Japanese Journal of Applied Physics
Vol. 46, No. 14, 2007, pp. L333–L335

Rapid and Localized Synthesis of Single-Walled Carbon Nanotubes on Flat Surface by Laser-Assisted Chemical Vapor Deposition

Keigo KASUYA[1,2*], Keisuke NAGATO[1,2], Yusuke JIN[1], Hiroshi MORII[1], Takeshi OOI[3], and Masayuki NAKAO[1]

[1]*Department of Engineering Synthesis, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2]*Research Fellow of the Japan Society for the Promotion of Science, 8 Ichibancho, Chiyoda-ku, Tokyo 102-8472, Japan*
[3]*Komatsu Ltd., 1200 Manda, Hiratsuka, Kanagawa 254-8567, Japan*

(Received December 5, 2006; revised February 19, 2007; accepted February 20, 2007; published online March 30, 2007)

The synthesis of single-walled carbon nanotubes (SWNTs) at a controlled position on a flat surface was demonstrated by laser-assisted chemical vapor deposition (CVD). The developed multilayer substrate including an energy-confining layer (ECL) enabled the efficient heating of catalysts on the surface, resulting in the rapid and localized syntheses of SWNTs. Using a Nd:YAG laser as a heat source, we achieved the rapid synthesis with laser irradiation for 1 s and the localized synthesis in an area of approximately 1 μm diameter. In addition, the scanning of the laser irradiation spot at a rate of 1 μm/s enabled the line-patterned synthesis of SWNTs at a linewidth of 2 μm. The resulting synthesis of SWNTs on a flat surface by laser-assisted CVD will lead to the easy and controllable fabrication of SWNT-based nanodevices. [DOI: 10.1143/JJAP.46.L333]

KEYWORDS: single-walled carbon nanotube, laser-assisted chemical vapor deposition, position control, line-patterned synthesis, multilayer substrate, energy-confining layer

Single-walled carbon nanotubes (SWNTs) have attracted considerable interest due to their novel electrical, optical, and mechanical properties, and they are expected to be promising materials for a wide variety of nanodevices, such as electric circuits, field emitters, sensors, and optical components.[1)] SWNTs have been synthesized by arc discharge,[2)] laser vaporization,[3)] and chemical vapor deposition (CVD).[4)] Among these methods, CVD is widely used because of its advanced feature enabling the synthesis of SWNTs directly on a surface. One of the difficulties in the development of practical applications is controlling the position of SWNTs on the surface. Position-controlled synthesis has been achieved by the patterning of catalysts in CVD.[5,6)] Recently, laser-assisted CVD has been reported as an alternative technique for the position control. Rohmund *et al.* synthesized carbon nanotubes on a millimeter scale using a focused CO_2 laser and $Fe(CO)_5$ catalysts.[7)] Fujiwara *et al.* synthesized SWNTs with a diameter of 5 μm using an Ar-ion laser and catalysts consisting of $Fe(NO_3)_3 \cdot 9H_2O$, $MoO_2(acac)_2$, and alumina nanoparticles.[8)] The advantage of this technique is that it enables the heating of desired points locally. This local heating reduces heat-induced damage to the surface, which enables the synthesis of SWNTs on substrates including low-melting-point materials or device components. Furthermore, this technique enables the synthesis of SWNTs independently at each position on one substrate. By changing irradiation conditions[9,10)] or applying an electric field,[11,12)] it has the potential of arranging SWNTs with different lengths, diameters or directions on one substrate. This form-selected synthesis at individual positions cannot be achieved by global heating in conventional CVD. However, the synthesis of SWNTs on flat surfaces by laser-assisted CVD has not been performed yet. Towards the goal of fabricating SWNT-based nanodevices, SWNT synthesis on flat surfaces should be required.

In this study, we performed the laser-assisted CVD synthesis of SWNTs on a flat substrate employing an energy-confining layer (ECL). The ECL enables the efficient heating of catalysts on the surface, which results in the localization of a synthesis spot, a decrease in heat up time and the growth of SWNTs on a flat Si substrate. We achieved the local synthesis of SWNTs in an area of about 1 μm diameter and their rapid synthesis with laser irradiation for 1 s. Using this rapid growth method, the line-patterned synthesis of SWNTs by scanning laser irradiation is also demonstrated.

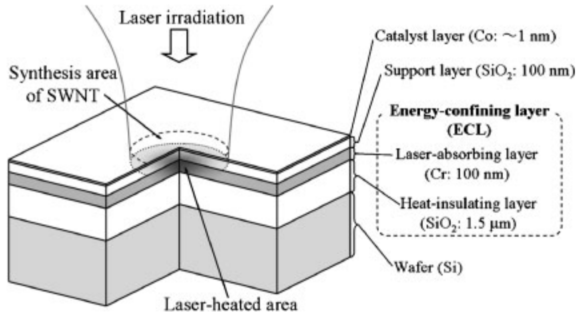

Fig. 1. Schematic of laser-assisted CVD synthesis of SWNTs on multilayer substrate with ECL.

