

Effect of growth temperature on the synthesis of carbon nanotube arrays and amorphous carbon for thermal applications

Quang N. Pham^{1,2}, LeighAnn S. Larkin¹, Carina C. Lisboa^{1,3}, Christopher B. Saltonstall^{1,4}, Lin Qiu^{*,1,5}, Jennifer D. Schuler², Timothy J. Rupert², and Pamela M. Norris¹

¹ Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, VA 22904-4746, USA

² Department of Mechanical and Aerospace Engineering, University of California-Irvine, Irvine, CA 92697, USA

³ Centro Tecnológico da Marinha em São Paulo, Av. Prof. Lineu Prestes, 2468, Cidade Universitária, São Paulo 05508-000, SP, Brazil

⁴ Sandia National Laboratories, P.O. Box 5800 Box 5800, Albuquerque, New Mexico 87185, USA

⁵ School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

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* Corresponding author: e-mail qiulin111@sina.com, Phone/Fax: +86 10 623 32743

Though carbon nanotube (CNT) arrays have tremendous potential due to their attractive mechanical, electrical, and thermal properties, the growth kinetics of CNTs are still not fully understood. Thus, we report on the effect of synthesis parameters, such as growth temperature, on the resulting arrays. In this work, CNT arrays were synthesized using catalytic chemical vapor deposition (CCVD) with furnace temperatures varying from 680 to 900 °C. Microscopy was used to investigate the effect of growth temperature on the structural properties, such as tube diameter, array length, and the amount of amorphous carbon produced at the top of the canopy as a growth by-product. Additionally, Raman spectroscopy was used to elucidate the effect growth temperature has on the resulting purity of the CNTs. It was

then revealed that crystalline inhomogeneity exists along the length of the tubes with respect to crystallinity. Transmission electron microscopy (TEM) further determines the degree of tube crystallinity as well as the thickness of amorphous carbon coating around the nanotubes. Through both microscopy and spectroscopy, we found two distinct temperature regimes within the range of 680–900 °C. Below 800 °C, the growth of tube length and diameter remained relatively stagnant followed by a rapid growth rate above 800 °C with the highest tube crystallinity obtained within the regime of 800–840 °C. This indicates the presence of an important transitional temperature for CNT CCVD growth. Additionally, growth temperature was determined to play an important role in the amount of the resulting amorphous carbon by-product.

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1 Introduction The promising thermal [1–3] and elastic [4, 5] properties of carbon nanotube (CNT) arrays allow them to withstand mismatched coefficients of thermal expansion at solid-solid interfaces during thermal cycling without mechanical degradation. Thus, numerous studies have proposed CNT arrays as ideal candidates for advanced thermal interface materials (TIMs) [6–8], media placed at the interface to enhance conduction, often between a heat source and a sink. For integration of CNTs as TIMs, the thermal conductivity of CNTs must be high. The thermal conductivity of a single CNT can be as high as

3000 Wm^{−1}K^{−1}, but the thermal conductivity of arrays has been measured and estimated to be two to three orders of magnitude lower. The reduction in thermal conductivity is due to inhomogeneities and amorphous carbon (a-C), both resulting from the growth process. Several investigations have attempted to rid arrays of a-C with various post-processing treatments, but these are often damaging to the arrays [9–12]. In addition to excess a-C, reduced crystallinity of the tubes and a large number of concentric walls can enhance phonon scattering thus reducing the thermal conduction. Therefore, it is of great interest to be

able to synthesize repeatable, high-quality CNT arrays by a systematic study of growth parameters to modulate the structural characteristics and eliminate the as-produced layer of a-C and tube inhomogeneities, nondestructively.

In this study, we systematically modulate growth temperature from 680 to 900 °C in increments of 20 °C in a catalytic chemical vapor deposition (CCVD) growth technique to determine the effect of growth temperature on three key resulting characteristics (array height, tube diameter, and tube crystallinity) of CNT arrays. To the best of our knowledge, this is the largest presented temperature range with such small increments, used to study the temperature effects on CNT growth using chemical vapor deposition in detail. Special attention will be focused on the resulting array structure and crystallinity at growth temperature ranges of ~780–850 °C since these are commonly reported temperatures for CCVD CNT synthesis [14, 17]. Scanning electron microscopy (SEM) was used to examine array heights, tube diameters, and the a-C content on the canopy of the arrays. Raman spectroscopy was used to measure structural defects and crystallinity of the tubes. High resolution transmission electron microscopy (HRTEM) was used to determine interlayer spacing, the number of concentric walls, iron nanoparticle size, crystallinity, inner and outer CNT diameter, and amorphous coating thickness surrounding the nanotubes. Through this level of characterization, we are able to report on the effect of growth temperature on CCVD grown CNTs.

