

Localized synthesis of single-walled carbon nanotubes on silicon substrates by a laser heating catalytic CVD

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Abstract. Synthesis of high-purity single-walled carbon nanotubes (SWNTs) is demonstrated by a laser heating catalytic CVD method. This method makes it possible to produce SWNTs without the use of an electric furnace or hot filament. SWNTs were synthesized from alcohol using Fe/Co catalyst particles supported on zeolite and Mo/Co particles deposited directly on a substrate. Synthesis of high purity SWNTs was confirmed by *in situ* Raman scattering analysis and AFM and FE-SEM observations.

1. Introduction

The development of single-walled carbon nanotube (SWNT) synthesis techniques is one of the most important subjects for realizing practical applications. Following the first report of SWNT synthesis [1], several techniques, such as laser-furnace [2] arc-discharge [3] and various catalytic chemical vapor deposition (CCVD) techniques [4] have been reported. Through these studies, it was found that a high reaction temperature (such as 800 °C) is necessary for SWNT synthesis, and this high reaction temperature prohibits direct growth of SWNTs on semiconductor devices. Therefore, new techniques that allow synthesis of SWNTs at a lower temperature are desired.

As one possible approach, we have proposed a catalytic CVD technique using alcohol as the carbon source (ACCVD), which has been shown to produce high-quality SWNTs [5] and can be performed at a significantly lower temperature compared with other catalyst CVD techniques. However, a reaction temperature of 550 °C or more is still necessary for SWNT growth. Recently, we proposed an even simpler version of ACCVD without resorting to an electric furnace or a hot filament [6], where high-purity SWNTs were grown from Fe/Co particles supported on zeolites by Joule heating of a silicon substrate. Even though the silicon substrate was heated to 850°C, the surrounding environment remained at room temperature. This result indicated the possibility of position-controlled synthesis of SWNTs by heating only a specific area. Very recently, ACCVD by laser irradiation was demonstrated by Y. Fujiwara *et al.* [7]. In this study, we demonstrate the possibility of controlled growth of SWNTs at a specific position by laser heating catalytic CVD method. Laser beam irradiation was used to heat a silicon substrate, on which catalysts prepared by 2 kinds of methods were supported. The synthesis of

SWNTs was examined by Raman spectroscopy, atomic force microscope (AFM) and field emission scanning electron microscope (FE-SEM) observation.

2. Experiment

In this study, 2 kinds of the catalysts were used for SWNT synthesis. One is Fe/Co metal particles supported by zeolites dispersed on a silicon substrate [5], and the other is Mo/Co particles directly loaded onto a silicon substrate using a dip-coating technique [8]. Fig. 1 shows a schematic of the experimental apparatus. An AFM measurement system inside a vacuum chamber (SII, SPA300HV), was built with micro Raman capabilities (Seki Technotron). Not only could AFM images and Raman scattering spectra be obtained at the same time, but also the sample environment could be controlled during measurements [6].

After evacuating the chamber, ethanol vapor (0.1~1.0 Torr) was supplied from a reservoir at room temperature through a gas port, and a silicon substrate on an AFM sample stage was irradiated by a laser beam. The lasers used were a CW-Ar ion laser (wavelength: 488.0 nm, 40.0 mW) and a CW-He-Ne laser (632.8 nm, 30.0 mW). The heating laser was also used as Raman excitation. Upon laser irradiation, the temperature of the metal catalyst immediately increased to the SWNT growth temperature (laser heating CVD). The synthesized SWNTs were characterized by AFM and FE-SEM observation as well as *in situ* micro Raman spectroscopy.

3. Results and discussions

3-1. Synthesis of SWNTs from Fe/Co particles supported on zeolites

After laser irradiation (632.8 nm, 15 min) in an ethanol gas atmosphere (0.6 Torr), the color of the zeolite particles inside the laser spot varied from yellow-brown to black (the size of the blackened area was about 30 μm in diameter). Fig. 2 shows Raman scattering from the center (a) and the edge (b) of the blackened area (488.0 nm excitation laser). The peak around 1592 cm^{-1} is the G-band, the peak at 1350 cm^{-1} is the D-band and peaks from 100 to 300 cm^{-1} are radial breathing mode (RBM) peaks. The split G-band comes from SWNTs and the D-band comes from defects in the graphitic structure. The Raman scattering in Fig. 2 shows high-quality SWNTs were generated by this laser heating CVD method, indicated by the high G/D intensity ratio. RBM peaks indicate the SWNT diameter distribution, where the following correlation between the diameter d and the RBM Raman shift ν was used for the diameter axis: $d/\text{nm} = 248/(\nu/\text{cm}^{-1})$ [9]. The diameter distribution of SWNTs synthesized at

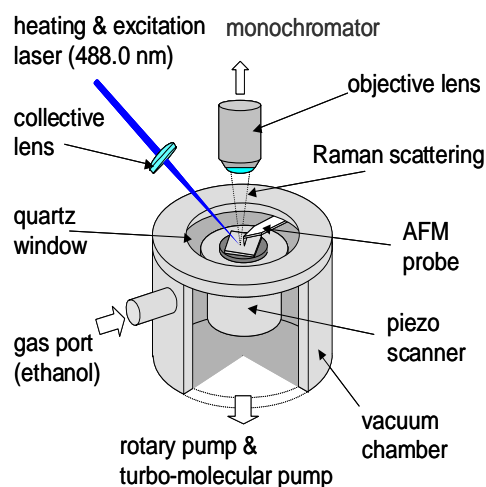


Fig. 1. A schematic of the experimental apparatus. A vacuum chamber unit for a scanning probe microscope was combined with a micro Raman system.

