

Selective Growth of Aligned Carbon Nanotubes on a Silver-Patterned Substrate by the Silver Mirror Reaction

Shaoming Huang* and Albert W. H. Mau

CSIRO Division of Molecular Science, Bag 10, Clayton South, Victoria 3169, Australia

Received: February 3, 2003

It was found that carbon nanotubes prepared by the pyrolysis of iron(II) phthalocyanine (FePc) can selectively grow on a SiO₂ surface when the SiO₂ wafer is patterned by silver. A combination of the micro-contact printing (μ CP) technique and chemical reaction (classical silver tollens reaction, also called silver mirror reaction) has been applied to generate a silver pattern with micro/nanoscale resolution on a quartz glass substrate (silver selectively deposits on hydrophilic regions), and an aligned carbon nanotubes (CNTs) pattern with the same resolution can be fabricated by the pyrolysis of FePc on the basis of the selective growth. This new method represents a great advantage of controlled fabrication of a micro/nanoscale aligned CNT pattern on a conducting surface (silver) by combination of soft-lithography and chemical approach for various device applications, requiring high-resolution pattern and conducting surface.

Introduction

Because of paramount importance in many applications of CNTs, e.g., flat panel display, nanoelectronics, nanosensors, etc., orienting and patterning CNTs have attracted much attentions in recent years.¹ Aligned CNTs could be generated by postsynthesis fabrication,² by chemical vapor deposition of hydrocarbons over prelocated catalysts on substrates,^{3–6} or by pyrolysis of some organometallic compounds, e.g., ferrocene^{7,8} and metal phthalocyanine,⁹ which contains both metal and a carbon source for nanotube growth on substrates. Various techniques including offset printing,¹⁰ standard lithography,^{5,11,12} soft-lithography,^{13–15} and self-assembly¹⁶ have been applied to pattern aligned/nonaligned CNTs on various substrates by prepatterning catalysts or prepatterning substrates for site selective growth of CNTs.^{11,17–19} For example, Dai et al. patterned single-walled carbon nanotubes (SWNTs) on 4 in. SiO₂/Si wafers by patterning photolithographically Fe-Mo/Al₂O₃ followed by pyrolyzing methane.¹² Ajayan reported site selective growth of aligned CNTs by pyrolysis of xylene/ferrocene on a patterned SiO₂/Si substrate generated by photolithography and wet and/or dry etching.¹⁹

Recently we developed a simple method to generate free-standing aligned CNTs film by pyrolysis of organometallic compounds (such as iron(II) phthalocyanine, abbreviated FePc).⁹ Furthermore, a few technologies including photolithography and soft lithography have been developed to fabricate two- and three-dimensional aligned CNT patterns on the basis of selective growth on a substrate patterned by carbonized polymer.^{9,15,17,20} Soft-lithography has recently become a very promising technique for micro/nanostructuring a wide range of materials. Micro-contact printing (μ CP) is one of the commonly used techniques. Using a poly(dimethylsiloxane) (PDMS) elastomer stamp, μ CP has been shown to be a convenient and effective way to generate self-assembled monolayer (SAM) patterns of certain “molecular inks” (e.g., alkanethiol, alkylsiloxane) on appropriate substrate surfaces (e.g., gold, silver, silicon dioxide, etc.).²¹ The silver

tollens test (also called the silver mirror reaction) is a classical reaction for identifying aldehyde groups of organic compounds. Here we report a new approach to fabricate aligned CNT micropatterns by selective growth of nanotubes by pyrolysis of FePc on silver-patterned substrates soft-lithographically by a combination of μ CP and the silver mirror reaction. The resolution of the pattern generated can be down to the micro-scale. Figure 1 represents the general procedure of fabricating the micro/nanopattern of aligned nanotubes by silver. It involves first the formation of a silver pattern by selective deposition of silver on an OTS-patterned substrate by μ CP of alkylsiloxane on a quartz substrate using the PDMS elastomer stamp, subsequently selective growth of aligned CNTs on silver-free region by pyrolyzing FePc.