2 Experimental CNT arrays were synthesized using CCVD [20]. An electric furnace with a horizontal quartz tube, 20 mm in inner diameter, was used (see Fig. 1 for experimental set-up). Ethylene, helium, and a gas mixture of argon and hydrogen were introduced into the furnace system from mass flow rate controllers (MFC). According to Orbaek White et al., keeping the SiO₂ substrate at a slight angle of attack toward the introduced gas can help favor optimized CNT growth. In this study, a stainless steel

carrier boat was created to maintain the substrate at an angle of attack of approximately 2° relative to a parallel along the length of the tube. The substrate and its stainless steel carrier boat were loaded in the middle of the furnace. A hot plate at 180 °C was placed in contact with 0.6 g of ferrocene to sublime the iron catalyst precursor, which was then transported into the growth chamber by carrier gas helium, flowing at 600 sccm. The furnace temperature was varied from 680 to 900 °C in 20 °C increments. When the furnace reached the desired temperature, a gas mixture of 9.5:0.5 ratio of Ar:H was introduced at 900 sccm for 10 min, and the helium flow was ceased [21]. The hot plate was then removed to terminate further ferrocene sublimation, and the initiation of CNT array growth occurred when ethylene was introduced at 50 sccm. CNT growth continued for 10 min before ethylene and Ar:H mixture flows were terminated. As the furnace cooled down, 600 sccm of helium was used to protect the sample in an inert atmosphere.

Oliver et al. [22] noticed that CNT arrays grown at identical experimental procedures can vary from sample to sample due to unaccounted factors, such as ambient humidity and barometric pressure. In order to support the consistency and repeatability of our results, two sets of samples were synthesized under identical control conditions.

The method outlined above, with the catalyst (ferrocene) and the hydrocarbon (ethylene), both containing carbon species, is common in CCVD set-ups for CNT growth. Several recent groups have shown that the ferrocene catalyst can initiate CNT growth, without the presence of an additional hydrocarbon [23, 24]. Thus, in addition to the experiment outlined above, three additional samples, one at low temperature (700 °C), one at intermediate temperature (800 °C), and one at high temperature (880 °C), were grown, where ethylene was never introduced. These samples aid in understanding of the role of both ferrocene and ethylene in CNT growth as a function of growth temperature.

2.2 Characterization CNT length and diameter were measured using a cross-sectional view of the array with SEM. Several CNT length measurements were made along the cross-sectional areas of the array, while obvious conglomerations of a-C near the top array were avoided in the analysis. Tube diameter measurements were conducted with high magnification cross-sectional SEM (see Fig. 2 as example), which permit statistically rigorous approximation through averaging over 200 tubes for each reaction temperature.

SEM was also used to quantify the amount of a-C produced on a microscopic level using SEM. Top-view micrographs obtained from SEM showed the array surface contained areas of large visible aggregation of a-C (Fig. 3), and were used to compute a total percentage of a-C coverage. To our knowledge, there have been limited reports on characterization of a-C present from the growth processes, other than using Raman spectroscopy and thermo-gravimetric analysis (TGA). Although this micro-quantification of a-C may not provide a representative

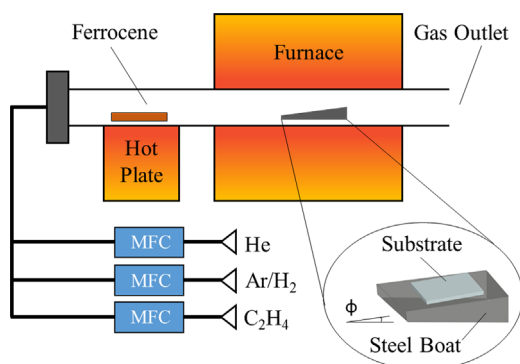


Figure 1 Schematic diagram of tube furnace set-up used for CNT array synthesis. A slightly angled steel boat carries the SiO₂ substrate for enhanced exposure to the catalyst and hydrocarbon sources.

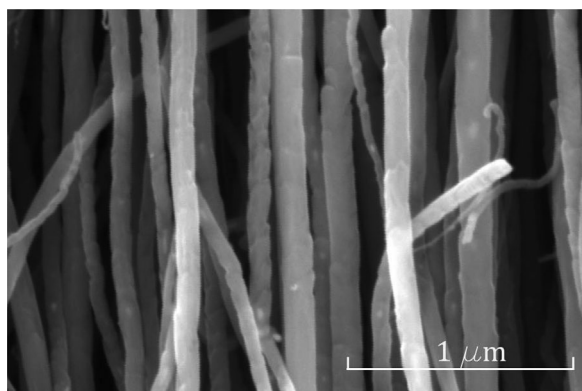


Figure 2 Sample SEM cross-sectional micrograph taken of CNT array. This particular sample was grown at 820 °C with an ethylene flow rate of 50 sccm.

analysis of overall CNT structural purity, it can provide visible evidence of an increase in a-C particulate formation at varying temperatures.

