

Growth of high-quality single-wall carbon nanotubes without amorphous carbon formation

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We report an alternative way of preparing high-quality single-wall carbon nanotubes (SWCNTs). Using a triple-layer thin film of Al/Fe/Mo (with Fe as a catalyst) on an oxidized Si substrate, the sample is exposed to a single short burst (5 s) of acetylene at 1000 °C. This produced a high yield of very well graphitized SWCNTs, as confirmed by transmission electron microscopy and Raman spectroscopy. We believe that the high temperature is responsible for the high crystallinity/straightness of the nanotubes, and the rapid growth process allows us to achieve a clean amorphous carbon (*a*-C) free deposition which is important for SWCNT device fabrication. The absence of *a*-C is confirmed by Auger electron spectroscopy, Raman spectroscopy, and electrical measurements. © 2004 American Institute of Physics. [DOI: 10.1063/1.1639509]

The remarkable electronic and mechanical properties of carbon nanotubes have generated an intense interest in their deposition methods over the past few years.¹ Arc discharge and laser ablation are some of the initial deposition techniques that demonstrate the growth of these one-dimensional structures.^{2,3} Since then, much effort has been made to exert a certain degree of control on the type, location, and chirality of the tubes. Recently, chemical vapor deposition (CVD) on patterned catalysts has proven to be one of the most promising methods of controlling the growth position of single and multiwall carbon nanotubes.⁴⁻⁷ In this letter, we demonstrate an alternative way of achieving high-quality single-wall carbon nanotubes (SWCNTs) on substrates without the deposition of amorphous carbon (*a*-C) by using a high temperature coupled with very rapid growth. The issue of *a*-C is one which has not been extensively studied in SWCNT growth, although it is of prime importance in fabricating a working SWCNT electronic/electrical circuit, because unwanted *a*-C can cause short circuits. The *a*-C is deposited due to the decomposition (thermal pyrolysis) of the hydrocarbon gases used. Some attempts have been made to prevent the formation of *a*-C such as the addition of hydrogen (which etches *a*-C) into the deposition process together with the hydrocarbon gas or by performing growth at very high gas pressures (>1 atm) which would inhibit the “C” species from sticking to the substrates and therefore prevent the accumulation of carbon.^{4,6} In these cases, the presence of *a*-C has been stud-

ied using transmission electron microscopy (TEM) and atomic force microscopy (AFM).^{4,6} However, TEM studies the nanotubes directly (not the substrate) and AFM cannot confirm the chemical composition (e.g., no *a*-C) on the substrate.

For electronic device applications, a fast and “clean” growth method for SWCNTs without the presence of *a*-C is essential. In this work, an approach based on high temperature (1000 °C) and rapid growth (~5 s of acetylene, C₂H₂) is used to achieve high-quality SWCNTs without *a*-C. This technique takes advantage of the high growth rates that have been observed previously for SWCNTs (>1 μm/s).^{8,9} Suspended SWCNTs were grown across a network of pillars; such structures enable the possibility of fabricating electronic devices using SWCNTs. The absence of *a*-C was confirmed using Auger depth profile spectroscopy and electrical measurements on the noncatalyst regions of the substrate surface. In our previous work, Auger spectroscopy was used to verify the presence or absence of *a*-C on the substrate during growth of vertically aligned multiwall carbon nanotubes by dc-plasma enhanced CVD.¹⁰

The SWCNTs were grown by thermal CVD using a 1 in. quartz tube vacuum furnace. Initially, the oxidized silicon substrates are coated with a thin-film catalyst [Al(10 nm)/Fe(1 nm)/Mo(0.2 nm)]¹¹ by sputtering and these are placed in the quartz tube which is evacuated to 0.2 mbar. Thin-film catalyst layers have been used for depositing SWCNTs¹¹⁻¹³ and this technique allows reliable and accurate patterning of the catalyst using lithographic techniques. The samples are heated up to 1000 °C for 35 min and maintained at 1000 °C