Experimental Section

To start with, all quartz glass was first cleaned by piranha solution (a mixture of 98% H₂SO₄ and 30% H₂O₂ at 7:3 v/v) for ca. 30 min, followed by thoroughly rinsing with deionized water. [**Caution!** Piranha solution is a very strong oxidizing agent and reacts violently with organic compounds. It should be handled with extreme care.] A PDMS stamp with microscale resolution parallel lines prepared by Sylgard 184 on master prepared by photolithography and cured at 60 °C for 4 h was used for the region specifically transferring a SAM of octadecyltrichlorosilane (OTS) onto the cleaned quartz surface. In a typical experiment, the PDMS stamp, precoated with the OTS “molecular ink” (0.2% w/w of OTS in hexane) was kept in contact with the substrate for 20–40 s. After the condition of the tollens reaction was optimized, the OTS patterned substrate was then immersed in a solution of 5–10% (w/w) D-glucose. Subsequently, a fresh tollens solution (Ag(NH₃)₄OH solution) was added into the aldehyde solution (1:10 v/v). The mixed solution was kept at room temperature for 5–10 min. Then the substrate was rinsed with deionized water and dried at room temperature. Growth of aligned CNTs on a silver-patterned substrate was carried out by pyrolyzing FePc under an Ar/H₂ atmosphere (1:1 v/v, $V_{\text{total}} = 40\text{--}60$ mL/min) at 800 °C using a conventional tube furnace as described in our previous paper.⁷

* Corresponding author. Present address: Chemistry Department, Duke University, NC 27708. E-mail: smhuang@duke.edu.

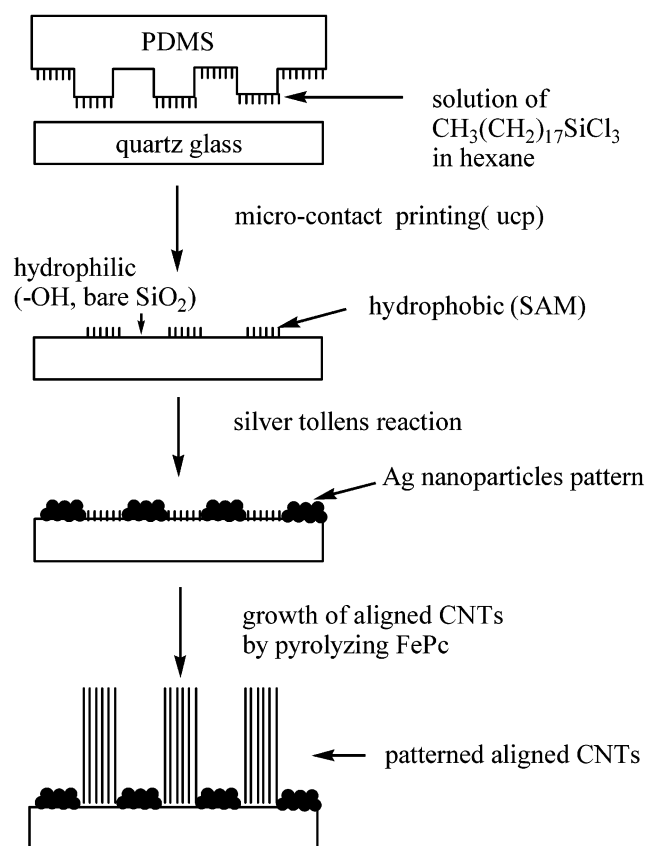


Figure 1. Schematic representation of the micropattern formation of aligned carbon nanotubes (CNTs) on a silver-patterned substrate by the silver mirror reaction.

Here we used one furnace. The FePc and quartz substrate were quickly moved into the high-temperature zone when the furnace temperature reached 800 °C under the Ar/H_2 atmosphere, and the pyrolysis lasted 5–10 min. By applying this method, perpendicularly aligned carbon nanotubes with lengths ranging from 0.5 to 100 μm on the substrate could be generated depending on experimental conditions (the amount of FePc used, flow rate of Ar/H_2 , pyrolysis time, and temperature). The samples were characterized by scanning electron microscopy (SEM, XL-30 FEG, Philips at 5 Kv), energy-dispersive X-ray analysis (EDX) associated with SEM, and transmission electron microscopy (TEM, JEOL 2010).

Results and Discussion

Initially, we grew CNTs on a silver-patterned substrate by sputter coating silver using the TEM grid with a low resolution of 40 μm as a physical mask. It was very interesting to find that silver did not support the growth of CNTs from the pyrolysis of FePc. Figure 2a gave the low magnification SEM image of the as-synthesized perpendicularly aligned CNTs pattern on quartz glass. The CNTs have a uniform length of ca. 5 μm , and most of the nanotubes have diameters of 40–60 nm. The inset in Figure 2a is the SEM image of the boundary of the aligned CNTs pattern and the silver layer. It was very clear to see that the aligned nanotubes are normal to the substrate and only grow on the silver-free area. After some of the CNTs were removed from the substrate by using stick tape, it was noted that the density of the nanotubes in the center (insert in Figure 2b) is higher than that near the boundary and straighter as well. For nanodevice application of patterned aligned CNTs, it is strongly desired to integrate CNTs on a substrate to realize the intermolecular junction as well as to attach an electrode to the nanotubes. From the SEM observation the density of the CNTs