Raman spectroscopy was used to characterize the microstructure of the CNT arrays. Key characteristics of the Raman spectra of graphitic-like carbon allotropes are two sharp peaks, a so called “D peak” at around 1300 cm^{-1} and a G peak around 1600 cm^{-1} [25]. The G peak arises from zone centered sp^2 vibrations present in graphite, hence G or graphite peak. The lower frequency D peak originates from the K-point phonons, a prohibited Raman active mode in perfectly ordered graphite, but disorder relaxes this constraint to produce a D, or disorder, peak. The relative and integrated intensities of the D and G peaks, that is A_D/A_G , is a method for characterization of the disorder present in the system at the length scales penetrable by the 785 nm laser, that is a few nanometers. In the present study, Raman spectroscopy was collected at

the top of the canopy and along the length of the tubes. Three cross-sectional Raman spectra measurements were made at randomly chosen locations on the sample in order to remove the effects of any local noncrystalline carbonaceous species that may be present at some positions in the sample. The ratio of the integrated intensity of the D to G peaks at the top and center points corresponds to the average between the three separate measurements at the same height, either at the top of the tubes (omitting any clear a-C layer), or at the center point, halfway along the length, of the tubes, respectively. The average point represents the average of all cross-sectional measurements made for that sample. The A_D/A_G ratios at the top and bottom of the tubes, as well as the average A_D/A_G value, computed along the length of the tubes, can be seen in Fig. 4.

HRTEM provides opportunities to observe the tubular structure of CNTs as well as quantify the degree of their crystallinity through analyzing selected area electron diffraction (SAED) patterns. In this work, images are collected from an FEI Titan operating at 300 kV. Estimates of tube diameter distribution provided by SEM are corroborated through TEM inspection of the tube inner and outer diameters. TEM is also used to quantify the size and crystallinity of the encapsulated iron nanoparticles, number of concentric tube walls, interlayer spacing, and amorphous coating thickness around the outer layer of the tubes.

3 Results and discussion The structural properties of array height and tube diameters are measured by SEM and the results are shown in Figs. 5 and 6, respectively. From Fig. 5, we see that below 800 °C, the array heights consistently remain between 25 and 35 μm . This stable region is followed by rapid growth rates at higher temperatures, peaking between 840 and 860 °C with drastic reduction in height afterward. Likewise, as we see in

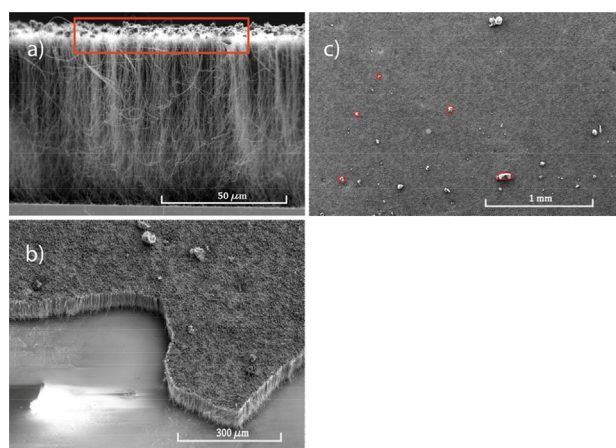


Figure 3 The presence of a-C conglomerations is shown in a) and b) scattered above the CNT array. The surface area of these relatively large a-C groupings is estimated as shown in c). These micrographs represent a sample grown at reaction temperature of 840 °C.

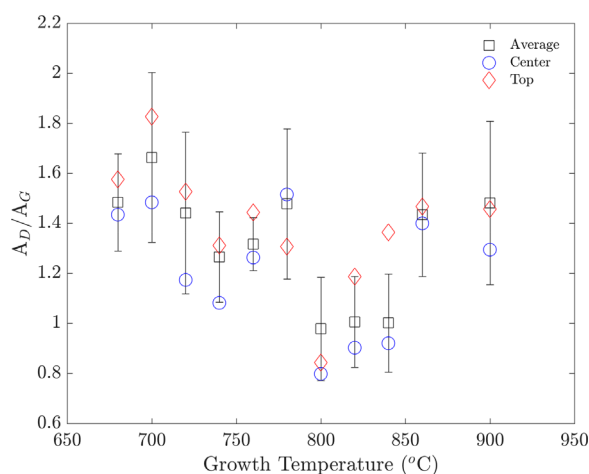


Figure 4 Three cross-sectional Raman spectra were taken along the height of CNT arrays. The A_D/A_G ratios from the center and top of the array shown along with the total average ratio values and their error bars.

