Applied Physics Letters

# Diagnostics and growth control of single-walled carbon nanotube forests using a telecentric optical system for in situ height monitoring

Satoshi Yasuda, Don. N. Futaba, Motoo Yumura, Sumio Iijima, and Kenji Hata

Citation: Appl. Phys. Lett. **93**, 143115 (2008); doi: 10.1063/1.2987480

View online: http://dx.doi.org/10.1063/1.2987480

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v93/i14

Published by the American Institute of Physics.

# Diagnostics and growth control of single-walled carbon nanotube forests using a telecentric optical system for *in situ* height monitoring

Satoshi Yasuda,[a)] Don. N. Futaba, Motoo Yumura, Sumio Iijima, and Kenji Hata[b)]
*Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan*

(Received 28 July 2008; accepted 21 August 2008; published online 10 October 2008)

An *in situ* telecentric height monitoring system was employed as a standard characterization tool for *in situ* height monitoring of nanotube forests. We demonstrated that the system possesses a wide dynamic range beyond the centimeter scale, high resolution of 1 $\mu$m, free from routine maintenance, simple installation, and use in contrast to previous methods. These features were highlighted by the monitoring of a 5 mm tall forest, the examination of the effect of gas species on growth rates, and the automatic control forest height. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2987480]

Vertically aligned carbon nanotube (CNT) forests with properties of high purity, vertical alignment, and millimeter-scale height have shown exceptional promise as a powerful industrial material for various applications: spanning actuators, energy storage, and sensors.[1–11] In order to fully realize the potential for these applications, it is crucial to understand the critical factors determining nanotube forest growth dynamics to further improve and to control nanotube growth. The key to further cultivate our understanding of CNT forest growth dynamics is an *in situ* monitoring system capable of measuring the height progression of the forest during growth with both millimeter-scale range and high resolution. While several measurement systems have already been proposed to investigate the growth dynamics, based on different optical methods such as optical interference, absorption, and diffraction,[12–16] none have simultaneously overcome the basic obstacles of high resolution, wide dynamic range, easy installation into conventional chemical-vapor deposition (CVD) furnaces, and free from constant adjustment.

One simple approach has been to directly image the forests with cameras.[14] However, for normal lenses used in cameras, the magnification varies with the distance (and changes the dynamic range), the image shape differs away from the optic axis, and sample focusing is required for each growth. These intrinsic shortcomings make accurate and reproducible height measurement difficult, while maintaining wide dynamic range. Therefore, although their importance is well acknowledged, *in situ* monitoring systems have not yet become a standard characterization tool for CNT forests as reflection high-energy electron diffraction has become for molecular beam epitaxy growth.

Here, we propose the use of a telecentric optical system as a standard characterization tool for *in situ* height monitoring of nanotube forests and demonstrate that the system possesses a wide dynamic range beyond the centimeter scale, high resolution of 1 $\mu$m, free from routine maintenance, simple installation, and use in contrast to previous methods.

CNT forests were synthesized in a 1 in. quartz tube furnace by water-assisted CVD, "supergrowth" at 750 °C with a $C_2H_4$ carbon source, and an $Al_2O_3$ (10 nm)/Fe (1 nm) thin-film catalyst on silicon wafers.[1,12] We used He with $H_2$ as the carrier gas [total flow of 1000 SCCM (SCCM denotes standard cubic centimeter per minute at 1 atm)] with a controlled amount of water vapor. Growth was performed at 750 °C with ethylene (75 SCCM). Vertically aligned single-walled CNTs grew from the substrate, forming a CNT forest.

Figure 1 shows a schematic of the telecentric optical monitoring system (top and side views). This monitoring system is commercial and available (LS7030M, Keyence). The monitoring system consists of a transmitter and a receiver. The transmitter produces a brilliant parallel green light flow from a GaN light-emitting diode (LED) source. The parallel light is transmitted into the furnace via a small rectangle slit and meets the forest and substrate from the side. The projected shadow of the forest progresses to the receiver and is refocused onto a charge coupled device (CCD) through the telecentric optical system. The separation of the two light-shadow interfaces on the CCD is the measured height, which allows for real-time data analysis and is monitored on a computer with a sampling frequency of 1 Hz.