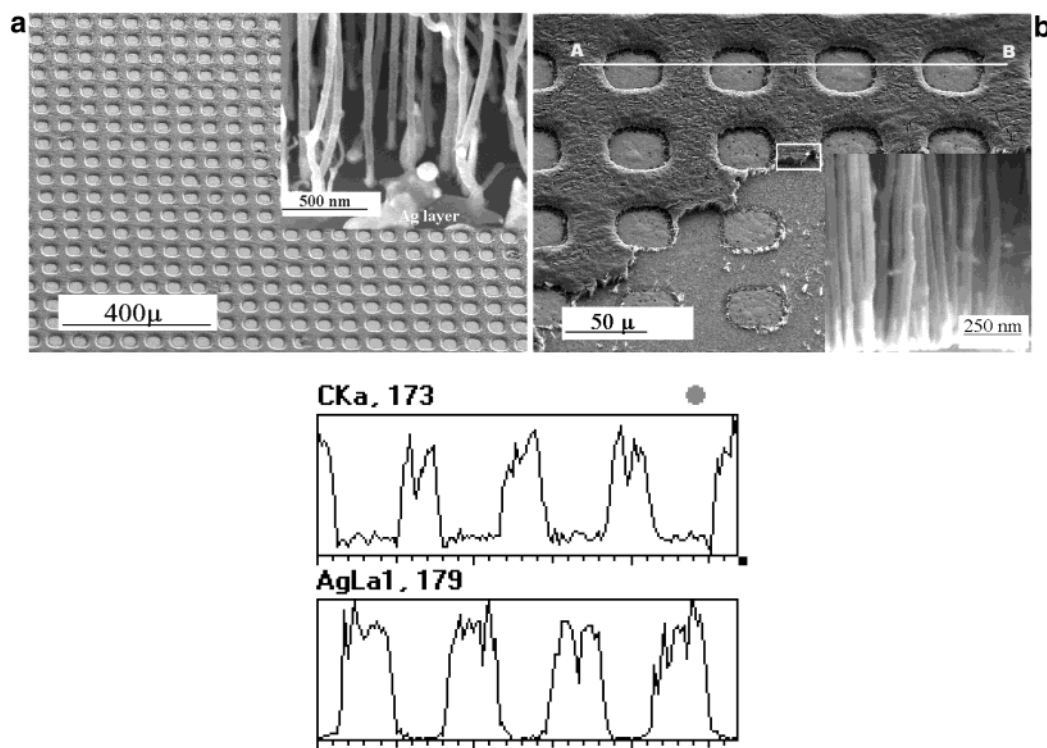


Figure 2. (a) Low magnification scanning electron microscope (SEM) image of the aligned CNTs pattern on silver-patterned quartz glass prepared by sputter coating silver using a transmission electron microscopy (TEM) grid as a physical mask. The inset is the SEM image of the boundary of the CNTs pattern and silver layer. (b) SEM image of partially screened aligned CNT pattern. The inset is the amplified image from as indicated by rectangle. (c) Energy-dispersive X-ray (EDX) profiles of C K α and Ag L α . The scanning path for the line analyses is indicated by the line between points A and B in Figure 2b.

