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Citation: [Applied Physics Letters](#) **87**, 033103 (2005); doi: 10.1063/1.1995961

View online: <http://dx.doi.org/10.1063/1.1995961>

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Patterned growth of carbon nanotubes on Si substrates without predeposition of metal catalysts

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(Received 7 February 2005; accepted 16 June 2005; published online 11 July 2005)

Aligned carbon nanotubes (CNTs) can be readily synthesized on quartz or silicon-oxide-coated Si substrates using a chemical vapor deposition method, but it is difficult to grow them on pure Si substrates without predeposition of metal catalysts. We report that aligned CNTs were grown by pyrolysis of iron phthalocyanine at 1000 °C on the templates created on Si substrates with simple mechanical scratching. Scanning electron microscopy and x-ray energy spectroscopy analysis revealed that the trenches and patterns created on the surface of Si substrates were preferred nucleation sites for nanotube growth due to a high surface energy, metastable surface structure, and possible capillarity effect. A two-step pyrolysis process maintained Fe as an active catalyst. © 2005 American Institute of Physics. [DOI: 10.1063/1.1995961]

A large quantity growth of carbon nanotubes (CNTs) on predesigned patterns and at desired locations on different substrates is an important approach for integrating CNTs into nanoscale devices and sensors in large scale. Aligned and patterned CNTs on silica (SiO₂) substrates have been synthesized using various chemical vapor deposition (CVD) methods.^{1–4} Brilliant three-dimensional architectures of organized CNTs have been created on SiO₂ substrates using a CVD process with the precursor of a mixture of ferrocene and xylene,^{5–9} however, it is difficult to grow patterned CNTs on pure Si substrates using the same method without a predeposition of metal catalysts.^{8,9} It has been found that CNTs grow selectively on SiO₂ substrates but not on Si substrates, because patterned growth of CNTs on substrates is strongly influenced by the surface states of substrates such as different materials, roughness, crystallinity, and porosity.¹⁰ The selective growth of CNTs on SiO₂ rather than Si was interpreted by the different reactivities between catalyst Fe and the substrates. In the case of SiO₂, Fe particles do not react with SiO₂ and thus the catalytic γ -Fe structure remains active; in the case of Si, Fe particles react with Si during the CVD process at a temperature above 1000 °C with the formation of noncatalytic Fe-Si alloys.^{9,10} We report in this work that aligned and patterned CNTs can be formed on pure Si wafer on the specific areas scratched with a diamond pen, and a two-step pyrolysis process can effectively prevent the reaction between Si and Fe.

We used iron phthalocyanine (FePc) as the precursor material because it contains both the carbon source and the metal catalyst required for carbon nanotube growth. Furthermore, aligned CNTs have been successfully synthesized using the same precursor material on quartz substrates previously.^{4,11} To enhance nanotube growth process, a high-energy ball milling treatment was used before the annealing process. Ball milling of FePc at room temperature has been found to be able to increase significantly nanotube formation yield. In addition, high-energy mechanical grinding reduces the vaporization temperature from 400 to 200 °C by creating an activated structure in FePc.¹¹ The lower vaporization tem-

perature helps vapor deposition and CNT growth, which will be discussed in details later. Two grams of FePc powders were milled in a vertical planetary ball mill with a steel vessel and several steel balls for 100 h in Ar gas at a pressure of 300 kPa. The Ar gas prevents oxidation during the milling process. The milling time can be reduced using a higher milling intensity. The milled samples were then heated in a quartz tube furnace for pyrolyzing and CNT growth under an Ar-5% H₂ gas flow (50 cm³/min). A piece of Si wafer was used as substrate. Templates of different patterns were created by scratching the wafer surface with a diamond pen. The patterned Si substrate was then placed inside a quartz furnace tube next to a combustion boat containing the milled FePc sample. The distance between the substrate and the boat is in the range of 5–15 cm depending on Ar gas flow that serves as material carrier. The heating process was programmed to two heating stages: the temperature was first increased from ambient temperature to 500 °C at a rate of 20 °C/min and held for 2–5 min; a blue vapor of FePc was generated inside the quartz furnace tube and disappeared in a few minutes. Then, the temperature was increased again up to 1000 °C and held for 15 min for nanotube growth. The morphology of as-grown CNTs and the surface of the patterned Si substrate were examined using field-mission scanning electron microscopy (SEM) (Hitachi S4500 instrument). Elemental analysis was conducted using an x-ray energy-dispersive spectrometer (EDS) equipped with an Oxford ISIS EDXA system attached to a JEOL (JSM6400) scanning electron microscope. Nanotubular structures were investigated using transmission electron microscopy (TEM) (300 keV Philips CM300 instrument).