Our system has two major advantages. First, the telecentric optical system operates with an infinite focal distance (magnification is independent of distance) which allows for

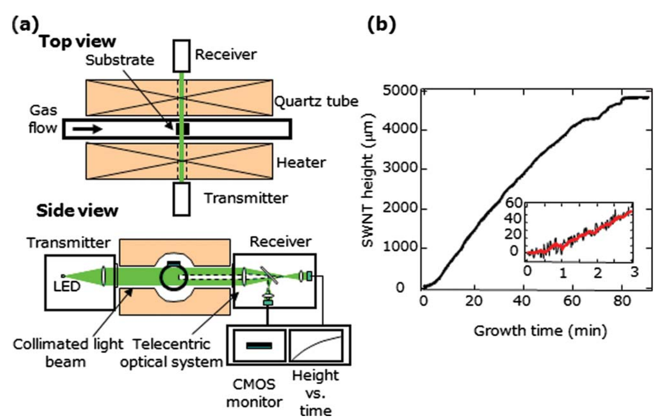


FIG. 1. (Color online) (a) A schematic of the top and side views of the telecentric optical monitoring system installed into our nanotube CVD furnace. (b) Time evolution of SWNT forest growth curve with 5 mm height. Inset graph shows the raw height data measured at a sampling frequency of 1 Hz (black curve). Red curve is smoothed curve by *in situ* filtering.

[a)]Electronic mail: satoshi-yasuda@aist.go.jp.
[b)]Electronic mail: Kenji-hata@aist.go.jp.

 

easy operation and accurate measurement. This differs from normal lens. No readjustment is required despite changes in sample-lens distance, sample size, or sample loading position because telecentric lenses create same sized images for objects observed at any distance. The second advantage is the bright parallel light flow produced from a LED source, which improves the stability and reliability of the system. The light intensity enabled *in situ* height monitoring even at severe growth conditions where the furnace tube became dirty and opaque. Additionally, the use of green light was important to minimize interference from the intense red and infrared lights from the hot furnace.

We demonstrate the durability and performance of our system by monitoring an entire 80+ min growth curve [Fig. 1(b)] for a forest with 5 mm height, which illustrates both the wide dynamic range and the durability of this system. (Growth termination occurred prior to reaching the measurement range of the system.) As a result of this extended growth time, the furnace quartz tube became very dirty and the interior was invisible to the naked eye. In this case, conventional optical cameras would have been unable to image the forest; however, the bright parallel illumination was transmitted through the opaque furnace tube and was detectable. This advantage was critical to enable the monitoring growth of tall forests.

Inset of Fig. 1(b) also shows the raw height data measured. The signal fluctuation [$\pm 6$ $\mu$m (standard deviation: $2\sigma$)] results from thermal fluctuation of air in the light path and system vibration and was smoothed by *in situ* filtering (red curve). From the filtered growth curve, the resolution of the system was estimated as $\pm 1$ $\mu$m (standard deviation: $2\sigma$). These data confirm that our monitoring system using telecentric optical system yields wide dynamic range with high resolution and high stability, and is appropriate for diagnostics and control of the forest.

By using the *in situ* monitoring system, we can further expand our knowledge of forest growth by examining the effect of ambient gas species on the catalyst. Figure 2(a) shows growth curves of multiple stop-and-go growth cycles,[17–19] defined by a 3 min growth and 3 min interruption. For each examination, different gas species were used during the growth interruption: He, $H_2$, and water (concentration of 100–150 ppm in He). From the growth curves, the growth rates at each cycle were normalized to the initial growth rate (average growth rate during the time period of 0–3 min) and plotted against the total growth time, as shown Fig. 2(b). Generally, the growth rates decreased with each successive growth, but the rate at which they dropped differed significantly with the gas species during the interruption. For the case of He, the growth rate dropped by about 50% for each successive growth, which quickly led to virtually complete deactivation by only the fourth growth cycle. By comparison, water exposure completely deactivated the growth by only the second growth cycle. In sharp contrast, hydrogen exposure during the growth interruption showed a tendency to maintain the growth rate for at least several cycles. The two following cycles after the initial onset of growth exhibited nearly identical growth rates. Moreover, these growth rates were even higher than for an uninterrupted forest growth. These results imply that the catalyst activity drops significantly in the neutral gas ambient of He and in the excess water ambient despite the absence of carbon. However, hydrogen tends to preserve the catalyst activ-