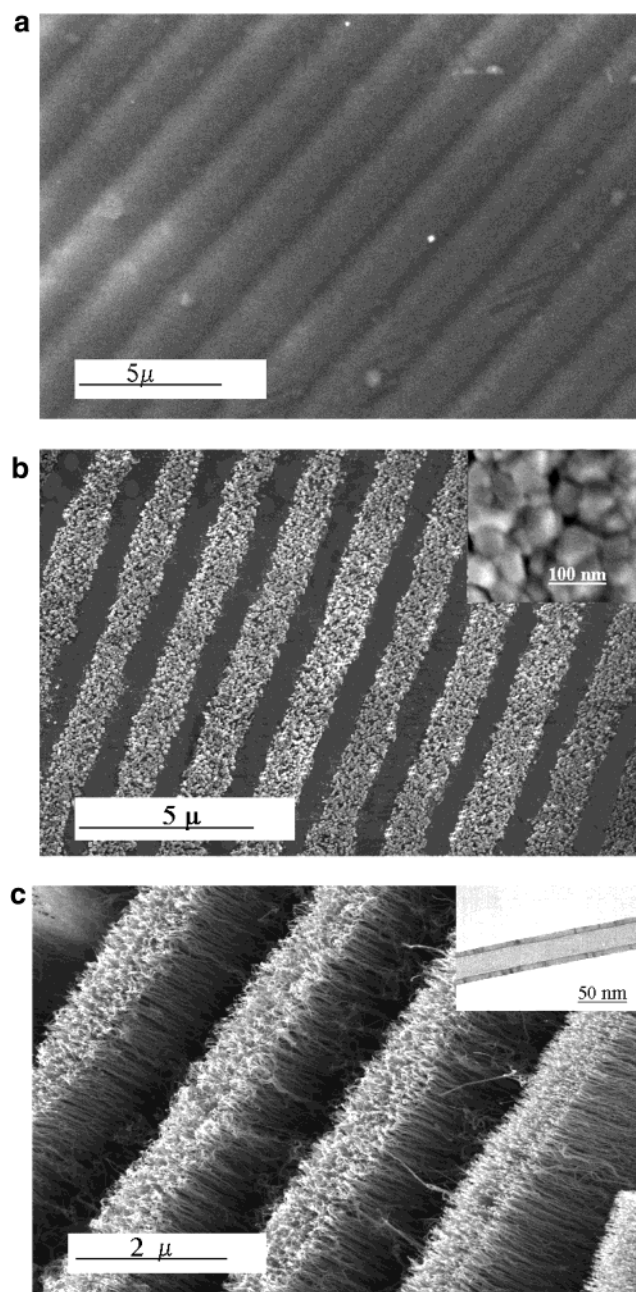


Figure 3. SEM images of (a) a parallel line octadecyltrichlorosilane (OTS) pattern on quartz substrate by micro-contact printing (μ CP), (b) a parallel line silver pattern formed by selective deposition of silver on OTS-free regions by the silver mirror reaction (inset: high magnification of SEM image showing the densely packed silver nanoparticles), and (c) aligned CNTs grown on silver-free regions by pyrolyzing iron(II) phthalocyanine (FePc) (inset: TEM image of individual nanotubes).

is so high that CNTs can attach with each other. SEM observation also showed that most of the carbon nanotubes at the edge of the pattern are still aligned and have good contact with the silver layer (Figure 2a inset), which is important for electronic device application of the patterned aligned CNTs. The selective growth of nanotubes was also confirmed by the EDX line analysis shown in Figure 2c. EDX line analysis of C K α and Ag L α scanning from point A to B in Figure 2b showed a preferential deposition of iron from the decomposition of FePc and carbon on the silver-free area, indicating that the silver surface does not support the growth of CNTs. The growth mechanism of the aligned nanotubes produced by the pyrolysis of FePc has been described previously.^{9a} The selective growth

of nanotubes on a silver-patterned substrate seems to be due to two main reasons. One is the selective location of iron particles during decomposition of FePc. The preferred partition of iron on the SiO₂ surface could be related to the different adhesion energies of the iron particles on SiO₂ and the silver surface. A similar situation was observed on Si and SiO₂ substrates.¹¹ Another reason may be that the localized surface energy of the silver surface effect on the nucleation of Fe particles^{9b,22} is such that the nanotubes cannot grow on the silver surface even though some iron particles are located on the surface.

Based on the above experimental result, further patterning of silver with microscale resolution by combining μ CP SAM of OTS and silver mirror reaction was developed. By optimizing the reaction condition, we can generate densely packed silver nanoparticles having parallel line pattern with microscale resolution. Parts a and b of Figure 3 reproduce SEM images of the parallel line OTS pattern with microscale resolution and the resulting silver pattern by selective deposition of silver on the OTS-patterned substrate by the silver mirror reaction, respectively. SEM observation showed that silver nanoparticles were densely packed with diameters ranging from 10 to 80 nm (see inset in Figure 3b). Most of the silver particles were located on OTS-free regions where the surface is hydrophilic. After growth of CNTs by pyrolyzing FePc, as expected, CNTs grew only on the silver-free regions; thus well-patterned aligned nanotube arrays with features of microscale parallel lines were fabricated (Figure 3c). As demonstrated earlier,^{9a} the constituent straight aligned multiwalled CNTs are densely packed and have well-graphitized structures with uniform diameters of 40–60 nm, which is also confirmed by TEM observation, as shown in the inset in Figure 3c. Both the geometry and the spatial resolution of the generated aligned CNTs micropattern are limited mainly by the resolution of the silver pattern formed. Basically, we can fabricate the PDMS stamp with any patterns and control the silver mirror reaction conditions to fabricate a conducting silver pattern on the substrate. This could open a new approach to fabricate controlled micro/nanopatterns of aligned CNTs on patterned conducting substrates on a large scale for various applications, particularly for nanoelectronic device fabrication, which requires a high conducting surface. And our method should be also suitable for other CNT growth systems using organometallic compounds such as ferrocene and metal carbonyl as catalyst.