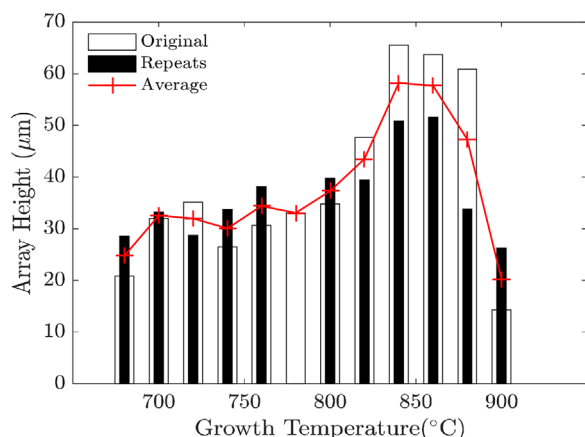


Figure 5 The array height as a function of reaction temperature is measured and averaged from the two data sets.

Fig. 6, the average CNT diameter is separated in a step function manner into two prominent temperature regimes (680–800 °C and 820–900 °C), which has never been observed due to the lack of wide temperature ranges from previous studies. The transition step in between is indicated by a dramatic diameter increase of ~25 nm, which correlated well with data presented by Schünemann et al. [13]. While the SEM analysis shows the structural properties exhibiting a clear change at ~800 °C, SEM has limited accuracy at the nanometer length scale, so a TEM analysis of the structural properties was also performed (as shown in Figs. 7–9). Again, a dramatic increase is observed at 800 °C in the diameter of the ferrocene particles, as seen in Fig. 8, and in the number of concentric walls, as seen in Fig. 9. This suggests there exists a transition at ~800 °C, where different phenomena become active in contributing to the growth of CNTs when using CCVD.

To fully understand the growth mechanisms in the two temperature regimes, we consider the samples grown without ethylene. As mentioned above in the Experimental

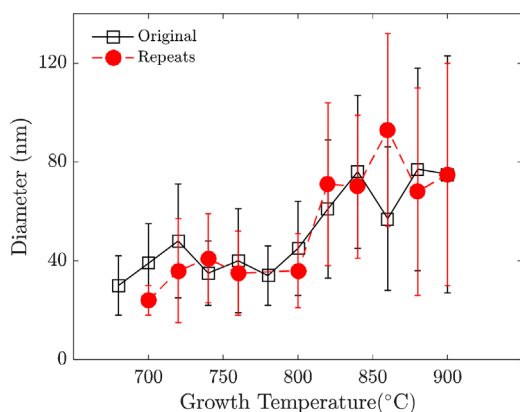


Figure 6 Average tube diameters and their associated standard deviations for both the original and repeats trials, as measured by cross-sectional SEM. As reaction temperature increases, the variation in the distribution of diameters also increases.

Section, three samples were grown at varying temperatures without the introduction of ethylene, our hydrocarbon source. With only ferrocene present, synthesis of CNT arrays is observed at high growth temperatures, above 800 °C (see Supplementary Information). Above 800 °C, the gaseous ferrocene decomposes via molecular bond fragmentations into the catalyst iron nanoparticles and carbon clusters, and these carbon clusters can become a feedstock for CNT growth. At 880 °C, we observe even longer ferrocene-grown tubes [25, 26]. The lack of CNT growth below 800 °C without ethylene suggests this temperature is not sufficient for the carbon within ferrocene to fully decompose and initiate catalysis. It is thus suggested that there exist two mechanisms for CNT growth within the current CCVD set-up: (i) at low temperatures (below 800 °C), CNT growth occurs only after the introduction of ethylene, but (ii) at high temperatures (greater than 800 °C), a 2-stage growth process occurs where ferrocene facilitates the initial growth and the introduction of ethylene accelerates further CNT growth.

In the low temperature regime, the iron nanoparticles are deposited in small, consistently sized clusters (see Fig. 8), and the hydrocarbons present in the ferrocene do not disassociate to the extent where there is excess carbon to initiate CNT growth. When ethylene is introduced, the decomposition rate in this regime is fairly slow, especially when compared to higher temperatures. The result is a lack of temperature dependence in structural properties. In the higher temperature regime, 800 °C marks an important transition for the ferrocene deposition. The increased furnace temperatures enhance the collision frequency of catalyst particles to produce larger conglomerations of catalysts. In Fig. 8, a sudden increase in catalyst diameter size is seen at 800 °C, which has long been correlated to an increased CNT diameter size and distribution [16, 17]. The catalyst sites are not only larger, but these temperatures enable the hydrocarbons in ferrocene to begin forming CNTs. The introduction of ethylene builds upon the ferrocene-grown tubes, which increase in length as the growth temperature increases. This two-step growth process creates temperature dependent structural properties. At even higher temperatures (around 860 °C), a significant side effect of disproportionate hydrocarbon decomposition is the deposition of an as-produced graphitic shell around the catalyst particles, preventing further reaction from the carbon feedstock needed for growth and thus reducing catalyst lifetime (often referred to as catalyst poisoning) [14–17], which causes growth termination. We see evidence of this catalyst poisoning at temperatures above 860 °C, which show a sudden drop in array height.