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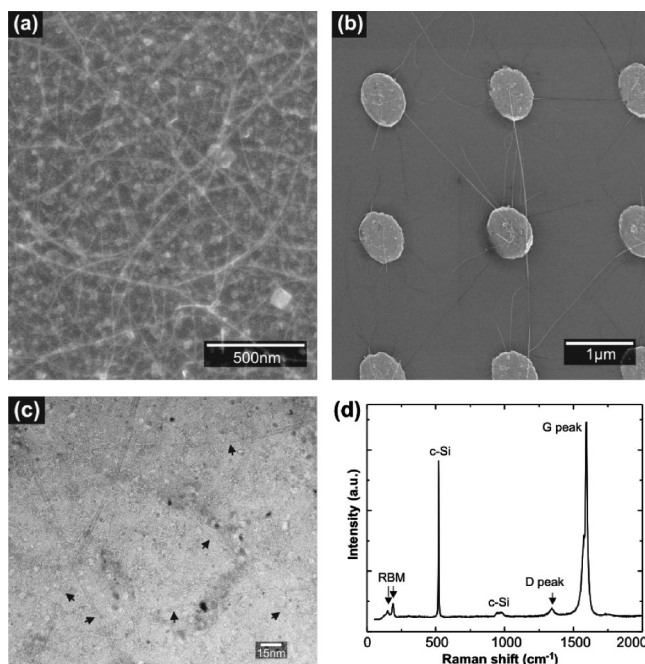


FIG. 1. (a) Scanning electron microscopy (SEM) image of a SWCNT prepared with a rapid growth process (~ 5 s). (b) SWCNT grown between pillars containing the triple-layer catalyst. (c) TEM image showing SWCNTs. (d) Example of high-quality Raman spectrum of SWCNT.

for 10 min, in 500 sccm of flowing helium at 15 mbar. The helium is then shut off and the tube is evacuated (< 1 mbar) before the introduction of a single burst of acetylene (~ 5 s) into the chamber. The acetylene flow rates used ranged from 50 sccm to 250 sccm, corresponding to chamber pressures of 0.7 to 2.7 mbar. After this, He is introduced into the system again and the chamber is cooled to room temperature. The flowing He was found to be crucial as it removes residual oxygen which could cause the nanotubes to be removed/burned from the substrate at temperatures greater than 800°C .

Figure 1 shows an example of the rapid growth process on a substrate prepared with the triple-layer metal catalyst [Fig. 1(a)] and straight SWCNTs grown from patterned catalyst dots [Fig. 1(b)]. It is important to note that the yield of nanotubes observed is high despite the short deposition time (~ 5 s). Nanotubes with lengths in the range of $5\text{--}10\ \mu\text{m}$ s were observed which gives a deposition rate of about $1\text{--}2\ \mu\text{m/s}$. This deposition rate is similar to that found by other authors.^{8,9} The existence of SWCNTs was confirmed by TEM. The TEM samples were prepared by performing CVD depositions on the triple-layer catalyst deposited onto SiN grids. Figure 1(c) shows a TEM image of single-wall tubes. An important observation of the TEM study is that most of the SWCNTs were found to be isolated or to exist in bundles, and that isolated nanotubes had a diameter of ~ 1.3 nm. On rare occasions, double-wall nanotubes were encountered. The Raman investigation [Fig. 1(d)] shows the signatures of well-crystallized SWCNTs, namely a strong presence of radial breathing modes at $183\ \text{cm}^{-1}$ (which is indicative of SWCNTs with diameters of 1.3 nm), a very small disorder peak (*D*) and narrow graphitic peak (*G*) with characteristic *G* splitting.¹⁴ We found that at temperatures from $700\text{--}800^\circ\text{C}$, the majority of the structures were curly mul-

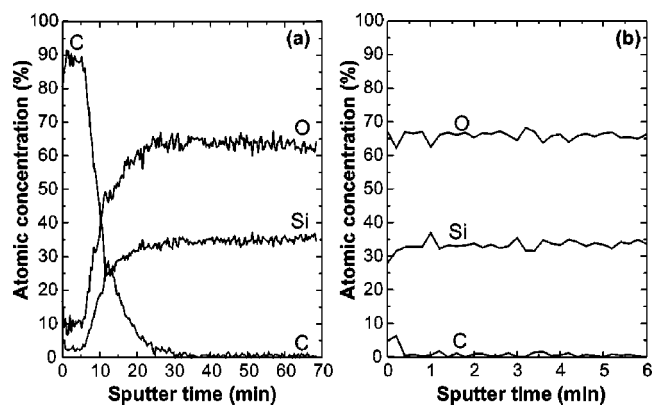


FIG. 2. Auger depth profile of the unpatterned SiO_2 with (a) 30 nm *a*-C for a deposition of 10 min, and (b) 1 nm *a*-C for a very fast growth (~ 5 s).

tiwall carbon nanotubes. At 900°C , curly SWCNTs were observed but with a significant number of multiwall nanotubes among the SWCNTs. The best temperature condition for growing straight SWCNTs was 1000°C . Our findings are similar to that found in metallocene-assisted CVD of hydrocarbons.¹⁵ This method produces multiwall carbon nanotubes at lower temperatures ($\sim 700^\circ\text{C}$) and a combination of multiwall and single-wall nanotubes are produced at much higher ($> 900^\circ\text{C}$) temperatures.

