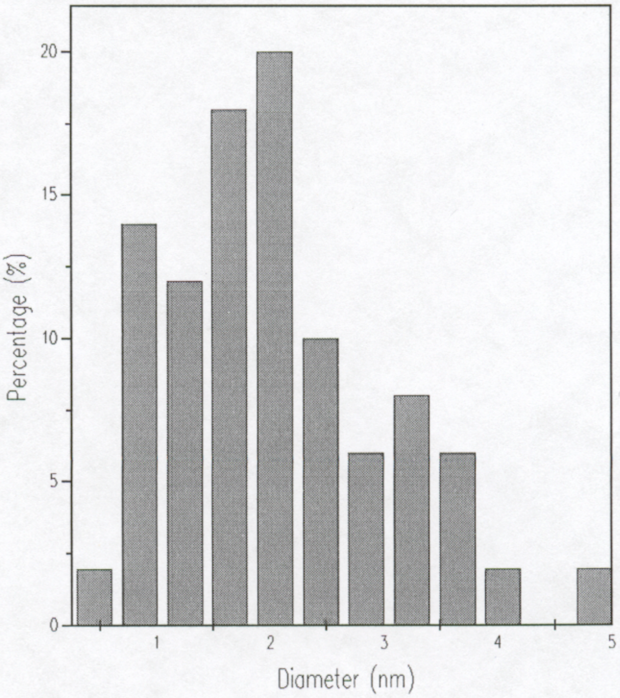

Fig. 4. Diameter distribution of single-walled carbon nanotubes based on AFM height profile measurements.

The minimum diameter of SWCNTs observed so far is 0.4 nm,[24,25] which grows out of half of a C_{20} dodecahedron. SWCNTs with larger diameters are energetically more favorable due to their smaller bond-bending strain, but mechanically they are less stable. Such SWCNTs may easily be distorted because of van der Waals forces between tube and substrate, and as a result the diameter could be underestimated from AFM height profile measurements but overestimated from TEM images. This agrees well with our observations since we found a diameter distribution with larger size by HRTEM. SWCNTs with larger diameters may be suitable for gas adsorption.[26]

After carbon nanotube growth, the porous structure of the catalyst disappeared. Based on TEM measurements, it appears that the porous structure can be preserved and can increase the growth yield only at the beginning of carbon nanotube growth. Further HRTEM measurements on as-grown samples investigating the structure of active catalyst grains for carbon nano-

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tube growth will shed more light on growth mechanisms of SWCNTs.

3. Conclusions

In summary, the CVD growth of single-walled carbon nanotubes from methane and hydrogen on catalyst patterns prepared by microcontact printing on thin silicon nitride substrates is reported for the first time. When hydrogen was introduced during deposition, a high yield of single-walled carbon nanotubes was obtained. The as-grown nanotube arrangement was studied by atomic force microscopy and transmission electron microscopy, revealing high-quality single-walled carbon nanotubes with a broad diameter distribution.

4. Experimental

Stamps and Substrate: Patterned PDMS stamps were prepared from Sylgard 184 (Dow Corning, Midland, MI) and cured for at least 12 h at 60 °C on masters prepared by UV-lithography and fluorinated with a monolayer of (1,1,2,2,-tetrahydroperfluorodecyl)-trichlorosilane. The thickness of the stamps was 4–5 mm. An O_2 plasma treatment was used to render the surface of stamps and substrates hydrophilic before inking.

Substrate, Catalyst, Inking, and Printing: Silicon nitride membranes (20 nm thick) were prepared according to [27]. SWCNTs could also be grown on SiO_2/Si substrates. The liquid-phase catalyst was prepared by stirring $AlCl_3$ (0.65 g) in 2-butanol (20 mL) while heating to 50 °C overnight. Ethanol (10 mL) was then added together with 0.5 g of block copolymer $H(–OCH_2CH_2–)_x[–OCH(CH_3)–CH_2–]_y(–OCH_2CH_2–)_zOH$ with a number-average molecular weight M_n of 5800, $FeCl_3$ (54 mg), and MoO_2Cl_2 (2 mg). A drop of liquid catalyst was placed onto the patterned stamps for about 10 s and the stamp was dried with a continuous stream of Ar. Printing using such wet-inked stamps was performed by placing the stamps on substrates and removing them by hand. The time of conformal contact was about 5 s. The substrate was then calcined at 500 °C with a heating rate of 5 °C/min for 10 h in ambient air to remove the copolymer.