The SEM image in Fig. 1(a) shows three letters, “ANU,” written on a Si substrate with a diamond pen. After annealing at 1000 °C, the three letters were covered by a layer of CNTs. The SEM images in Figs. 1(b)–1(d) were taken on the letter “N” area with higher magnifications. A very high density of CNTs on the letter areas and few CNTs on the surrounding surfaces can be seen clearly. Some CNT samples were removed from the substrate and deposited directly on a TEM copper grid for TEM analysis. TEM revealed a multi-walled cylindrical structure of the CNTs and a diameter around 50 nm (Fig. 2). The TEM image in Fig. 2(b) shows

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FIG. 1. SEM images of patterned CNTs grown on a Si substrate: (a) Three letters, "ANU," written with a diamond pen covered by CNTs. (b)–(d) SEM images taken from the letter "N" area with higher magnifications showing selective and patterned growth of CNTs.

some Fe particles inside the nanotubes, suggesting these Fe particles act as catalysts during nanotube growth.¹²

Vertical aligned CNTs can be grown on a large area of Si substrate in different patterns, as shown in Figs. 3(a) and 3(b), under controlled gas flow rates and the positions of the substrate inside the furnace tube. The patterned templates were also created with a diamond pen. By controlling the width and depth of trenches and/or scratches, the density of CNTs can be adjusted and the growth location can be carefully positioned, as shown in Fig. 3(c). The SEM image in Fig. 3(d) shows that CNTs can be grown on a single straight line. Neither FePc nor C was deposited on unscratched surfaces because EDS analysis did not detect any C.

The above results clearly show a preferred nucleation of CNTs at the scratched areas. The SEM image in Fig. 4(a) shows typical rough surface of the scratches with broken crystalline planes, edges, and steps. It has been reported that phase transformation with the formation of metastable Si phases could occur on the wafer surface under such severe mechanical treatment.^{13,14} Compared with the perfect, smooth surface of Si substrate, FePc or C vapor prefers the special structure of the scratched areas for vapor deposition and nanotube nucleation because of a higher surface energy and the metastable structure. Indeed, Fig. 4(b) shows a row of CNTs rooted inside a trench of a substrate surface. To further confirm this mechanism, one substrate coated with patterned CNTs was first heated in air to remove all CNTs via oxidation. EDS analysis was then performed on the oxidized substrate. Fe was detected at the scratched areas, but not on the untouched surfaces, indicating the scratched areas as the nucleation site of the CNTs. This result is in agreement with previous research on enhanced nucleation of diamond

FIG. 2. TEM images showing (a) a multiwalled cylindrical structure and (b) catalyst Fe particles encapsulated inside nanotube tips.

FIG. 3. SEM images of vertically aligned and patterned CNTs on Si substrates: (a) top view, (b) side view, (c) precisely deposited CNTs, and (d) a higher magnification image of (c).