In order to control the position and to a certain extent the density of nanotubes, a network of pillars [$\text{W}(50\ \text{nm})/\text{SiO}_2(30\ \text{nm})/\text{Al}(10\ \text{nm})/\text{Fe}(1\ \text{nm})/\text{Mo}(0.2\ \text{nm})$], $500\ \text{nm}$ in diameter and $2\ \mu\text{m}$ pitch was fabricated using electron-beam lithography. As shown in Fig. 1(b), suspended straight SWCNTs were found to grow out of the pillars. In addition, the nanotubes tend to self-assemble across the network of pillars forming nanotube bridges, which has also been reported by other authors.^{7,16} Employing further lithographic steps, two point contacts of aluminum were contacted onto individual nanotubes.

The presence of *a*-C was first investigated by Auger electron spectroscopy (AES) using a Physical Electronic PHI 680 Auger nanoprobe. For this purpose, an *in situ* 2 keV Ar-ion gun was used to sputter the surface and provide depth-resolved chemical analysis. In literature, nanotubes are typically grown using CVD methods with hydrocarbon gases (methane, ethylene, and acetylene) at temperatures ranging from 700 to 1000°C with deposition times varying between 1 and 10 min.^{8,9,11–13} At such temperatures, the thermal hydrocarbon decomposition may cause deposition of amorphous carbon on the noncatalyst regions of the substrate. Figure 2(a) shows the Auger depth profile of the surface for a deposition of 10 min with acetylene at 1000°C in the thermal CVD system. This condition produced 30 nm of *a*-C on the SiO_2 surface which indicates significant pyrolysis of C_2H_2 at 1000°C . With a very short deposition time (~ 5 s), no surface carbon layer is observed as shown in Fig. 2(b). Micro-Raman was also performed on the noncatalyst substrate surface for the 10 min deposition and 5 s deposition. As shown in Fig. 3, the 10 min deposition produced *a*-C on the surface, characterized by the *D* and *G* broad peaks, whereas the 5 s deposition yielded no detectable *D* and *G* peaks. Both spectra were normalized to the first-order crystalline-silicon peak ($\sim 500\ \text{cm}^{-1}$) for a realistic com-

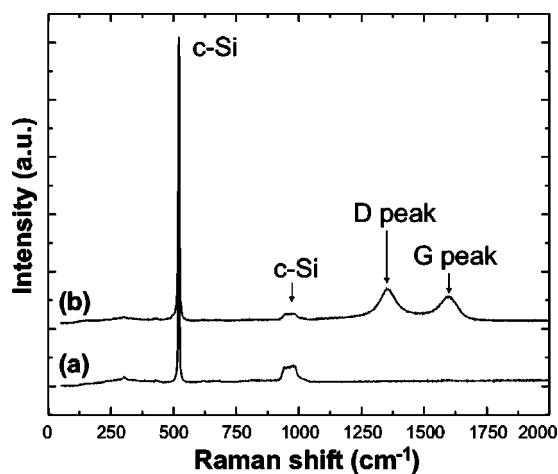


FIG. 3. Raman spectra showing the presence and absence of *a*-C for a very fast (a) and long deposition (b) growth time, respectively.

parison. These findings show that an *a*-C film was not deposited on the surface. Macroscopic probes connected to a multimeter were also used to test the resistivity across the SiO₂ substrate surface. In the case of the 5 s deposition, a large resistance (>Mohms to out of range) was found whereas at longer deposition times (>1 min), a surface resistance as low as 1 kΩ was measured. It is important to note that the low resistance of surface *a*-C can affect the fabrication and characterization of SWCNT devices. Current-voltage (*I*-*V*) measurements were also performed on two point contacts on individual nanotubes and on the substrate, see inset in Fig. 4. In areas where the substrate was contacted without nanotubes, no current was detected (i.e. <1 pA). Where the nanotubes were contacted, the nanotube resistance could be measured. The *I*-*V* plot for a Al-contacted SWCNT gives resistivity values of 100 to 500 kΩ, see Fig. 4. The high resistance of the nanotubes measured here is probably due to the poor contact resistance of Al and recent findings indicate that Pd would have been a much better choice as a contact material (~tens of kΩ).¹⁷

