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To cite this article: Yasuyuki Fujiwara et al 2005 Jpn. J. Appl. Phys. 44 1581

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

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(Received October 15, 2004; accepted December 9, 2004; published April 8, 2005)

Single-walled carbon nanotubes (SWNTs) were synthesized by chemical vapor deposition using Ar-ion laser irradiation as a source of heat. The circular area corresponding to the position of the laser spot in the growing process was characterized by Raman scattering spectroscopy and scanning electron microscopy. The results revealed that SWNTs can be synthesized at exactly controlled positions and localized regions. The regions of SWNT growth strongly depended on the power of the laser; therefore, only suitable power from laser irradiation could synthesize SWNTs over an entire circular area. By making a partial improvement to the apparatus, the optical instrument and the laser power, we finally synthesized SWNTs in an extremely localized area of approximately 5 μm in diameter.

KEYWORDS: single-walled carbon nanotubes, laser-irradiated chemical vapor deposition, position control, local synthesis, Raman spectroscopy, scanning electron microscopy

1. Introduction

Single-walled carbon nanotubes (SWNTs) are the most promising candidates for nano-scale devices due to their unique electric and mechanical properties and small shapes.1 Generally, SWNTs have been synthesized by arc discharge,2 laser vaporization3 and chemical vapor deposition (CVD).4 CVD methods have been widely used from the view point of their productivity, efficiency and position-controlled growth using patterned catalysts. It has been difficult to synthesize SWNTs at precise positions on catalysts by general CVD techniques, since SWNTs were grown from the catalysts over a wide range of regions on the substrates.5–7

In this paper, we describe a laser-irradiated CVD method to synthesize SWNTs using laser irradiation as a source of heat without electric furnaces,5 hot filaments6 or resistive heaters.7 Since laser irradiation heats the catalysts locally, they can become hot or cold immediately. As a result, it is possible to synthesize SWNTs one after another at localized selective positions. Using the laser-irradiated CVD method, we have demonstrated the growth of SWNTs at exactly controlled positions and localized regions. Therefore, the laser-irradiated CVD method can be useful to produce nano-scale devices with SWNTs as integrated circuits.

2. Experimental

A schematic illustration of a laser-irradiated CVD apparatus is shown in Fig. 1. Because the new CVD apparatus uses laser irradiation as a source of heat, an extremely simple apparatus can be realized. The 514.5-nm line of an Ar-ion laser was used for the laser irradiation. First, the catalyst, which consists of Fe(NO3)3·9H2O, MoO2(acac)2 and alumina nanoparticles in a liquid phase, was deposited on Si(100) substrates (10 × 10 mm2), and then the substrates were heated to 120°C for 5 min.8 Second, the substrate was put into a vacuum chamber, and the chamber was evacuated by rotary pump. Then ethanol vapor was supplied from a room-temperature reservoir. Finally, the substrate was irradiated with the Ar-ion laser for 1 min to heat the catalyst on the substrate locally. After that, laser irradiation was stopped and the substrate was moved to another point to be irradiated with a different power. The circular areas corresponding to the position of the laser spot in the growing process were investigated by Raman scattering spectroscopy (514.5-nm excitation) and scanning electron microscopy (SEM).

3. Results and Discussion

Figure 2(a) shows SEM images of the circular area after laser irradiation at a power of 180 mW by laser-irradiated CVD; the diameter of the area was about 40 μm. The SEM image reveals the obvious difference between the center of the circle and the surrounding area. At the center of the circular area, neither SWNTs nor catalytic nanoparticles were fabricated, as shown in Fig. 2(b). The SEM image in Fig. 2(c) reveals a remarkable border line between the center of the circle and the surrounding area. At the center side of
the border, neither SWNTs nor catalytic nanoparticles were observed as in the center of the circular area shown in Fig. 2(b). However, SWNTs were synthesized with high density and the catalytic nanoparticles were also obtained in the surrounding area, as shown in Fig. 2(d). At the edge of the circular area in Fig. 2(e), in spite of the formation of catalytic nanoparticles, synthesis of SWNTs was hardly observed.