In addition to the structural properties, the crystallinity of the tubes was also characterized as a function of growth temperature. Raman spectroscopy examines the crystallinity along the length of the tubes, that is a cross-sectional view. While, it is conventional to use Raman spectroscopy to probe the top of CNT arrays, our group recently revealed

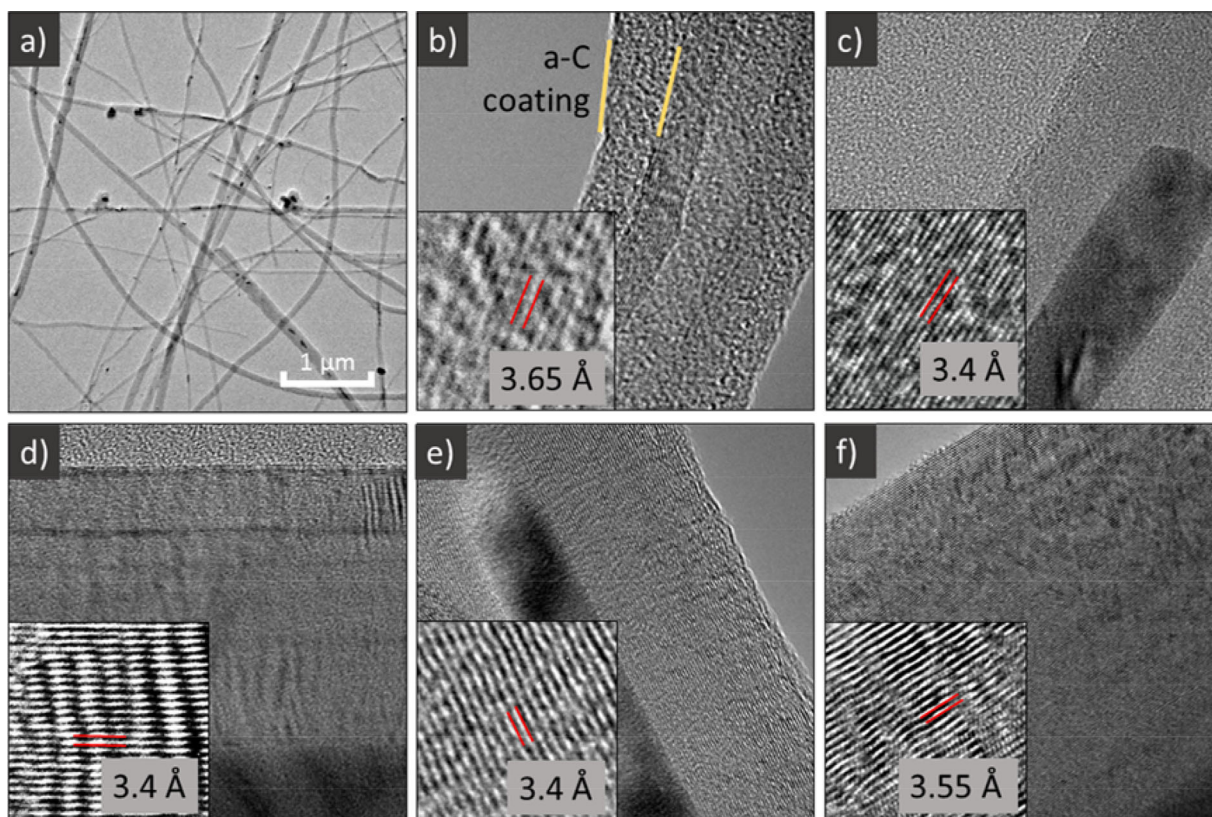


Figure 7 a) A representative TEM image at low magnification to view tubular structure as well as estimate tube diameter and catalyst nanoparticle size. b–f) High magnification TEM images of CNTs synthesized at 700, 800, 820, 840, and 900 °C, respectively, are used to determine tube inner diameters, number of concentric walls, and interlayer spacing. b) At 700 °C, amorphous carbon coating around the outer nanotube is more common and thicker in comparison to higher temperatures of c–f). The insets provide detailed view of the nanotube crystalline packing of graphite walls with the measured interlayer spacing displayed.

