Abrupt self-termination of vertically aligned carbon nanotube growth

Eric R. Meshot and A. John Hart[a)]
Department of Mechanical Engineering, University of Michigan, 2350 Hayward Street, Ann Arbor, Michigan 48109, USA

(Received 17 December 2007; accepted 8 February 2008; published online 18 March 2008)

Real-time height measurements demonstrate that growth of millimeter-high carbon nanotube (CNT) forests terminates abruptly after first exhibiting a steady decay in growth rate. Termination is accompanied by a distinct loss of alignment among the CNTs, which is quantified by small-angle x-ray scattering. Previously suggested diffusion-limited and decay-limited models of kinetics accurately fit the growth period, yet fail to capture the termination behavior and incorrectly predict that growth will continue for much longer durations than observed. It appears that structural disorder is a distinct chemical and/or mechanical signature of self-terminated CNT forest growth. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2889497]

Organization and growth of a vertically aligned (VA) carbon nanotube (CNT) "forest" by chemical vapor deposition (CVD) involves decomposition of carbon at individual nanoscale catalyst sites, along with mechanical interactions among large numbers ($\sim 10^{10}$–$10^{12}/\mathrm{cm}^2$) of CNTs. Therefore, understanding temporal evolution of the catalyst performance, along with evolution of the structural characteristics of the CNTs, is vital for elucidating the limiting mechanisms of growth. These limiting mechanisms must be fully understood to enable growth of aligned CNTs to macroscopic lengths, is a fascination for possible high-strength CNT cables and high-conductivity CNT wires, as well as for efficient manufacturing of large-area CNT forests for use as thermal, electrical, and mechanical interface layers.[1,2]

Previous studies have suggested that the growth rate and terminal height of VA-CNT forests can be limited by several mechanisms, which depend on process parameters such as the substrate, catalyst, precursor chemistry, and reaction temperature. Apparent limitations by the reaction rate at the catalyst,[3] by diffusion of the precursor to the catalyst,[4,5] by decay of the catalyst activity,[6] and/or by poisoning of the catalyst by products of gas-phase carbon pyrolysis,[7] have been observed. By methods used in these studies, forests of single-wall CNTs and multiwall CNTs (MWNTs) are routinely grown to heights of several millimeters; however, growth beyond these lengths has not been reported. Further, while relatively few studies have revealed the kinetics of CNT forest growth by precise time-resolved measurements, the dominant hypothesis is that the growth rate decays gradually with reaction time, and that this kinetic is represented by a parabolic or exponential decay. However, the precise mechanism of termination has not been identified. In this work, we demonstrate by *in situ* kinetics measurements that thermal CVD growth of VA-CNT forests terminates abruptly, and that this event is accompanied by a loss of structural order among the CNTs. This suggests that a sudden mechanism is responsible for termination of forest growth.

Forests of small-diameter MWNTs are grown on silicon substrates by atmospheric pressure thermal CVD, using a desktop reactor (SabreTube, Absolute Nano) where the substrate is seated on a suspended resistive heater,[8] mounted inside a quartz tube. The gas passes through a heated pipe before entering the chamber. Although the gas cools before reaching the substrate, this pre-treatment step significantly increases the growth rate (and is inherently present in a conventional tube furnace) by forming reactive precursors from the initial C_2H_4/H_2 mixture.[9] Forests are grown on (100) silicon substrates coated with 100 nm thermally grown SiO_2, and 1/10 nm Fe/Al_2O_3 deposited by electron beam evaporation.[10] For each experiment, the chamber is first flushed with He, then the substrate is heated to $T_s = 825\ ^\circ\mathrm{C}$ under 310/300 SCCM (SCCM denotes cubic centimeter per minute at STP) H_2/He to anneal the catalyst, then growth is performed under 120/310/180 SCCM $C_2H_4/H_2/He$.