Figure 3 shows the Raman spectra measured at different positions: the center of the circular area and the surrounding area. At the center of the circular area, small G- (about 1600 cm\(^{-1}\)) and D-band (about 1350 cm\(^{-1}\)) signals were observed and radial breathing mode (RBM) signals that are specific to SWNTs were not found. On the other hand, in the surrounding area, RBM signals were clearly observed around 100–200 cm\(^{-1}\) and the G-band signal was larger than in the center. These results indicate that SWNTs were synthesized in the surrounding area, which is consistent with SEM images in Fig. 2.

These results in Figs. 2 and 3 are attributed to a nonuniform temperature distribution in the circular area during laser irradiation at a power of 180 mW. Figure 4 shows a schematic illustration of the temperature distribution in the circular area during laser irradiation at 180 mW by laser-irradiated CVD. At the center of the circular area in Fig. 2(b), which had the highest temperature in the circular area, the temperature was too high to form catalytic nanoparticles of suitable size for SWNT growth. As a result, SWNTs were not synthesized at the center of the circular area. On the other hand, both SWNTs and catalytic nanoparticles were produced in the surrounding area, as shown in Fig. 2(d), suggesting that the temperature was sufficient to make both catalytic nanoparticles and SWNTs. Since SWNTs are grown more slowly at lower temperature,
SWNTs were rarely synthesized at the edge of the circular area in spite of the formation of catalytic nanoparticles, as shown in Fig. 2(e). To summarize: laser-irradiated CVD at a laser power of 180 mW generates SWNTs in a doughnut-shaped region.

Figure 5 shows SEM images of the circular area after laser irradiation at 160 mW by laser-irradiated CVD; the diameter of the circle was about 30 µm. There were hardly any differences between the center of the circular area and the surrounding area, as shown in Fig. 5(a), in contrast to the circular area after laser irradiation at 180 mW, as shown in Fig. 2(a). This result reveals that the catalytic nanoparticles were formed in the entire circular area. Figure 5(b) shows the high-density growth of SWNTs in the center of the circular area. SWNTs were also synthesized in the surrounding area, as shown in Fig. 5(c), although the density of SWNTs was lower than in the center.

Figure 6 shows the Raman spectra measured at different positions: the center of the circular area and the surrounding area. At the center of the circular area, the Raman intensity ratio of the G- to D-band structures, the so-called G/D ratio, was clearly larger than that in Fig. 3(b), and RBM signals were clearly observed. In the area surrounding the circle, the G/D ratio was almost the same as in the center, and RBM signals were also clearly observed, although G- and D-band signals were a little smaller than in the center. These results indicate that SWNTs exist in almost the entire circular area, which is consistent with SEM observations.

Figure 7 shows a schematic illustration of the temperature distribution in the circular area during laser irradiation at 160 mW by laser-irradiated CVD. Catalytic nanoparticles were formed over the entire circular area, as shown in Fig. 5(a), in contrast to the area after laser irradiation at 180 mW, as shown in Fig. 2(a), indicating that the temperature at the entire circular area was sufficient to form catalytic nanoparticles. As previously mentioned, the density distribution of SWNTs is a result of the temperature distribution. Since SWNTs grow more rapidly in a higher temperature region, high-density growth of SWNTs was observed at the center of the circular area. On the other hand, the density of SWNT growth in the surrounding area was lower than that in the center, as shown in Fig. 5(c). To summarize: laser-irradiated CVD with laser irradiation at a suitable power (160 mW) produces SWNTs over the entire circular area.

To synthesize SWNTs in a more localized area, we made
a partial improvement to the apparatus, the optical instrument and the laser power. Then, we finally succeed in localizing the growth area of SWNTs to a circle about 5 μm in diameter as shown in Fig. 8. This result indicates that the growth area of SWNTs can be localized by choosing a suitable laser power and reducing the laser spot size.

4. Conclusions

We have proposed a laser-irradiated CVD method using laser irradiation as a source of heat, and SWNTs were synthesized at selective, localized regions on catalysts in a room-temperature chamber. In this method, the growth area of SWNTs strongly depended on the laser power, and only laser irradiation of suitable power can produce SWNTs over an entire circular area. By changing the laser spot size and the laser power in the growing process, it may be possible to reduce the region to less than 1 μm in diameter. Since the laser-irradiated CVD method also has a special feature that makes it possible to synthesize SWNTs one after another at a different position on the catalyst without patterning the catalyst repeatedly, this method is considered to be useful for applications involving nanoscale devices.