films on mechanically polished Si wafers during hot-filament CVD process.¹⁵

The selective growth over the scratched surface on Si substrate is a typical self-assembly process possibly driven by a capillary force. The deposition from the FePc blue vapor onto the templates at low-temperature range (200–500 °C) seems to be a critical step. Under the controlled gas flow, a thin layer of FePc was formed over the template areas but not on unscratched smooth surfaces due to a capillarity force. Because the temperature (500 °C) is not high enough for pyrolyzing, no CNTs were formed yet. When the temperature reached 1000 °C, CNTs grew out from the FePc layers deposited on the template. The two-step heating process probably avoided direct contacts and reactions between Fe particles and Si surface to form noncatalytic FeSi alloys. When the FePc layer was first deposited on the Si surface at 500 °C, Fe had not been decomposed from FePc because the temperature was not high enough; when pyrolysis occurred, fresh Fe was involved directly in CNT formation. X-ray diffraction was conducted on the scratched area where CNTs were formed, and neither Fe–Si alloys nor SiC compounds were detected. Some reactions between metastable Si phases created by mechanical treatment and free C and Fe atoms during the annealing might occur. Nevertheless, the SEM, EDS, and XRD results demonstrated that CNTs were formed on the scratched areas with the help of Fe catalysts. The selective growth over the scratches suggests a very simple technique for preparing a template on a smooth substrate surface. The detailed nucleation mechanism needs further investigation using TEM.

In summary, we have demonstrated that aligned and patterned CNTs can be readily grown using a pyrolysis process at a patterned template on pure Si substrates prepared by simple scratching. This simple technique does not require a predeposition of metal catalysts. The fractured Si atomic

FIG. 4. SEM images of (a) rough surface of scratched area on a Si substrate without CNT deposition, and (b) a row of CNT root inside a trench indicating the trenches as the nucleation sites.

planes at the scratched areas sink FePc vapor due to capillarity effects and act as the preferred nucleation sites for CNT growth. A two-step pyrolysis process avoids reactions between catalyst Fe particles and Si surface with the formation of inactive FeSi catalysts.

The authors gratefully thank Dr. John Fitzgerald and the staff at the Electron Microscopy Unit for the assistance in microscopy analysis. This work is supported in part by the Australian Research Council under Centre of Excellence and Discovery research projects.

- ¹W. Z. Li, S. S. Xie, L. X. Quian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, *Science* **274**, 1701 (1996).
- ²M. Terrones, N. Grobert, J. Olivares, J. P. Zhang, H. Terrones, K. Kordatos, W. Hsu, J. Hare, P. Townsend, K. Prassides, A. Cheetham, H. K. Kroto, and D. Walton, *Nature (London)* **388**, 52 (1997).
- ³Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, *Science* **282**, 1105 (1998).
- ⁴S. M. Huang, L. M. Dai, and A. W. H. Mau, *J. Phys. Chem. B* **103**, 4223

(1999).

- ⁵Z. J. Zhang, B. Q. Wei, G. Ramanath, and P. M. Ajayan, *Appl. Phys. Lett.* **77**, 3764 (2000).
- ⁶X. F. Zhang, A. Cao, B. Q. Wei, Y. Li, J. Wei, C. Xu, and D. Wu, *Chem. Phys. Lett.* **362**, 285 (2002).
- ⁷C. J. Lee, S. C. Lyu, H. Kim, C. Park, and C. Yang, *Chem. Phys. Lett.* **359**, 109 (2002).
- ⁸B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath, and P. M. Ajayan, *Nature (London)* **416**, 495 (2002).
- ⁹Y. J. Jung, B. Q. Wei, R. Vajtai, and P. M. Ajayan, *Nano Lett.* **3**, 561 (2003).
- ¹⁰J. W. Ward, B. Q. Wei, and P. M. Ajayan, *Chem. Phys. Lett.* **376**, 717 (2003).
- ¹¹Y. Chen and L. T. Chadderton, *J. Mater. Res.* **19**, 2791 (2004).
- ¹²D. Li, L. Dai, S. Huang, A. W. H. Mau, and Z. L. Wang, *Chem. Phys. Lett.* **316**, 349 (2000).
- ¹³Y. Gogotsi, C. Baek, and F. Kirscht, *Semicond. Sci. Technol.* **14**, 928 (1999).
- ¹⁴D. B. Ge, V. Domnich, and Y. Gogotsi, *J. Appl. Phys.* **95**, 2725 (2004).
- ¹⁵B. V. Spitsyn, in *Handbook of Crystal Growth*, edited by D. T. J. Hurle (Elsevier, Amsterdam, 1994), pp. 401–456.