In conclusion, we have demonstrated a simple way to deposit single-wall carbon nanotubes by CVD without the co-deposition of unwanted *a*-C. By using a shot burst of acetylene, a high yield of highly crystallized, straight single-wall nanotubes could be obtained without the simultaneous growth of *a*-C as was verified by Auger depth profile, Raman spectroscopy, and electrical measurements. We found here that the catalytic deposition of SWCNTs occurs at a substantial rate (deposition rates of 1–2 μm per second) compared to the self-pyrolysis of the hydrocarbon gas used, and this can be advantageously employed for the industrial growth of carbon nanotubes. By coupling of a *fast* annealing time altogether with a *fast* deposition process, another route for the rapid production of carbon nanotubes on substrates will be possible.

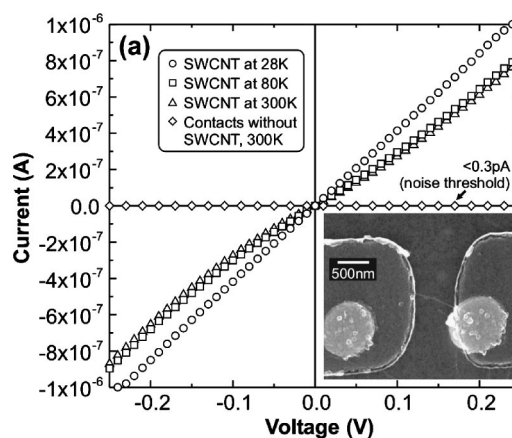


FIG. 4. *I*-*V* curves of the SWCNT at different temperatures. A reference *I*-*V* from Al electrodes without a nanotube shows that the current is in the noise threshold (<0.3 pA). This confirms that there is no leakage from the substrate (i.e. no surface carbon from deposition process). The inset shows a SEM image of a suspended SWCNT grown with the rapid growth technique, which is then contacted using two Al electrodes.

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- ¹ *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*, edited by M. S. Dresselhaus, G. Dresselhaus, and P. Avouris (Springer, New York, 2001).
- ² A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, *Science* **273**, 483 (1996).
- ³ C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. L. delaChapelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer, *Nature (London)* **388**, 756 (1997).
- ⁴ J. Kong, A. M. Cassell, and H. Dai, *Chem. Phys. Lett.* **292**, 567 (1998).
- ⁵ J. H. Hafner, M. J. Bronikowski, B. R. Azamian, P. Nikolaev, A. G. Rinzler, D. T. Colbert, K. A. Smith, and R. E. Smalley, *Chem. Phys. Lett.* **296**, 195 (1998).
- ⁶ N. R. Franklin, Y. Li, R. J. Chen, A. Javey, and H. Dai, *Appl. Phys. Lett.* **79**, 4571 (2001).
- ⁷ Y. Homma, Y. Kobayashi, T. Ogino, and T. Yamashita, *Appl. Phys. Lett.* **81**, 2261 (2001).
- ⁸ W. Kim, H. C. Choi, M. Shim, Y. Li, D. Wang, and H. Dai, *Nano Lett.* **2**, 703 (2002).
- ⁹ S. Huang, X. Cai, and J. Liu, *J. Am. Chem. Soc.* **125**, 5636 (2003).
- ¹⁰ K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, D. G. Hasko, G. Pirio, P. Legagneux, F. Wyczisk, and D. Pribat, *Appl. Phys. Lett.* **79**, 1534 (2001).
- ¹¹ L. Delzeit, B. Chen, A. Cassell, R. Stevens, C. Nguyen, and M. Meyyapan, *Chem. Phys. Lett.* **348**, 368 (2001).
- ¹² Y. J. Yoon, J. C. Bae, H. K. Baik, S. Cho, S. Lee, K. M. Song, and N. S. Myung, *Chem. Phys. Lett.* **366**, 109 (2002).
- ¹³ R. Seidel, M. Liebau, G. S. Duesberg, F. Kreupl, E. Unger, A. P. Graham, W. Hoenlein, and W. Pompe, *Nano Lett.* **3**, 965 (2003).
- ¹⁴ A. Jorio, R. Saito, J. H. Rafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. Lett.* **86**, 1118 (2001).
- ¹⁵ R. Sen, A. Govindaraj, and C. N. R. Rao, *Chem. Mater.* **9**, 2078 (1997).
- ¹⁶ N. R. Franklin and H. J. Dai, *Adv. Mater. (Weinheim, Ger.)* **12**, 12 (2000).
- ¹⁷ A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, *Nature (London)* **424**, 654 (2003).