The CNT forest height is measured in real-time using a laser displacement sensor (LKG-152, Keyence), which is mounted above the reaction chamber (Fig. 1). A Si_3N_4-coated "cap" substrate is placed on the catalyst substrate, and the beam reflects from this substrate, which is lifted as the CNT forest grows. One contact electrode is mounted on rollers to reduce drift of the substrate assembly due to thermal expansion ($<2\ \mu\mathrm{m/min}$). Our previous stud-

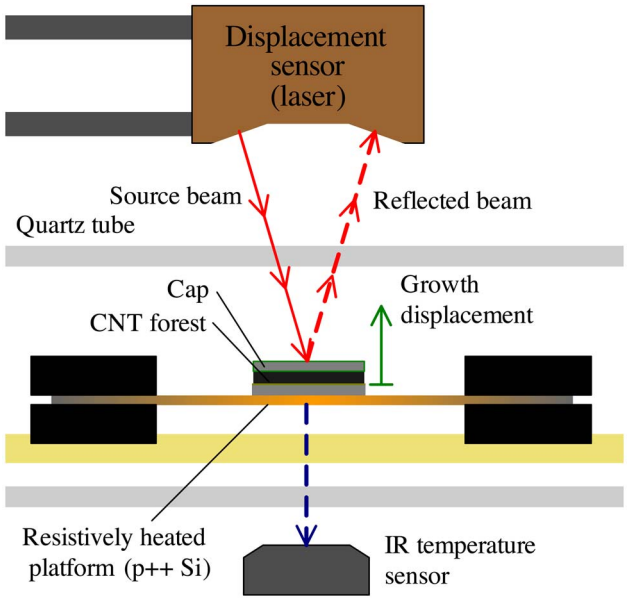

FIG. 1. (Color online) Schematic of real-time CNT forest kinetics measurement, using laser displacement sensing of upward motion created by growth.

[a)]Electronic mail: ajohnh@umich.edu.

 © 2008 American Institute of Physics
Author complimentary copy. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

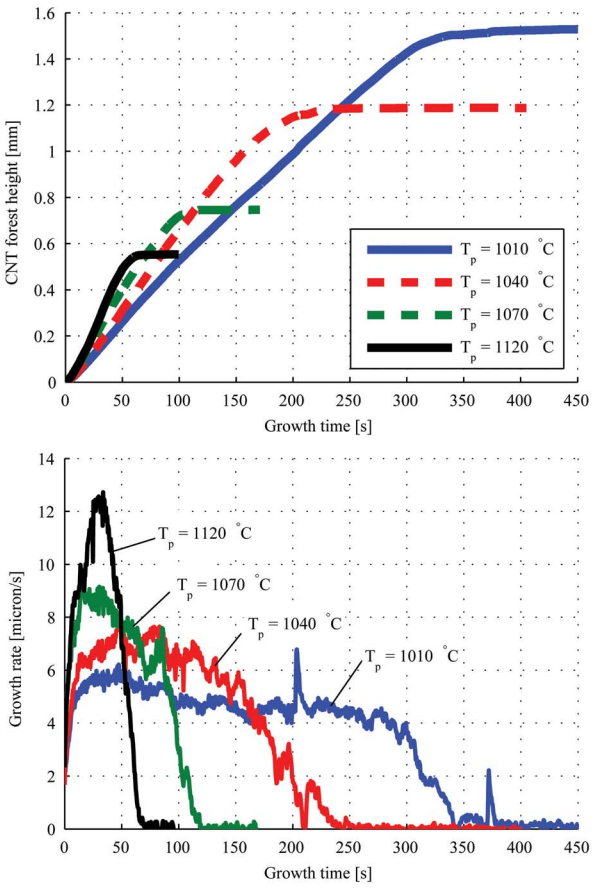

FIG. 2. (Color online) Growth kinetics of thick CNT forests, demonstrating initial acceleration, followed by a steadily declining growth rate, followed by abrupt termination.