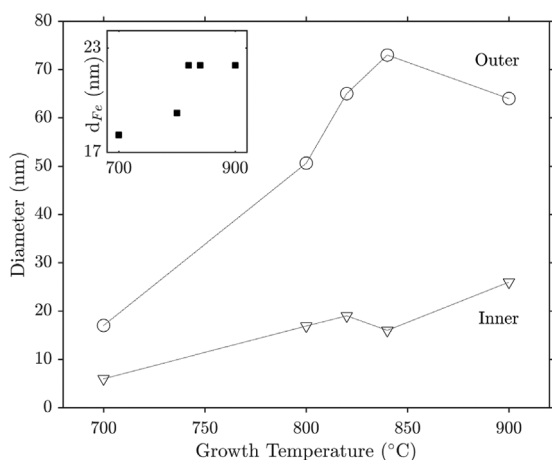


Figure 8 Encapsulated iron catalyst particle diameters measured from HRTEM images are presented in the inset. While the inner diameter (triangles) of the CNTs has minor changes with increasing temperature, the catalyst particle size seems to strongly determine the outer diameter (circles) of the nanotubes.

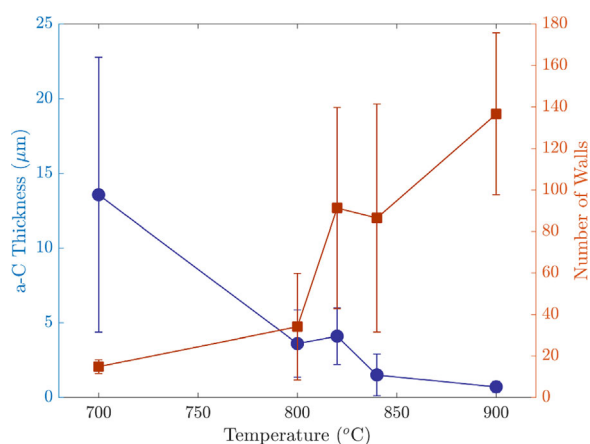


Figure 9 Using HRTEM, the a-C layer thicknesses (circles) and number of concentric tube walls (squares) are determined. Prominent amorphous coating is present at 700 °C but significantly decrease at higher temperatures due to efficient decomposition of hydrocarbons for higher level of crystalline tube formations. This increased in growth reaction can be observed by the increasing number of concentric graphite walls that encase the catalytic nanoparticles.

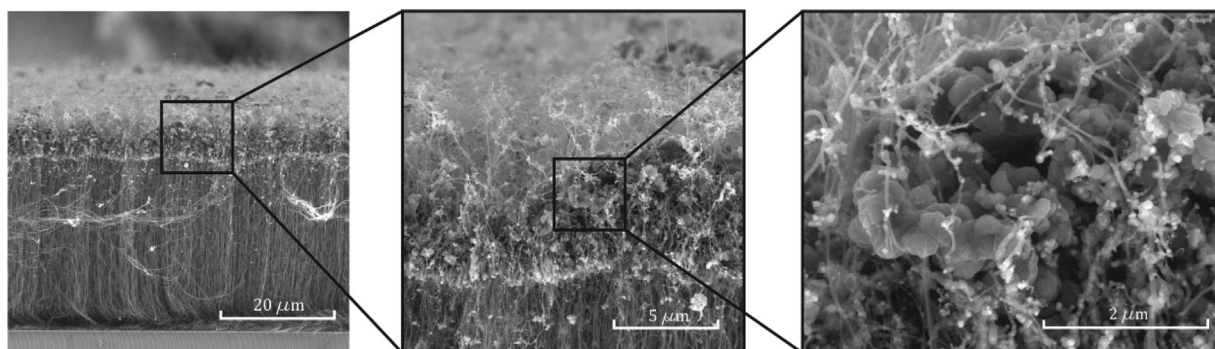


Figure 10 A cross-sectional SEM micrograph of a CNT array grown at 700 °C reveals a thick layer of a-C deposition. This helps validate the sharp peak of disorder found in Raman spectroscopy measurements.

that the crystallinity of the CNTs unexpectedly varies along the length [19]. Due to the inhomogeneity of CNTs, it becomes imperative to collect Raman spectra measurements along the array height in order to capture holistic information about purity data. When examining multiple points along the length of the array, Fig. 4 shows a region of high average disorder from 680 to 780 °C, peaking at 700 °C. In the SEM micrograph (Fig. 10), a clear, relatively thick layer of a-C resides near the top of the array canopy, and is the most prominent crust of a-C relative to the other samples. Above 780 °C, the A_D/A_G ratio drops with the lowest values approximately from 800 to 840 °C, suggesting a higher level of crystallinity in tube structure and catalyst formation, before increasing in disorder again.