Growth of Carbon Nanotubes: The substrate was placed in a tube furnace, which was heated to 950 °C in an argon (99.999 %) atmosphere. Afterwards H_2 (99.999 %) at a pressure of 1.1 bar was introduced at a flow rate of 500 sccm together with 500 sccm argon. 30 min later the argon gas was replaced by CH_4 gas (99.5 %) with a flow rate of 500 sccm and a pressure of 1.2 bar. After another 30 min the hydrogen and methane were switched off and the substrate was cooled to room temperature in an argon atmosphere.

Imaging and Instrumentation: The microstructures of the substrates were studied by AFM with a Nanoscope IIIa system (Digital Instruments) in tapping mode using commercial silicon cantilevers under ambient conditions, except for Figure 1A, which was performed using a Thermomicroscopes M5 atomic force microscope in non-contact (NC) AFM mode. High-resolution transmission electron micrographs were taken with a Philips CM200 microscope operated at 200 keV.

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[1] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. S. Smalley, L. J. Geerings, C. Dekker, *Nature* **1997**, *386*, 474.
[2] D. H. Cobden, M. Bockrath, P. L. McEuen, A. G. Rinzler, R. E. Smalley, *Phys. Rev. Lett.* **1998**, *81*, 681.
[3] S. J. Tans, A. R. M. Verschueren, C. Dekker, *Nature* **1998**, *393*, 49.
[4] R. Martel, T. Schmidt, H. R. Shea, T. Hertekl, P. Avouris, *Appl. Phys. Lett.* **1998**, *73*, 2447.
[5] H. Dai, J. Kong, C. Zhou, N. Franklin, T. Tombler, A. Cassell, S. Fan, M. Chapline, *J. Phys. Chem. B* **1999**, *103*, 11 246.
[6] J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, H. Dai, *Nature* **1998**, *395*, 878.
[7] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, H. Dai, *Science* **1999**, *283*, 512.
[8] Y. Y. Wei, G. Eres, *Appl. Phys. Lett.* **2000**, *76*, 3759.
[9] A. Cassell, N. Franklin, T. Tombler, E. Chan, J. Han, H. Dai, *J. Am. Chem. Soc.* **1999**, *121*, 7975.
[10] A. Kumar, G. M. Whitesides, *Appl. Phys. Lett.* **1993**, *63*, 2002.
[11] Y. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, *37*, 550.
[12] H. A. Biebuyck, N. B. Larsen, E. Delamarche, B. Michel, *IBM J. Res. Dev.* **1997**, *41*, 159.
[13] H. Kind, J.-M. Bonard, C. Emmenegger, L.-O. Nilsson, K. Hernadi, E. Maillard-Schaller, L. Schlapbach, L. Forro, K. Kern, *Adv. Mater.* **1999**, *11*, 1285.
[14] P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chemelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, *282*, 2244.
[15] P. Yang, D. Zhao, D. Margolese, B. Chemelka, G. D. Stucky, *Nature* **1998**, *396*, 152.
[16] N. R. Franklin, H. Dai, *Adv. Mater.* **2000**, *12*, 890.
[17] M. Su, B. Zheng, J. Liu, *Chem. Phys. Lett.* **2000**, *322*, 321.
[18] R. T. K. Baker, *Carbon* **1989**, *27*, 315.
[19] G. G. Tibbetts, M. G. Devour, E. J. Rodda, *Carbon* **1989**, *25*, 367.
[20] S. Amelinckx, D. Bernaerts, X. B. Zhang, G. Van Tendeloo, J. Van Landuyt, *Science* **1995**, *267*, 1334.
[21] S.-T. Lee, Z. Lin, X. Jiang, *Mater. Sci. Eng. Rep.* **1999**, *25*, 123.
[22] C.-H. Kiang, W. A. Goddard, R. Beyers, J. R. Salem, D. S. Bethune, *J. Phys. Chem.* **1994**, *98*, 6612.
[23] X. Lin, X. K. Wang, V. P. Dravid, R. P. H. Chang, J. B. Ketterson, *Appl. Phys. Lett.* **1994**, *64*, 181.
[24] L. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, S. Iijima, *Nature* **2000**, *408*, 50.
[25] N. Wang, Z. K. Tang, G. D. Li, J. S. Chen, *Nature* **2000**, *408*, 50.
[26] S. D. M. Brown, G. Dresselhaus, M. S. Dresselhaus, *Mater. Res. Soc. Symp. Proc.* **1998**, *497*, 157.
[27] G. Philipp, T. Weimann, P. Hinze, M. Burgard, J. Weis, *Microelectron. Eng.* **1999**, *46*, 157.

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