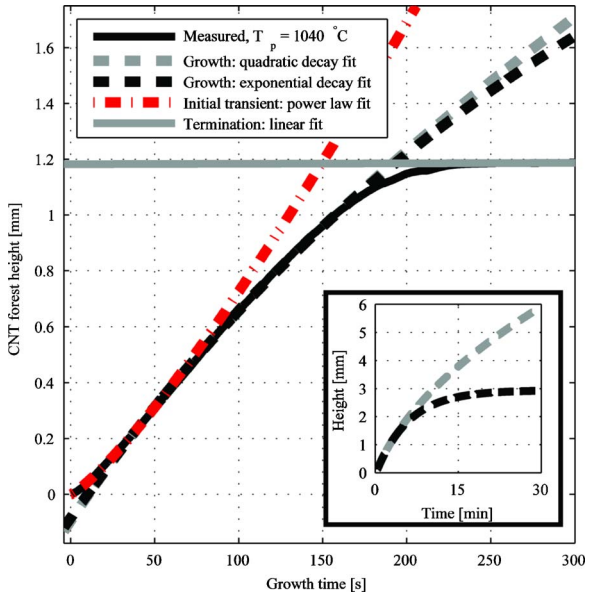

FIG. 3. (Color online) Curve fits to CNT forest growth kinetics, obtained at T_s=825 °C and T_p=1040 °C. The inset shows extrapolations of the exponential and quadratic decay fits, which predict terminal thicknesses which far exceed the measured result.

ies confirm that the weight of the cap substrate does not suppress growth, and that gas diffusion through the cap-substrate gap is sufficient for uniform growth over the 1×1 cm^2 substrate.[11] This simple real-time method enables detection of rapid kinetic events, compared to methods that estimate the average growth rate by dividing the forest height by the reaction time, or that pulse the reactant flow to introduce witness marks on the forest.[4,12] Other real-time approaches include single-slit laser diffractography,[13] optical interference,[14] and time-resolved reflectivity;[7] however, these are limited to relatively short forest heights and rely on the optical properties of the CNT forest, which can change with time and reaction conditions.

The growth kinetics [Fig. 2] in our system exhibit a nearly constant yet gradually decreasing growth rate, followed by abrupt termination at which time the growth rate drops to zero. Upon introduction of C_2H_4, it takes approximately 15 s for the growth rate to reach a maximum as the gas mixes to a steady composition in the chamber, and then the growth rate decreases before the termination event. The role of thermal activation of the reactant mixture is revealed by changing the temperature of the heated pipe, at otherwise identical conditions specified above, and this affects both the average growth rate and the terminal forest height. At heated pipe temperatures (T_p) of 1010, 1040, 1070, and 1120 °C, the average growth rates before termination are 4.7, 6.0, 7.2, and 8.5 μm/s, respectively. Gas-phase decomposition of C_2H_4 produces a large number of hydrocarbons ranging from alkenes to alkanes and polycyclic aromatic compounds,[15] and based on our observations, this population of hydrocarbons strongly affects both the CNT growth rate and the catalyst lifetime.

As real-time measurement of the forest height enables a precise measurement of the termination kinetics, we find that a piecewise curve-fit [Fig. 3] is more appropriate than the single quadratic decay[4] (diffusion-limited) or exponential decay[6] kinetics that have previously been proposed to fit the entire growth curve. In our experiments, the initial transient is captured by a power-law fit ($h=mt^n$), and this transitions to a second region which is captured by a quadratic decay ($h=0.5\sqrt{A^2+4Bt}-0.5A$) or exponential decay [$h=\beta\tau_0(1-e^{-t/\tau_0})$], which is then truncated by the termination event. The parabolic and exponential decay models almost identically fit the second region of the curve, yet greatly overestimate the terminal forest height. In this case, the exponential decay model predicts relatively slow termination at 2.9 mm after approximately 25 min, and the diffusion-limited model predicts continued growth past 6 mm height after 30 min. Futaba *et al.*[6] propose that the exponential decay model captures termination of forest growth in their H_2O-assisted process; however, it appears to us that their technique of sampling forest height at discrete intervals of several minutes does not adequately capture the termination kinetics.