The quantification of a-C via top-view SEM micrographs shows low a-C coverage above the CNT canopy at lower temperatures (Fig. 11). The proportion of a-C increased around 780 °C and dropped after 820 °C. The formation of non-crystalline carbon particles at elevated temperature can be explained by excessive pyrolysis. Aside

from a-C conglomerates on top of CNT arrays, several previous investigations report that such high rate of hydrocarbon decomposition also results in forming amorphous coatings around the surface of individual CNTs, rapidly increasing the nanotube diameters [13, 14]. Our side-view Raman spectroscopy (Fig. 4) and HRTEM analysis (Fig. 7) do not agree well with this traditional theory of tube diameter enlargement. Such an amorphous coated film around the tubes would have strongly impacted the Raman spectra measurements. For instance, samples grown at elevated temperature would have a higher A_D/A_G ratio similar to that of the noncrystalline carbonaceous species observed near the top CNT array of 700 °C (Figs. 4 and 10). Corroboration from TEM images additionally reveals that the amorphous coating thickness around the outer wall of the CNTs actually decreases with increasing temperature (Fig. 7). While the a-C coating thickness decreases around the tubes, the diameter of the CNTs continues to increase with increasing number of concentric walls, facilitated by larger catalyst particles. The A_D/A_G ratio is thus related to the number of walls and the thickness of a-C surrounding the tubes. The temperature range of 800–840 °C present both low number of walls as well as a-C thickness, which results in the lowest A_D/A_G ratio (Figs. 4 and 9). It is believed that activation energy, diffusion of carbon in iron particles, and conglomeration of nanoparticle sizes from atomic collision may play a major role in tube diameter enlargement rather than a-C thickening [18].

Samples from the low (700 °C), transitional (800–840 °C), and high (900 °C) growth temperature regimes are further examined with HRTEM (sample images in Fig. 7). Selected area electron diffraction (SAED) patterns from HRTEM are used to provide additional characterization for crystallinity of the CNTs and catalytic nanoparticles. The nanotubes are observed to be crystalline with d-spacings of approximately 3.4 Å in the $\langle 002 \rangle$ plane, which is previously observed in literature [26, 27]. The diffraction patterns of the iron catalysts reveal that the nanoparticles retained their crystalline structuring throughout in all temperature regimes.

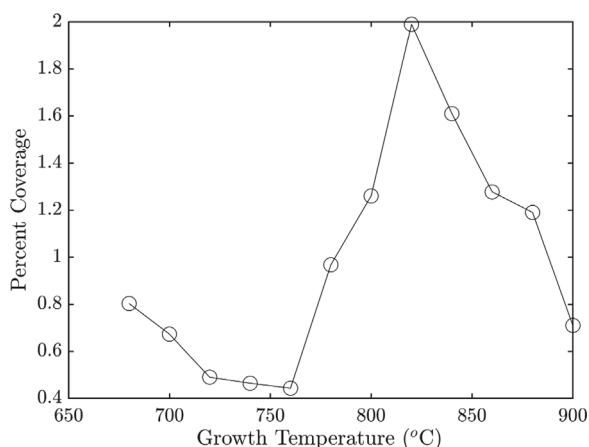


Figure 11 The estimated percentage coverage of a-C to the total working area shows a growth temperature zone (780–900 °C) that induces excessive pyrolysis. The aggregations of a-C in this region are much larger and prominent on the top surface of the arrays.

4 Conclusions In conclusion, we systematically varied a large range of growth temperatures and observed the incremental changes in array height, tube diameter, nanotube crystallinity, and percentage of a-C grown per unit area using SEM, HRTEM, and Raman spectroscopy. Overall, we report on an important transitional temperature regime (800–840 °C) within the CCVD CNT synthesis process. Array growth rate and tube diameter enlargement begin to significantly increase within this temperature range while producing highly crystalline CNT arrays. Above or below these transitional temperatures, CNTs with lower crystallinity and temperature-independent morphology were grown within their respective regimes. Since the majority of CCVD CNT syntheses are conducted within the range of 750–850 °C, better control of rapid and enhanced growth reactions at these transitional temperatures can ensure repeatable synthesis. In addition, we demonstrated the inhomogeneity in crystal structure along the length of the CNTs, suggesting that traditional Raman measurement from the top of CNT arrays is insufficient in providing representative crystallinity information about the arrays. The growth mechanism of high-quality CNT arrays must be better understood and controlled before they can be used for next-generation thermal management.

Supporting Information Additional supporting information may be found in the online version of this article at the publisher's web-site.