Figure 1 shows the multilayer substrate developed with the ECL. The substrate involves a sputtered Co thin film as a catalyst layer, a 100-nm-thick sputtered SiO_2 film as a support layer and the ECL, which consists of a 100-nm-thick sputtered Cr film as a laser-absorbing layer and a 1.5-μm-thick thermally oxidized film as a heat-insulating layer. When a laser irradiates the multilayer substrate, most of the laser energy, which has not been reflected on the surface, is absorbed by the Cr film and transformed to heat energy. Since the thermally oxidized thick film underneath prevents thermal conduction, the Co thin film over the irradiated area is efficiently heated and transforms into nanoparticles.[13)] Then SWNTs are synthesized on the surface within the irradiated area. Without the ECL, the laser beam is transmitted into the substrate due to the low absorption coefficients of Si and SiO_2, and the heat energy is dispersed into a large region in the Si substrate due to its high thermal conductivity. In this case, synthesis requires a high laser power, a long heat up time, and a large synthesis area.

Figure 2 shows the experimental apparatus for laser-assisted CVD. The multilayer substrate was placed in a

*E-mail address: kasuya@hnl.t.u-tokyo.ac.jp

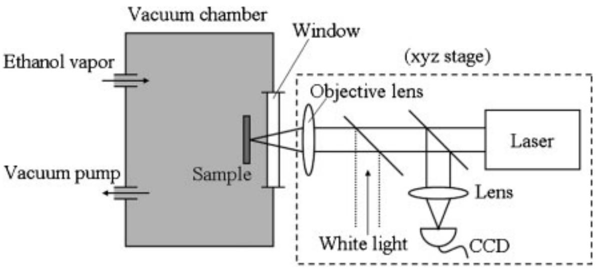

Fig. 2. Configuration of experimental apparatus for laser-assisted CVD synthesis of SWNTs.

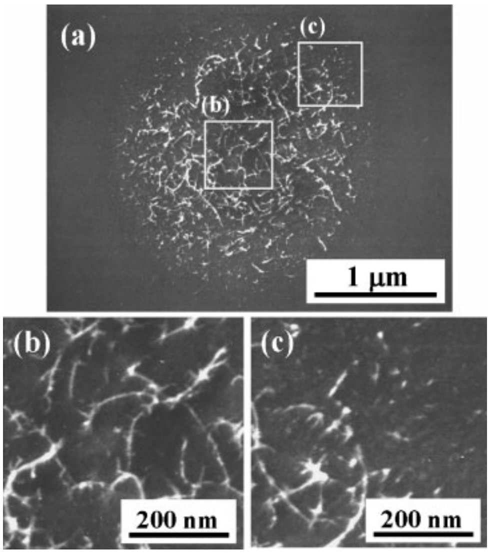

Fig. 3. SEM images of SWNTs synthesized by laser-assisted CVD for laser-irradiation time of 1 s: (a) entire circular area, (b) center and (c) edge of area.

vacuum chamber, and the chamber was evacuated to about 1 Pa. Then ethanol vapor[14)] was supplied to the chamber from a room-temperature reservoir. The pressure of the chamber was kept at 1.3 kPa. We used a continuous single-mode Nd:YAG laser (wavelength of 1064 nm) with a Gaussian profile intensity as a heat source. This laser was focused using an objective lens to the substrate through the window of the vacuum chamber. The entire optical assembly was set on an *xyz* stage beside the chamber to adjust the laser focus, spot site, and scan position of laser irradiation. We adjusted the laser focus and spot while monitoring the laser-irradiated region using a charge-coupled device (CCD) camera. The substrate was irradiated using the laser at a power of 50 mW and a beam spot diameter of about 3 µm. The irradiation time was varied from 1 s to 10 min. After irradiation, the irradiated spot was analyzed by scanning electron microscopy (SEM) and Raman spectroscopy with an excitation wavelength of 488 nm.