Further, we observe the morphology of the CNT forests by scanning electron microscopy (SEM, Philips XL30-FEG) (Fig. 4), and spatially map the diameter and alignment within the forest by small-angle X-ray scattering (SAXS).[16] For these growth conditions, the diameter typically ranges from 5.5–6.5 nm. The top of a forest shows a characteristic tangled "crust" that represents the initial stages of growth,[17] after which a relatively strong and uniform alignment persists until alignment is rapidly lost at the bottom of the forest. This loss of alignment coincides with the rapid termination event. Alignment is quantified by calculating the Hermans orientation parameter from SAXS patterns, and this abruptly drops to near zero (representing random orientation)

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

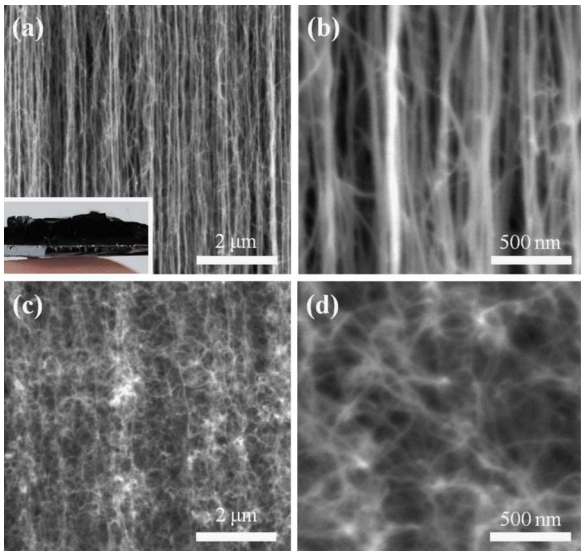

FIG. 4. (Color online) SEM images of CNT forest (T_p=1010 °C) morphology. (a) and (b) show aligned region (h=0.9 mm). (c) and (d) show highly disordered region near substrate. Inset to (a) shows optical image of forest resting on fingertip.

within the final 100 μm of growth (Fig. 5). Intentional stoppage of growth by discontinuing the C_2H_4 supply or reducing the substrate temperature also gives abrupt termination, yet in these cases the CNTs remain aligned at the bottom of the forest, indicating that the abrupt loss of alignment is a signature of self-terminated growth. We also observe this disordered bottom layer within forests grown to self-termination in a regular tube furnace. Liu *et al.* observed that a gradual decrease in carbon supply at the end of a growth process (presumably before self-termination) gives a micrometer-thick disordered layer at the bottom of the forest, whereas the CNTs remain strongly aligned at the substrate when the carbon supply is discontinued rapidly.[18] In our experiments, the carbon supply to the catalyst remains constant during termination, and the loss of order can be attributed to an instability of the growth process.

The highly disordered morphology of the forest base suggests that the CNTs at this location are highly defective, and/or are mechanically strained or buckled. As the catalyst activity decays or the supply of active precursor to the catalyst is restricted, the catalyst particles may suddenly transition to a state where growth is no longer energetically favorable and therefore terminates abruptly. Simulations of CNT nucleation from individual Fe particles suggest that a critical carbon concentration in the catalyst is needed for nucleation and growth,[19] and in principle growth may stop when this condition is no longer satisfied. Further, while these fluctuations may be localized, the CNTs within a forest are mechanically coupled by entanglement and van der Waals forces, and local fluctuations in growth rate can be spatially distributed by this coupling.[20] By applying mechanical pressure to a CNT forest during growth, we have shown that forces can introduce defects in CNTs and directly control the forest morphology during growth,[11] and thereby create a disordered morphology such as that observed in the termination regions of forests grown in this study.

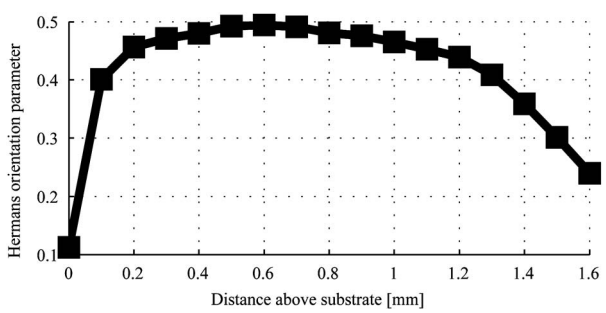

FIG. 5. Map of Hermans orientation parameter of a CNT forest grown to abrupt termination (T_p=1010 °C), verifying abrupt loss of structural order near the substrate.