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References

- [1] J. Hone, M. Whitney, C. Piskoti, and A. Zettl, *Phys. Rev. B* **59**, R2514 (1999).
- [2] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, *Phys. Rev. Lett.* **87**, 215502 (2001).
- [3] W. Yi, L. Lu, Z. Dian-lin, Z. W. Pan, and S. S. Xie, *Phys. Rev. B* **59**, R9015 (1999).
- [4] L. Cai, L. Song, P. Luan, Q. Zhang, N. Zhang, Q. Gao, D. Zhao, X. Zhang, M. Tu, and F. Yang, *Sci. Rep.* **3**, 3048 (2013).
- [5] R. S. Ruoff, D. Qian, and W. K. Liu, *C.R. Phys.* **4**, 993 (2003).
- [6] X. Liu, Y. Zhang, A. M. Cassell, and B. A. Cruden, *J. Appl. Phys.* **104**, 84310 (2008).
- [7] M. Panzer, G. Zhang, D. Mann, X. Hu, E. Pop, H. Dai, and K. E. Goodson, *Thermal. J. Heat Transfer* **130**, 1306 (2008).
- [8] H. Wang, J. Feng, X. Hu, and K. M. Ng, *J. Phys. Chem. C* **111**, 12617 (2007).
- [9] J. L. Zimmerman, R. K. Bradley, C. B. Huffman, R. H. Hauge, and J. L. Margrave, *Chem. Mater.* **12**, 1361 (2000).
- [10] A. C. Dillon, T. Gennett, K. M. Jones, J. L. Alleman, P. A. Parilla, and M. J. Heben, *Adv. Mater.* **11**, 1354 (1999).
- [11] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, and C. Galiotis *Carbon* **46**, 833 (2008).
- [12] S. Bando, A. M. Rao, K. A. Williams, A. Thess, R. E. Smalley, and P. C. Eklund, *J. Phys. Chem. B* **101**, 8839 (1997).
- [13] C. Schünemann, F. Schäffel, A. Bachmatiuk, U. Queitsch, M. Sparing, B. Rellinghaus, K. Lafdi, L. Schultz, B. Büchner, and M. H. Rummeli, *ACS Nano* **5**, 8928 (2011).
- [14] C. Ghemes, A. Ghemes, M. Okada, Y. Inoue, and H. Mimura, *J. Adv. Res. Phys.* **3**, 11207 (2012).
- [15] Q. W. Li, X. F. Zhang, R. F. DePaula, L. X. Zheng, Y. H. Zhao, L. Stan, T. G. Holesinger, P. N. Arendt, D. E. Peterson, and Y. T. Zhu, *Adv. Mater.* **18**, 3160 (2006).
- [16] T. Yamada, T. Namai, K. Hata, D. N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura, and S. Iijima, *Nat. Nanotechnol.* **1**, 131 (2006).
- [17] Y. Luo, X. Wang, M. He, X. Li, and H. Chen, *J. Nanomater.* **4** (2012).
- [18] S. K. Pal, S. Talapatra, S. Kar, L. Ci, R. Vajtai, T. Borca-Tasciuc, L. S. Schadler, and P. M. Ajayan, *Nanotechnology* **19**, 45610 (2008).
- [19] M. L. Bauer, Q. N. Pham, C. B. Saltonstall, and P. M. Norris, *Appl. Phys. Lett.* **105**, 151909 (2014).
- [20] Q. Zhang, J. Huang, M. Zhao, W. Qian, and F. Wei, *Appl. Phys. A* **94**, 853 (2009).
- [21] A. Orback White, Flow in the Field of Carbon Nanotube Growth. Symposium presented at the University of Virginia, Charlottesville, VA (Feb 5, 2014).
- [22] C. R. Oliver, E. S. Polsen, E. R. Meshot, S. Tawfik, S. J. Park, M. Bedewy, and A. J. Hart, *ACS Nano* **7**, 3565 (2013).
- [23] K. Elihn and K. Larsson, *Thin Solid Films* **458**, 325 (2004).
- [24] R. Bhatia and V. Prasad, *Solid State Commun.* **150**, 311 (2010).
- [25] A. C. Ferrari and J. Robertson, *Phys. Rev. B* **61**, 14095 (2000).
- [26] C. Liang-Chen, W. Li-Jun, T. Dong-Sheng, X. Si-Shen, and J. Chang-Qing, *Chin. Phys. Lett.* **18**, 577 (2001).
- [27] Y. Maniwa, R. Fujiwara, H. Kira, H. Tou, E. Nishibori, M. Takata, M. Sakata, A. Fujiwara, X. Zhao, S. Iijima, and Y. Ando, *Phys. Rev. B* **64**, 73105 (2001).