COMMUNICATIONS

Deposition of aligned bamboo-like carbon nanotubes via microwave plasma enhanced chemical vapor deposition

H. Cui, O. Zhou, and B. R. Stoner[a)]
Curriculum in Applied and Materials Science, University of North Carolina, Chapel Hill, North Carolina 27599

(Received 24 January 2000; accepted for publication 31 August 2000)

Aligned multiwall carbon nanotubes have been grown on silicon substrates by microwave plasma enhanced chemical vapor deposition using methane/ammonia mixtures. Scanning electron microscopy shows that the nanotubes are well aligned with high aspect ratio and growth direction normal to the substrate. Transmission electron microscopy reveals that the majority phase has a bamboo-like structure. Data are also presented showing process variable effects on the size and microstructure of the aligned nanotubes, giving insight into possible nucleation and growth mechanisms for the process. © *2000 American Institute of Physics.* [S0021-8979(00)04923-9]

Since their discovery approximately 10 yr ago,[1] carbon nanotubes have generated much enthusiasm and scientific curiosity due in part to their unique properties[2] and potential applications.[3–6] Their high aspect ratio for both single- and multiwalled varieties in combination with electronic properties that can be either conducting or semiconducting make these materials ideal for a number of electronic applications. The research presented here was driven primarily by an interest in the field emission and field-enhanced ionization properties of carbon nanotube (CNT) materials. The emission properties are thus strongly dependent upon both the physical and electronic properties of the nanotubes. It therefore becomes important to gain a better understanding of how to control these properties and the corresponding structure–process relationships. This research will focus on the nucleation and growth of multiwalled CNTs deposited via microwave plasma enhanced chemical vapor deposition (MPECVD).

One of the benefits of chemical vapor deposition (CVD) and surface deposition processes is that one can more easily control the nucleation site as well as differentiate between growth and tail ends of the nanotube. Furthermore, unlike the pulsed laser deposition processes, CVD may enable more control over such process factors as neutral gas temperature, substrate temperature, and carbon concentration. All of these factors make CVD an appropriate choice for the study of nucleation and growth processes in CNT deposition. In this communication, we report on the deposition of aligned carbon nanotubes via MPECVD on oxidized silicon substrates using an iron catalyst and methane/ammonia mixtures. CVD has been used in previous work to grow aligned carbon nanotubes.[7–11] Ammonia has also been shown in previous work to help stabilize the alignment of carbon nanotubes on nickel,[11] but twist-like defects also exist along carbon nanotubes. The ability to deposit aligned CNTs is technologically beneficial for the aforementioned applications,[12–15] however it should also facilitate fundamental studies of nucleation and growth mechanisms. The purpose of this communication is to report on the effects of growth temperature and gas phase chemistry variations on the nanotube nucleation and growth structure.

The deposition system used in this study was a 915 MHz MPECVD reactor with 10 kW maximum input power.[16] Process gas flows were adjusted with mass flow controllers. The substrate rested on a fused quartz plate, heated by a graphite element. The substrates were prepared by sputter depositing a 10 nm thick iron film onto oxidized Si wafers. The thermally grown oxide of approximately 100 nm was used as a diffusion barrier between the Si substrate and catalyst layer. Prior to deposition, the iron-coated substrates were pretreated in an ammonia gas plasma for approximately 4 min. The purpose of this pretreatment was to transform the smooth iron layer into discrete islands ranging in size from 100 to 200 nm. Following the pretreatment, the methane gas was introduced into the reactor for the start of the deposition stage. The pretreatment and deposition parameters are listed in Table I. Following deposition, surface morphology was examined by both scanning electron microscope (SEM) and transmission electron microscope (TEM). The TEM specimens were prepared from a cluster of nanotube deposit removed from the substrate and ultrasonically treated in methanol. A drop of the suspension was placed on a TEM grid and subsequently analyzed.

Figures 1(a) and 1(b) show SEM images of aligned CNTs deposited on the substrate. The nanotubes are almost parallel to each other and normal to the substrate. Misalignment at the edge is most likely caused by the damage from tweezers during handling. The density of CNTs was estimated to be about 10^8 cm^{-2} by analyzing SEM images.

Figure 2(a) shows TEM images of two different carbon nanotube structures. The tube without obvious bamboo-like

a)Author to whom correspondence should be addressed; electronic mail: stoner@physics.unc.edu

TABLE I. Pretreatment and deposition parameters.

	Pretreatment	Deposition
Gas	NH_3	CH_4/NH_3
Pressure(Torr)	21	⋯
Input microwave power (kW)	2.1	2.3
Time (min)	4	40
Flow rate (sccm)	50	150/150, 200/100, 240/60
Temperature (°C)	660–1000	⋯

structure appears to be concentrically hollow with wrinkles on the inside wall, suggesting that the inside layers are less stable. The bamboo-like structure resemble a series of stacked cones where the thickness of the inner wall increases from the tip to the body, approaching a uniform diameter. In each nanotube subsection, the outer thickness is fairly uniform, with the inner portion tapering to a tip. This pattern is repeated throughout the length of the bamboo-like nanotube. Figure 2(b) shows a particle at the end of the larger nanotube, with the tip of a bamboo layer surrounding the particle tip. This particle is most likely the iron-based catalyst, however elemental analysis was not performed as part of this study.

Figure 3 shows a plot of nanotube length as a function of deposition temperatures following 40 min growth with maximum lengths around 100 μm between 750 and 850 °C. At both temperature ends, the length of CNTs decreases.

The periodic bamboo-like structure seems to suggest a continual growth and renucleation mechanism is taking place. The distance between tips within a single tube is thus indicative of the time lag between renucleation events. At this stage the authors are uncertain as to whether the individual bamboo sections terminate on the inside or outside of the larger multiwalled structure. However given the continuous nature of the outer tip section shown in the TEM [Fig. 2(a)] we propose that the renucleated tip sections are continuous to the point where they terminate on the outer walls of the tube, forming a series of stacked cones. We expect that a combination of functional hydrocarbons and disordered carbon terminate the outer surfaces of these cones.

Growth models of bamboo-like structure have been proposed in prior work.[17,18] Saito suggested an intermittent growth model whereby layers of graphite would form on the catalyst surface until the accumulated stresses in the system would ‘‘propel’’ the nanotube (or catalyst particle) away from each other creating a fresh surface for subsequent graphite nucleation. An alternate proposal by Kovalevski and Safronov suggests that a bamboo-like structure can form when the new graphitic sheath grows more quickly than the catalyst moves away from the existing tube.[18] The latter proposal pertained to gas-phase nucleation where the catalyst particle is free to move, whereas in the present study it is fixed to the substrate surface. In the current study, we have evaluated the microstructural changes that arise from variations in both temperature and carbon concentration in the gas phase. Specifically we have evaluated variations in the interbamboo layer distance. This distance represents a renucleation of subsequent multiwalled nanotube segments and thus variations in this dimension may lead to better understanding of the process as a whole.

Figure 4 shows a plot of the interbamboo-layer distance for nanotubes grown from different methane/ammonia concentrations at a substrate temperature of approximately 810 °C. The data show an increase in spacing with partial pressure of methane. If the formation of the bamboo-layer sections is due to precipitation and renucleation at the catalyst surface, this increased spacing with carbon concentration suggests a possible diffusion limited process whereby the nanotube renucleation event is the rate-limited step. More experimental evidence, however, is required to confirm this

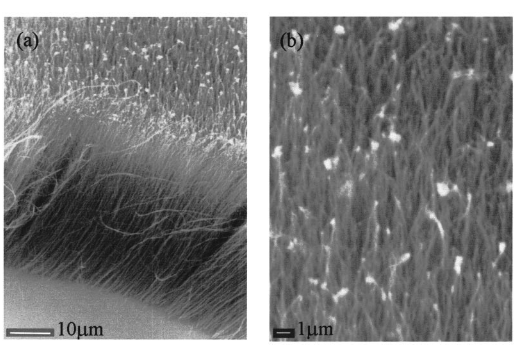

FIG. 1. (a) SEM micrograph of aligned carbon nanotubes on substrate, and (b) surface morphology of aligned carbon nanotubes. Misalignment on the edge could be caused by a tweezers scratch.

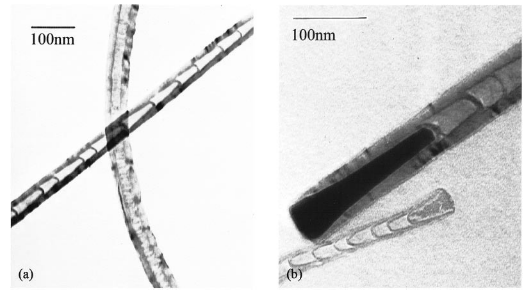

FIG. 2. (a) TEM image of bamboo-like and possible concentric hollow structures and (b) particle at the end of carbon nanotube. Bamboo-like structure exists at all depositions performed.

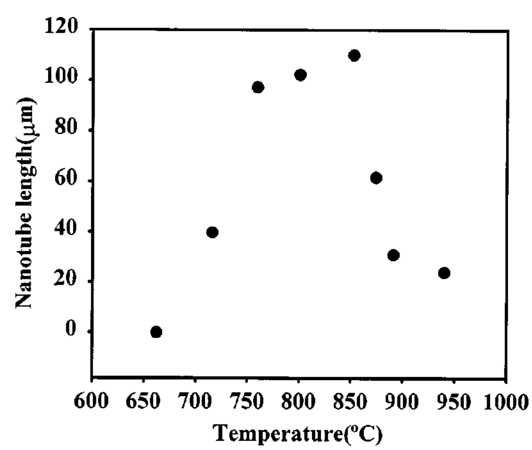

FIG. 3. CNT length at different temperatures with constant methane/ammonia ratio of 200/100 sccm.

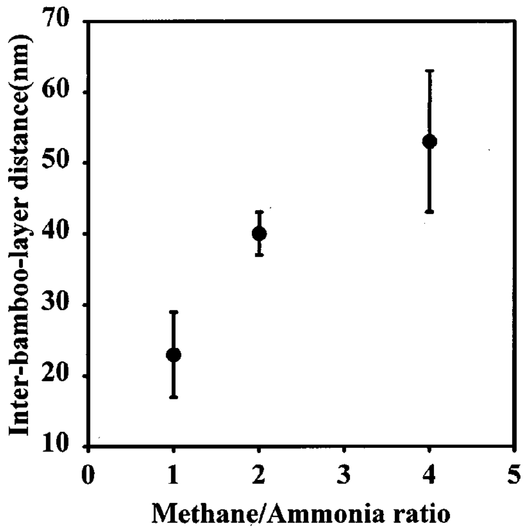

FIG. 4. Interbamboo-layer distances at different methane/ammonia ratios. Due to nanotubes tending to tangle together, the interbamboo-layer distance is averaged ranging from two to five nanotubes for each growth conditions. In each nanotube, at least five interbamboo-layer distances are measured and averaged and for the most ten interbamboo-layer distances are measured and averaged.

speculation, taking into account simultaneous variations in both tube length and diameter. Figure 5 shows the interbamboo-layer distance as a function of temperature for a constant methane/ammonia ratio. These data show a near exponential rise in the interbamboo-layer spacing with temperature. It is important to mention that neither the tube lengths nor their diameters were constant as a function of temperature, thus the interbamboo-layer spacing is indicative only of a dimensional variation and not relative rates of renucleation.

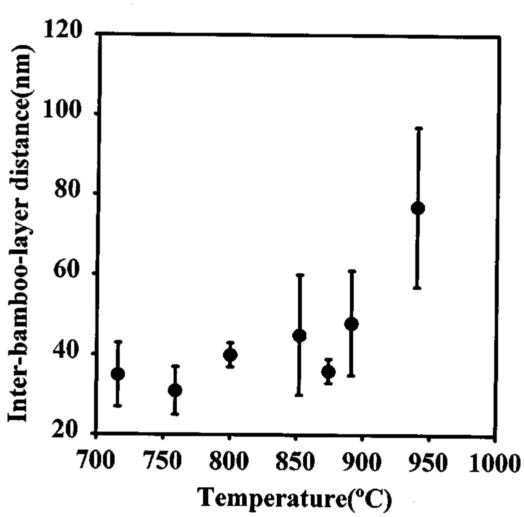

FIG. 5. Interbamboo-layer distances at different temperatures.

The reasons for this trend are not yet well understood. What we appear to have are two competing processes: the growth of the multiwalled segments and renucleation of subsequent segments. Future studies will focus on the differentiation between nucleation and growth modes with an emphasis on understanding the role of carbon incorporation at both basal and tip regions of the tube. Furthermore, we will evaluate the effects of nanotube nucleation and growth as a function of particle composition, allowing us to differentiate among the effects of carbon solubility, surface, and bulk diffusivities.

In summary, aligned CNTs have been deposited using methane/ammonia mixtures via MPECVD. Density of carbon nanotubes is about $10^8\ \mathrm{cm}^{-2}$. The majority phase is found to have a bamboo-like structure with concentric hollow structures also in existence. Further measurements such as high resolution TEM and elemental analysis are needed to confirm the structure and growth model. From the above discussion, both substrate temperature and carbon concentration in the gas phase have significant effects on the microstructure of aligned multiwalled tubes. It also must be emphasized that the above discussion does not include effects from nanotube diameter, a subject of future work.

The authors would like to thank Dr. Wallace Ambrose for assistance in SEM and TEM measurements. The project was supported in-part from ONR-MURI (Grant No. N00014-98-1-0597) and through donations by Raychem Corporation and Kobe Steel USA Inc.

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] M. S. Dresselhaus, Nature (London) **358**, 195 (1992).
[3] A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colbert, and R. E. Smalley, Science **269**, 1550 (1995).
[4] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, Nature (London) **386**, 377 (1997).
[5] C. Niu, E. K. Sichel, R. Hoch, D. Moy, and H. Tennent, Appl. Phys. Lett. **70**, 1480 (1997).
[6] S. J. Tans, A. R. M. Verschueren, and C. Dekker, Nature (London) **393**, 49 (1998).
[7] W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, Science **274**, 1701 (1996).
[8] M. Terrones *et al.*, Nature (London) **388**, 52 (1997).
[9] Z. P. Huang, J. W. Xu, Z. F. Ren, J. H. Wang, M. P. Siegal, and P. N. Provencio, Appl. Phys. Lett. **73**, 3845 (1998).
[10] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, Science **283**, 512 (1999).
[11] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, Science **282**, 1105 (1998).
[12] Y. Saito, S. Uemura, and K. Hamaguchi, Jpn. J. Appl. Phys., Part 2 **37**, L346 (1998).
[13] Q. H. Wang, T. D. Corrigan, J. Y. Dai, R. P. H. Chang, and A. R. Krauss, Appl. Phys. Lett. **70**, 3308 (1997).
[14] W. Zhu, C. Bower, O. Zhou, G. Kochanski, and S. Jin, Appl. Phys. Lett. **75**, 873 (1999).
[15] C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, and M. S. Dresselhaus, Science **286**, 1127 (1999).
[16] H. Cui, O. Zhou, and B. Stoner, Mater. Res. Soc. Symp. Proc. **593**, 39 (2000).
[17] Y. Saito, Carbon **33**, 979 (1995).
[18] V. V. Kovalevski and A. N. Safronov, Carbon **36**, 963 (1998).