In summary, real-time kinetic measurements have revealed that CNT forest growth terminates abruptly after first exhibiting a slow decay. The growth rate and catalyst lifetime are strongly affected by the generation of active gaseous precursors by thermal decomposition of C_2H_4/H_2. Termination is accompanied by loss of alignment among the CNTs, which is quantified by SAXS mapping of the forest structure, and this disorder is a distinct chemical and/or mechanical signature of self-terminated growth. Elucidating and overcoming the mechanisms of growth termination may enable macroscopic synthesis of aligned CNT strands as well as more efficient production of uniform CNT forests for many commercial applications.

We thank Eric Verploegen, Sang-Woo Han, Myounggu Park, Jong-Girl Ok, and Sameh Tawfick for assistance with x-ray scattering measurements, data processing, and equipment setup. Financial support was provided by the University of Michigan College of Engineering. Microscopy was performed at the University of Michigan Electron Microbeam Analysis Library (EMAL). X-ray scattering was performed at the Cornell High-Energy Synchrotron Source (CHESS), which is supported by the National Science Foundation and the National Institutes of Health under Grant No. DMR-0225180.

[1] R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, Science **297**, 787 (2002).
[2] M. Endo, T. Hayashi, Y. A. Kim, M. Terrones, and M. S. Dresselhaus, Philos. Trans. R. Soc. London **362**, 2223 (2004).
[3] L. B. Zhu, J. W. Xu, F. Xiao, H. J. Jiang, D. W. Hess, and C. P. Wong, Carbon **45**, 344 (2007).
[4] L. Zhu, D. W. Hess, and C. P. Wong, J. Phys. Chem. B **110**, 5445 (2006).
[5] O. A. Louchev, T. Laude, Y. Sato, and H. Kanda, J. Chem. Phys. **118**, 7622 (2003).
[6] D. N. Futaba, K. Hata, T. Yamada, K. Mizuno, M. Yumura, and S. Iijima, Phys. Rev. Lett. **95**, 056104 (2005).
[7] A. A. Puretzky, D. B. Geohegan, S. Jesse, I. N. Ivanov, and G. Eres, Appl. Phys. A: Mater. Sci. Process. **81**, 223 (2005).
[8] L. C. van Laake, A. J. Hart, and A. H. Slocum, Rev. Sci. Instrum. **78**, 083901 (2007).
[9] A. J. Hart, L. van Laake, and A. H. Slocum, Small **3**, 772 (2007).
[10] A. J. Hart and A. H. Slocum, J. Phys. Chem. B **110**, 8250 (2006).
[11] A. J. Hart and A. H. Slocum, Nano Lett. **6**, 1254 (2006).
[12] K. Liu, K. Jiang, C. Feng, Z. Chen, and S. Fan, Carbon **43**, 2850 (2005).
[13] L. M. Dell'Acqua-Bellavitis, J. D. Ballard, P. M. Ajayan, and R. W. Siegel, Nano Lett. **4**, 1613 (2004).
[14] D. H. Kim, H. S. Jang, C. D. Kim, D. S. Cho, H. S. Yang, H. D. Kang, B. K. Min, and H. R. Lee, Nano Lett. **3**, 863 (2003).
[15] G. D. Towell and J. J. Martin, AIChE J. **7**, 693 (1961).
[16] B. N. Wang, R. D. Bennett, E. Verploegen, A. J. Hart, and R. E. Cohen, J. Phys. Chem. C **111**, 5859 (2007).
[17] L. Zhang, Z. R. Li, Y. Q. Tan, G. Lolli, N. Sakulchaicharoen, F. G. Requejo, B. S. Mun, and D. E. Resasco, Chem. Mater. **18**, 5624 (2006).
[18] K. Liu, K. Jiang, Y. Wei, S. Ge, P. Liu, and S. Fan, Adv. Mater. (Weinheim, Ger.) **19**, 975 (2007).
[19] F. Ding, K. Bolton, and A. Rosen, J. Phys. Chem. B **108**, 17369 (2004).
[20] Q. Zhang, W. Zhou, W. Qian, R. Xiang, J. Huang, D. Wang, and F. Wei, J. Phys. Chem. C **111**, 14638 (2007).

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp