Growth of Suspended Single-Walled Carbon Nanotubes by Laser-Irradiated Chemical Vapor Deposition

Y Asai, Y Fujiwara, Y Ohno, K Maehashi, K Inoue and K Matsumoto

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

E-mail: asai11@sanken.osaka-u.ac.jp

Abstract. Single-walled carbon nanotubes (SWNTs) have been synthesized by a laser-irradiated chemical vapor deposition (LICVD), where a laser with 514.5 nm was used as a source of heat. The irradiation laser power dependence was investigated for growth of suspended SWNTs. On the basis of the results, the suspended SWNTs were formed between the patterned catalysts at irradiation power of 5 mW by LICVD method. The 514.5-nm Raman scattering spectroscopy measurement revealed that the radial breathing mode was clearly observed. As a result of the resonant effect, SWNTs, which are resonant to irradiation laser with 514.5 nm, might be easily bridged between the patterned catalysts.

1. Introduction

SWNTs have quasi one-dimensional structures, and unique electrical and mechanical properties [1]. By these special features, SWNTs are one of the most promising candidates for nanoscale devices [2-5]. A lot of methods were reported to synthesize SWNTs. Chemical vapor deposition (CVD) methods have been widely used from the view point of its productivity, efficiency and position-controlled growth by using patterned catalysts [6]. Generally, electric furnaces, hot filaments and resistive heaters are used as a source of heat in CVD methods. However, by these apparatuses, the wide region of devices is heated for a long time. For this reason, the devices are in danger of being hurt by high temperature during the CVD process. Furthermore, it has been difficult to grow SWNTs one after another at localized selective position without patterning catalysts repeatedly.

Recently, we have proposed a laser-irradiated CVD (LICVD) method using the laser irradiation as a source of heat to synthesize SWNTs [7]. Because only the laser-irradiated parts are heated, it is possible to grow SWNTs without heating the whole substrates. Moreover, condensing the laser spot, SWNTs can be formed at precise positions on catalysts. Therefore, the LICVD method is useful for applications involving nanoscale devices. In this paper, using LICVD method, we have investigated laser-power dependence for growth of suspended SWNTs. Using optimized laser-power, suspended SWNT bridges have been formed between patterned catalysts which are necessary to produce nanoscale devices. The suspended SWNTs have been also characterized by scanning electron microscopy (SEM) and Raman scattering spectroscopy.

2. Experiments

Figure 1 shows a schematic illustration of a LICVD apparatus. Since the laser irradiation is used as a source of heat, the apparatus is simple. In this study, the 514.5-nm line of an Ar-ion laser was used for
the laser irradiation. The following processes were employed. First, the catalyst, which consists of Fe(NO₃)₃·9H₂O, MoO₂(acac)₂ and alumina nanoparticles in a liquid phase, was patterned on Si(100) substrates (10 × 10 mm²), and then the substrates were heated at 120°C for 5 min. Second, the substrate was fixed in a vacuum chamber, and the chamber was evacuated by rotary pump. Then ethanol vapor was supplied from a room-temperature reservoir. Third, a laser spot was focused on the edge of the patterned catalyst and the substrate was irradiated with the Ar-ion laser for 10 min to heat the patterned catalyst on the substrate, as shown in Figure 2. After that, the laser irradiation was stopped and the substrate was moved to another point to be irradiated with a different power to find out the most suited laser power for growth of suspended SWNTs. The circular areas corresponding to the position of the laser spot in the growing process were investigated by SEM. Finally, on the basis of the laser-power dependence, the suspended SWNTs were grown under a specific condition by LICVD method. The suspended SWNTs were characterized by 514.5- and 633-nm Raman scattering spectroscopy and SEM.

3. Results and Discussion
First of all, SEM images were taken to investigate laser-power dependence by LICVD method for growth of suspended SWNTs. Figures 3(a), 3(b) and 3(c) show SEM images of the center area after laser irradiation at 10, 5, 2.5 mW, respectively. Figure 3(a) reveals that no SWNTs were observed and catalytic nanoparticles were not fabricated. However, the SEM images in the surrounding area exhibited that SWNTs were synthesized with high density. These results indicate that the surface temperature at laser irradiation power of 10 mW was too high to form SWNTs. On the other hand, at
an irradiation laser power of 5 mW, catalytic nanoparticles of suitable size for SWNT growth were formed and the high-density growth of SWNTs was found, as shown in Figure 3 (b). Some SWNTs whose length was enough to be bridged were also observed, as shown in Figure 3(b). Furthermore, as shown in Figure 3 (c), SWNTs were found with low density and short length at an irradiation laser power of 2.5 mW. Therefore, these results indicate that laser irradiation at a power of 5 mW is the most suitable for growth of suspended SWNTs by LICVD method. However, as shown in Figure 3 (b), most of long SWNTs, which grew from catalysts, reached at the substrate and then were curved. This result is consistent with a mechanism of self-directed growth which is explained by the swing of the nanotube cantilever [8]. Therefore, under this condition, it is difficult to form suspended SWNTs.

Next, in order to form suspended SWNTs, the following structure was fabricated, as shown in Figure 4. Ti/Fe (2 / 100 nm) mask was patterned on the substrate using conventional photolithography and metal lift-off processes. Next, the substrate was etched by CF$_4$ plasma for about 2 hours and the groove whose height was 4.4 $\mu$m and width was 3 $\mu$m was fabricated not to contact to the substrate for SWNTs. Finally, the catalysts were patterned on the substrate, as shown in Figure 4.

Using this substrate, the irradiation Ar-ion laser with a power of 5 mW was focused at the edge of the catalyses to form suspended SWNTs. Figure 5 shows the SEM image of the patterned catalysts on the substrate after laser irradiation at a power of 5 mW by LICVD method. The suspended SWNT was clearly observed in the red circle. Moreover, 514.5- and 633-nm Raman scattering spectroscopy were measured with one-line scan mode along the blue arrow in Figure 5. Figure 6 shows 514.5-nm Raman scattering spectra as a function of the position of every 1 $\mu$m, where the blue arrow in Figure 6 corresponds to the blue arrow in Figure 5. The strong peaks (about 520 cm$^{-1}$) from Si substrates were sharply observed at all positions. However, at only the one point, the radial breathing mode (RBM) was clearly found as shown in the red circle in Figure 6. This point just matched the position that the
SWNT was suspended between the patterned catalysts as shown in the red circle in Figure 5. This Raman spectrum was picked out in Figure 7(a). In addition, G-band peak was evidently obtained. These results indicate that the suspended SWNT was formed between the patterned catalysts at an irradiation power of 5 mW by LICVD method. From the peak position of RBM signal (165 cm⁻¹), as shown in Figure 7(a), the SWNT was estimated to be semiconducting and the diameter to be about 1.5 nm.

In contrast to the 514.5-nm Raman scattering spectrum, only strong peaks from the Si substrate were obtained. As shown in Figure 7(b), a Raman spectrum, which was measured with 633-nm line of a He-Ne laser, was also picked out, where the position of the Raman spectrum is the same as that of the suspended SWNT between the patterned catalysts. The Raman spectrum reveals that both RBM and G-band signals were not observed. These results indicate that the suspended SWNT was resonant to 514.5 nm wavelength.

Similar phenomena were obtained for other samples. Since SWNTs are one-dimensional materials, the SWNT density of states (DOS) is characterized by multiple van Hove singularities, which have sharp peaks [9, 10]. The DOS of SWNTs is strongly dependence on their chirality. When a sample is irradiated with the energy \( (h\nu) \) of the laser beam, absorption of the exciting beam can be strongly enhanced for the SWNTs with specific chirality, whose energies of the allowed electronic transitions match the energy \( (h\nu) \) of the incident photon. As a result of the resonant effect, SWNTs, which are resonant to irradiation laser with 514.5 nm, might easily become longer and be bridged between the patterned catalyst, as shown in Figures 5 and 6. Further experiments will be needed to clear the phenomena.

4. Summary
SWNTs were synthesized at selective, localized regions on catalysts in room-temperature chamber by LICVD method, where a laser with 514.5 nm was used as a source of heat. On the basis of the investigation of irradiation power dependence, we have succeeded in forming the suspended SWNTs between the patterned catalysts at irradiation power of 5 mW by LICVD method. The 514.5 nm Raman scattering spectroscopy measurement revealed that the G-band and RBM signals were clearly observed. As a result of the resonant effect, SWNTs, which are resonant to irradiation laser with 514.5
nm, might be easily bridged between the patterned catalysts. Consequently, LICVD method is useful for applications involving nanoscale devices.

Acknowledgements
This research was partially supported by Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Corporation (JST), and the New Energy and Industrial Technology Development Organization (NEDO). The one of the authors (K.I.) is partially supported by a Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science

References
[1] Dresselhaus M S, Dresselhaus G and Eklund P C 1996 Science of Fullerenes and Carbon Nanotubes (Academic Press, New York)
[2] Kaminishi D, Ozaki H, Ohno Y, Maehashi K, Inoue K, Matsumoto K, Seri Y, Masuda A and Matsumura H 2005 Appl. Phys. Lett. 86 113115
[3] Maehashi K, Matsumoto K, Kerman K, Takamura Y and Tamiya E 2004 Jpn. J. Appl. Phys. 43 L1558
[4] Kerman K, Morita Y, Takamura Y, Tamiya E, Maehashi K and Matsumoto K 2005 Nanobiotechnol. 1 065
[5] Ohno Y, Narumi K, Maehashi K, Inoue K and Matsumoto K 2006 J. Physics: Conference Series 38 57
[6] Maehashi K, Ohno Y, Inoue K and Matsumoto K 2004 Appl. Phys. Lett. 85 858
[7] Fujiwara Y, Maehashi K, Ohno Y, Inoue K and Matsumoto K 2005 Jpn. J. Appl. Phys. 44 1581
[8] Homma Y, Kobayashi Y, Ogino T and Yamashita T 2002 Appl. Phys. Lett. 81 2261
[9] Saito R, Fujita M, Dresselhaus G and Dresselhaus M S 1992 Appl. Phys. Lett. 60 2204
[10] Rao A M, Richter E, Bandow S, Chase B, Eklund P C, Williams K A, Fang S, Subbaswamy K R, Menon M, Thess A et al 1997 Science 275 187