Figure 3 shows the SEM images of the synthesized SWNTs for 1 s irradiation. On the flat surface of the multilayer substrate, SWNTs were synthesized in a circular area with a diameter of approximately 2 µm. At the center of the circular area, dense SWNT bundles were clearly observed [Fig. 3(b)]. Towards the outside of the circular area, the number of bundles decreased and finally disappeared at the edge [Fig. 3(c)]. Figure 4 shows the Raman spectrum of the

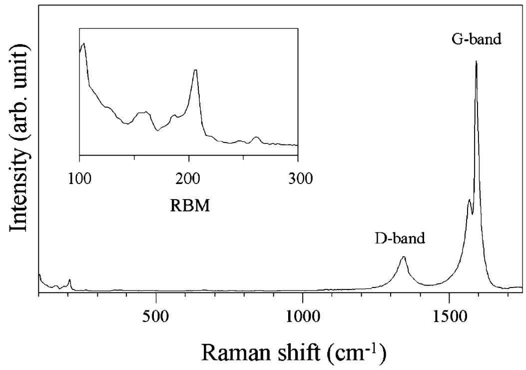

Fig. 4. Raman spectra of synthesized SWNTs. The excitation wavelength was 488 nm at a spot diameter of 4 µm.

synthesized SWNTs. Since the focus spot of Raman spectroscopy was about 4 µm in diameter, the measured spectrum was an average over the entire circular area. This spectrum shows distinct radial breathing modes (RBMs; 150–300 cm^{-1}) and a G-band with a zone-holding spread (about 1590 cm^{-1}), which indicates that SWNTs were successfully synthesized by laser-assisted CVD. Following the correlation between diameter d (nm) and the RBM Raman shift λ (cm^{-1}): $d = 248/\lambda$,[15,16)] the diameter of SWNTs was estimated to be 1.2–1.5 nm. However, the intensity of the D-band signal (about 1350 cm^{-1}) in the Raman spectrum was slightly higher than that of SWNTs synthesized by an alcohol CVD method.[9,17)] We assume that this D-band comes from SWNTs in the perimeter region of the circular area where the temperature is at the low end of the appropriate range for synthesis.

The irradiation up to 10 min also enabled the synthesis of SWNTs. The amount of SWNTs increased with time. However, the sizes of the circular area and their Raman spectra were similar. The rapid synthesis with 1 s irradiation is attributed to the short heat up time brought about by laser heating and the ECL. Since the laser enables the heating of a micrometer-sized area confined by the ECL, the temperature at the irradiated spot immediately increases and saturates. The laser power of around 50 mW was found to be optimal for the synthesis at the beam diameter of 3 µm. When we irradiated the substrates with a high laser power, the center of the circular area was ablated. SWNTs were synthesized around this center forming a doughnut-shaped area. The size of the circular area could be controlled by changing the laser power and spot diameter. We realized the localized synthesis within a diameter of about 1 µm, as shown in Fig. 5. Further localization can be realized by choosing appropriate laser powers and spot diameters.

We calculated the temperature distribution on the surface of the multilayer substrate by a finite difference method. We estimated thermal conduction in a two-dimensional axisymmetric cylinder model with the radius and depth of 15 µm. The center of its surface was constantly irradiated using a laser. The laser power was 50 mW and it had a Gaussian profile intensity with a diameter of 3 µm at which the intensity became $1/e^2$. The temperature at the boundary was set to be 300 K (27 °C). Figure 6(a) shows the calculated temperature distribution on the surface. Predicting the actual value is difficult because the physical properties of the sub-

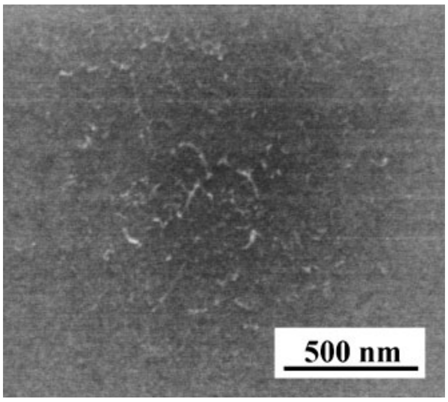

Fig. 5. SEM image of localized synthesis of SWNTs in area of about 1 μm diameter.

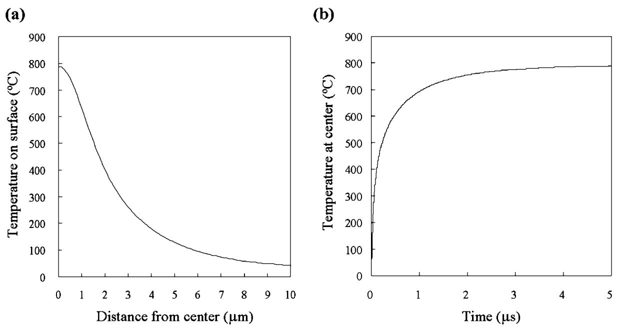

Fig. 6. (a) Calculated temperature distribution on surface of multilayer substrate. (b) Calculated time variation of temperature at center of surface.

strate change with temperature. This calculated distribution should be understood qualitatively. The highest temperature was achieved at the center of the irradiated spot. Towards the outside, the temperature gradually decreased. SWNTs are synthesized within the area where the temperature is suitable for synthesis. The distribution explains the resulting synthesis of SWNTs in the circular area. Figure 6(b) shows the time variation of the temperature at the center. The temperature was saturated in a period of microsecond order, which explains the rapid synthesis of SWNTs. The thickness or materials of the ECL can be changed to meet the requirement of the applications. With the optimization of the design of the ECL and synthesis conditions, SWNTs can be synthesized on substrates other than a Si substrate.