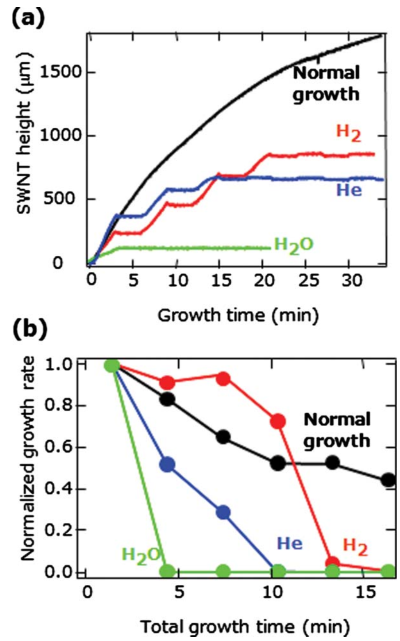


FIG. 2. (Color online) (a) Growth curves of multiple stop-and-go growth cycles, defined by a 3 min growth and 3 min interruption. The flow gas during the interruption were $H_2$ (red curve), He (blue curve), and concentration of 100–150 ppm in He (green curve), respectively. (b) Plot of the growth rates normalized to the initial growth rate at each cycle as a function of the total growth time.

ity. We believe that water deactivation occurred through oxidation of the catalysts while hydrogen reduced and reactivated them. While initially puzzling, we believe that the deactivation observed while flowing neutral He gas is not an intrinsic effect of He itself, but rather effects from either the residual gas impurities in the He [~5 ppm oxygen and ~10 ppm water included in He gas (99.995% purity)] or the water and ethylene supply imbalance created when the growth is interrupted. This unique approach provides fascinating insight into further fundamental studies to maintain catalyst lifetime.

Finally, the potential of our monitoring system to control the growth was explored by automatically synthesizing nanotube forests with predetermined height. The height is one of the most important structural parameters of the forest because electrochemical, mechanical, electrical, and thermal properties are all expected to depend on the height.[10,20] For applications, synthesizing forests with optimum height for each application is paramount to fully realize the potential of each application. Therefore, the ability to grow forests with precisely determined height is valuable for both fundamental science and practical applications. To control the growth with high precision, the output of the *in situ* monitoring system was used as feedback to the full-automated CVD furnace, and when the forest height reached the programmed height the growth was stopped automatically. Figure 3(a) shows a series of nanotube forests automatically synthesized with set heights of 10, 100, 400, 800, and 2000 $\mu$m, respectively. For 10 and 100 $\mu$m short forests, the ethylene flow rate was decreased to 20 SCCM to increase the controllability. The actual heights were measured by scanning electron microscopy (SEM) [Figs. 3(b)–3(f)] and were 12, 108, 420, 828, and 2022 $\mu$m, respectively. The observed deviations were lower than 10% except when the height was on the order of the system resolution [Fig. 3(g)]. The wide dynamic range,

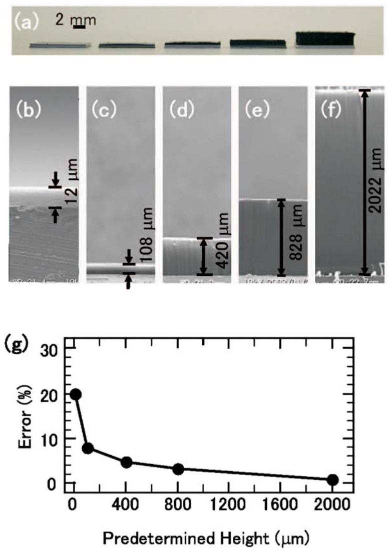


FIG. 3. (Color online) (a) A series of nanotube forests automatically synthesized with set heights of 10, 100, 400, 800, and 2000 $\mu$m, respectively, and [(b)–(f)] their SEM images. (g) Plot of the error between the programmed and actual heights as a function of the programmed height.

high resolution, accurate, and real-time *in situ* monitoring of our system enabled precise control of the growth over a very wide range from a couple of micrometers to over a millimeter. We believe that the ability to control the growth of forests with our monitoring system would open up numerous opportunities in the future to explore the science and applications of nanotube forests.