Conclusion

Our work has demonstrated that a silver surface does not support the growth of CNTs from pyrolysis of FePc. A new feasible method to fabricate large-scale aligned CNT micro/nanopatterns on quartz substrate on the basis of selective growth by combination of microcontact printing and silver mirror reaction has been developed. The resolution of the nanotube pattern can be down to the microscale. This, together with a patterned conducting metal (silver) substrate, will represent a great advantage in controlled fabrication of aligned CNT patterns for some applications of nanotubes that require high-resolution patterns and conducting surfaces, e.g., field emission, sensors, artificial muscle, electrochemical modification of nanotubes, etc.

References and Notes

- (1) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*; Springer, Heidelberg, 2001.
- (2) Ajayan, P. M.; Stephan, O.; Colliex, C.; Trauth, D. *Science* **1994**, 265, 1212.

- (3) Li, W. Z.; Xie, S. S.; Qian, L. X.; Chang, B. H.; Zhous, B. H.; Zhou, W. Y.; Zhao, R. A.; Wang, G. *Science* **1996**, 274, 1701.
- (4) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Provencio, P. N. *Science* **1998**, 282, 1105.
- (5) Fan, S.; Chapline, M.; Franklin, N.; Tombler, T.; Cassell, A.; Dai, H. *Science* **1999**, 283, 512.
- (6) Bower, C.; Zhu, W. Z.; Jin, S.; Zhou, O. *Appl. Phys. Lett.* **2000**, 77, 830.
- (7) Rao, C. N. R.; Sen, R.; Satishkumar, B. C.; Govindaraj, A. *Chem. Commun.* **1998**, 1525.
- (8) Zhang, Z. J.; Wei, B. Q.; Vajtai, R.; Ward, J.; Ramanath, G.; Ajayan, P. M. *Adv. Mater.* **2001**, 13, 1767.
- (9) (a) Huang, S.; Dai, L.; Mau, A. W. H. *J. Phys. Chem. B* **1999**, 103, 4223. (b) Huang, S.; Dai, L.; Mau, A. W. H. *J. Mater. Chem.* **1999**, 9, 1221. (c) Li, D.; Dai, L.; Huang, S.; Mau, A. W. H.; Wang, Z. L. *Chem. Phys. Lett.* **2000**, 316, 349.
- (10) Sohn, Y.; Lee, S.; Song, Y.; Choi, S.; Cho, K.; Nam, K. *Appl. Phys. Lett.* **2001**, 78, 901.
- (11) Zhang, J. Z.; Wei, B. Q.; Ramanath, G.; Ajayan, P. M. *Appl. Phys. Lett.* **2000**, 77, 3764.
- (12) Franklin, N. R.; Li, Y.; Chen, R. J.; Javey, A.; Dai, H. *Appl. Phys. Lett.* **2001**, 79, 4571.
- (13) Cassell, A. M.; Franklin, N. R.; Tombler, T. W.; Chan, E. M.; Han, J.; Dai, H. *J. Am. Chem. Soc.* **1999**, 121, 7975.
- (14) Kind, H.; Bonard, J.-M.; Emmenegger, C.; Nilsson, L. O.; Hernadi, K.; Maillard-schaller, E.; Schlapbach, L.; Forro, L.; Kern, K. *Adv. Mater.* **1999**, 11, 1285.
- (15) Huang, S.; Mau, A. W. H.; Turney, T. W.; White, P. A.; Dai, L. *J. Phys. Chem. B* **2000**, 104, 2193.
- (16) Burghard, D.; Duesberg, G.; Philipp, G.; Muster, J.; Roth, S. *Adv. Mater.* **1998**, 10, 584.
- (17) (a) Yang, Y.; Huang, S.; He, H.; Mau, A. W. H.; Dai, L. *J. Am. Chem. Soc.* **1999**, 121, 10832. (b) Huang, S.; Dai, L.; Mau, A. W. H. *Adv. Mater.* **2002**, 14, 1140.
- (18) Ago, H.; Murata, K.; Yumura, M.; Yotani, J.; Uemura, S. *Appl. Phys. Lett.* **2003**, 82, 811.
- (19) Wei, B. Q.; Vajtai, R.; Jung, Y.; Ward, J.; Zhang, Y.; Ramanath, G.; Ajayan, P. M. *Nature* **2002**, 416, 495.
- (20) Chen, Q.; Dai, L. *J. Nanosci. Nanotechnol.* **2001**, 1, 43.
- (21) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 551.
- (22) Ohara, P. C.; Gelbart, W. M. *Langmuir* **1998**, 14, 3418.