The rapid synthesis with the ECL enabled the line-patterned synthesis of SWNTs by scanning the laser irradiation spot. Figure 7 shows the SEM images of the demonstrated line-patterned synthesis of SWNTs. The irradiation spot was scanned on the substrate using the *xyz* stage at a scanning speed of about 1 μm/s and a laser power of 50 mW. SWNTs were synthesized in a designed pattern of a line at linewidth of 2 μm. At the center of the line, distinct SWNT bundles were observed. This line-patterned synthesis can be used for the production of various SWNT-based nanodevices as an easy and versatile method.

In summary, we have synthesized SWNTs by laser-assisted CVD on a flat surface employing an ECL. The ECL enabled the efficient heating of catalysts on the surface, resulting in rapid synthesis for 1 s and localized synthesis

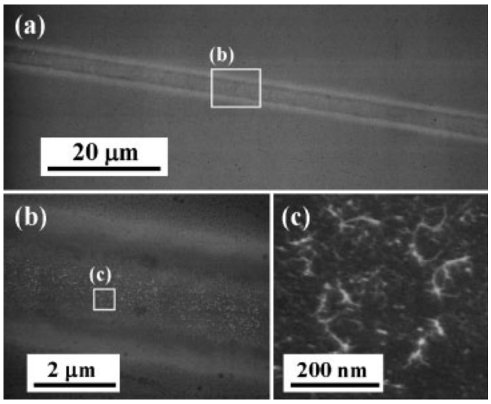

Fig. 7. SEM images of line-patterned synthesis of SWNTs by scanning of laser-irradiation spot: (a) entire region, (b) enhanced area, and (c) highly magnified image of enhanced area.

in an area of 1 μm diameter. The rapid synthesis using the ECL also enabled the synthesis of SWNTs in a desired line pattern by scanning irradiation spot. This novel fabrication method is expected to facilitate the development of various SWNT-based devices.

Acknowledgements

We would like to thank Dr. S. Chiashi, Tokyo University of Science, and Professor S. Maruyama, The University of Tokyo, for the Raman spectroscopy measurements and discussions.

1) M. S. Dresselhaus, G. Dresselhaus, and G. Avouris: *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications* (Springer, Berlin, 2001).
2) C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. L. Chapelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer: Nature **388** (1997) 756.
3) A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer, and R. E. Smalley: Science **273** (1996) 483.
4) H. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley: Chem. Phys. Lett. **260** (1996) 471.
5) J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, and H. Dai: Nature **395** (1998) 878.
6) M. Ishida, H. Hongo, F. Nihey, and Y. Ochiai: Jpn. J. Appl. Phys. **43** (2004) L1356.
7) F. Rohmund, R.-E. Morjan, G. Ledoux, F. Huisken, and R. Alexandrescu: J. Vac. Sci. Technol. B **20** (2002) 802.
8) Y. Fujiwara, K. Maehashi, Y. Ohno, K. Inoue, and K. Matsumoto: Jpn. J. Appl. Phys. **44** (2005) 1581.
9) S. Maruyama, E. Einarsson, Y. Murakami, and T. Edamura: Chem. Phys. Lett. **403** (2005) 320.
10) K. Maehashi, Y. Ohno, K. Inoue, and K. Matsumoto: Appl. Phys. Lett. **85** (2004) 858.
11) Y. Zhang, A. Chang, J. Cao, Q. Wang, W. Kim, Y. Li, N. Morris, E. Yenilmez, J. Kong, and H. Dai: Appl. Phys. Lett. **79** (2001) 3155.
12) A. Ural, Y. Li, and H. Dai: Appl. Phys. Lett. **81** (2002) 3464.
13) S. Noda, Y. Tsuji, Y. Murakami, and S. Maruyama: Appl. Phys. Lett. **86** (2005) 173106.
14) S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, and M. Kohno: Chem. Phys. Lett. **360** (2002) 229.
15) H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, and Y. Achiba: Synth. Met. **103** (1999) 2555.
16) A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus: Phys. Rev. Lett. **86** (2001) 1118.
17) Y. Murakami, Y. Miyauchi, S. Chiashi, and S. Maruyama: Chem. Phys. Lett. **377** (2003) 49.