In summary, we have employed a telecentric optical system to diagnose and control the growth of nanotube forests. The growth curve could be easily measured with much higher accuracy and wider dynamic range than conventional measurement systems. The wide dynamic range with high resolution was highlighted by monitoring the entire growth evolution of a 5 mm forest with a resolution of 1 $\mu$m. Lastly, the system versatility beyond monitoring the growth was demonstrated by (1) diagnosing the growth kinetics for differing gas ambients and (2) using the monitored height as feedback for the CVD system to set the forest growth with precisely predetermined height. We believe that this monitoring system would become a standard characterization tool for nanotube forest growth.

Support from the Nanotechnology Program "Carbon Nanotube Capacitor Development Project" (2006–2010) by the New Energy and Industrial Technology Development Organization ("NEDO") is acknowledged.

[1]K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, Science **306**, 1362 (2004).
[2]S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, Science **283**, 512 (1999).
[3]S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, and M. Kohno, Chem. Phys. Lett. **360**, 229 (2002).
[4]M. Cantoro, S. Hofmann, S. Pisana, V. Scardaci, A. Parvez, C. Ducati, A. C. Ferrari, A. M. Blackburn, K.-Y. Wang, and J. Robertson, Nano Lett. **6**, 1107 (2006).
[5]H. J. Jeong, K. K. Kim, S. Y. Jeong, M. H. Park, C. W. Yang, and Y. H. Lee, J. Phys. Chem. B **108**, 17695 (2004).
[6]J. Liu, R. Czerw, and D. L. Carroll, J. Mater. Res. **20**, 538 (2005).
[7]S. J. Jeong, K. A. Park, S. H. Jeong, H. J. Jeong, K. H. An, C. W. Nah, D. Pribat, S. H. Lee, Sr., and Y. H. Lee, Nano Lett. **8**, 2178 (2007).
[8]M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, and R. H. Baughman, Science **309**, 1215 (2005).
[9]Y. Yun, V. Shanov, Y. Tu, M. J. Schulz, S. Yarmolenko, S. Neralla, J. Sankar, and S. Subramaniam, Nano Lett. **6**, 689 (2006).
[10]D. N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura, and S. Iijima, Nature Mater. **5**, 987 (2006).
[11]J. K. Holt, H. G. Park, Y. Wang, M. Stadermann, A. B. Artyukhin, C. P. Grigoropoulos, A. Noy, and O. Bakajin, Science **312**, 1034 (2006).
[12]D. N. Futaba, K. Hata, T. Yamada, K. Mizuno, M. Yumura, and S. Iijima, Phys. Rev. Lett. **95**, 056104 (2005).
[13]D. B. Geohegan, A. A. Puretzky, I. N. Ivanov, S. Jesse, G. Eres, and J. Y. Howe, Appl. Phys. Lett. **83**, 1851 (2003).
[14]A. J. Hart, L. V. Laake, and A. H. Slocum, Small **5**, 772 (2007).
[15]S. Maruyama, E. Einarsson, Y. Murakami, and T. Edamura, Chem. Phys. Lett. **403**, 320 (2005).
[16]L. M. Dell'Acqua-Bellavitis, J. D. Ballard, P. M. Ajayan, and R. W. Siegel, Nano Lett. **4**, 1613 (2004).
[17]L. Zhu, Y. Xiu, D. W. Hess, and C.-P. Wong, Nano Lett. **5**, 2641 (2005).
[18]X. Li, A. Cao, Y. J. Jung, R. Vajtai, and P. M. Ajayan, Nano Lett. **5**, 1997 (2005).
[19]T. Iwasaki, J. Robertson, and H. Kawarada, Nano Lett. **8**, 886 (2008).
[20]Z. L. Wang, D. W. Tang, X. B. Li, X. H. Zheng, W. G. Zhang, L. X. Zheng, Y. T. T. Zhu, A. Z. Jin, H. F. Yang, and C. Z. Gu, Appl. Phys. Lett. **91**, 123119 (2007).