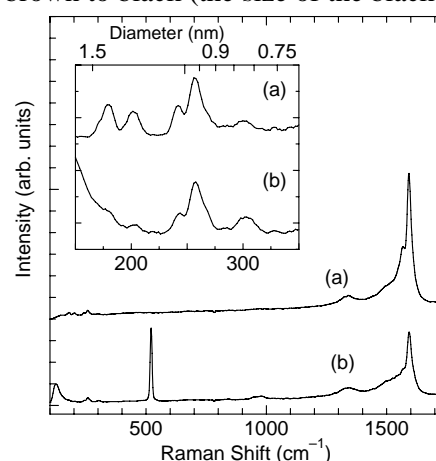


Fig. 2. Raman scattering from the laser spot (488.0 nm excitation laser). The spectra (a) and (b) were measured at the center and the edge, respectively. The peak at 521 cm^{-1} comes from the silicon substrate.

the edge was narrower than at the center. Moreover, the G/D ratio in spectrum (b) was smaller than in spectrum (a). These different features in Raman scattering were caused by the temperature distribution in the laser spot. The temperature at the center was higher than that at the edge, due to the heat transfer along the radial direction in the laser spot. Judging from the CVD temperature dependence reported in Ref. 5, the temperature of the metal catalyst supported with zeolites at the center and the edge were estimated to be about 800 °C and 600 °C, respectively.

3-2 Synthesis of SWNTs directly on a silicon substrate

Using the laser heating CVD method, SWNTs were synthesized directly on a silicon surface from Mo/Co metal particles directly loaded onto the silicon surface by the so called ‘dip-coat’ method developed by Y. Murakami *et al.* [8]. It is difficult to heat only the laser spot area, because the thermal conductivity of silicon is so high that the heat input by laser irradiation is quickly transferred away from the laser spot. Therefore, the size of the silicon substrate was reduced (to about 150x150x200 μm) in order to heat the entire substrate. The heating laser was a CW-Ar ion laser (30.0 mW, 15 min) and the pressure of the ethanol vapor was 0.1 Torr. Raman scattering by this sample (Fig. 3(A)) indicates that high-quality SWNTs were generated by the laser heating CVD method, because of the high G/D ratio. The RBM peaks in the inserted panel of Fig. 3(A) were observed and the RBM signal features are quite similar to the spectra reported in Ref. 8.

Synthesized SWNTs were further characterized by FE-SEM observation, and an image is shown in Fig. 3(B). In this FE-SEM image, the surface is uniformly covered by many tangled SWNTs, which indicates that there was no temperature distribution on the silicon surface. We could not find by-products, such as multi-walled carbon nanotubes or amorphous carbon, during SEM observation, which is consistent with the purity indicated by the high G/D ratio in Raman scattering in Fig. 3(A). While for FE-SEM measurement, the sample was taken out of the synthesis vacuum chamber and was directly mounted on a sample holder, AFM observation was measured *in situ* without any treatment. An AFM image is shown in Fig. 4(A), which also shows many tangled SWNTs were generated on the silicon surface, as in the SEM image (Fig. 3(B)).

By using the heating laser as the Raman excitation laser, *in situ* Raman scattering measurements during the laser heating CVD process was performed. Raman scattering spectra were measured every second and the intensity of the silicon and G-band peaks were plotted in Fig. 4(B). The temperature of the silicon substrate was estimated from the temperature dependence of the silicon peak's Raman shift (520 cm^{-1} , 300 K) [10]. The substrate was heated by laser to about 830 °C in vacuum (at 0 min), and after the ethanol vapor (0.1 Torr) was supplied (at 1 min) the substrate temperature decreased to about 800 °C, due to heat transfer to the ethanol gas. At 1 min and 40 second, the G-band appeared and its intensity increased with time until about 10 min, while the intensity of silicon was almost constant

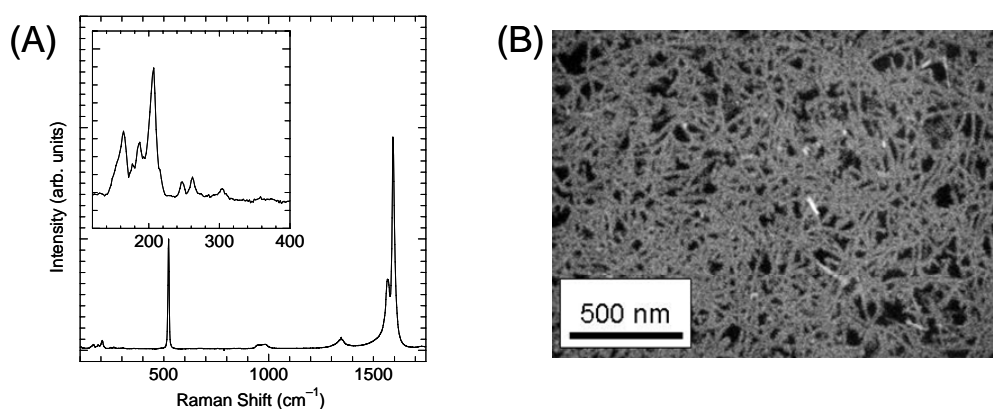


Fig. 3. (A) Raman scattering from SWNTs generated from Co/Mo particles on a silicon substrate by the laser heating CVD method. An Ar ion laser (488.0 nm) was used as the excitation laser. (B) SEM image of the sample. SWNTs were synthesized uniformly over the silicon surface because there was no temperature gradient, due to the thermal conductivity of silicon (about 30 W/mK at 800 °C).

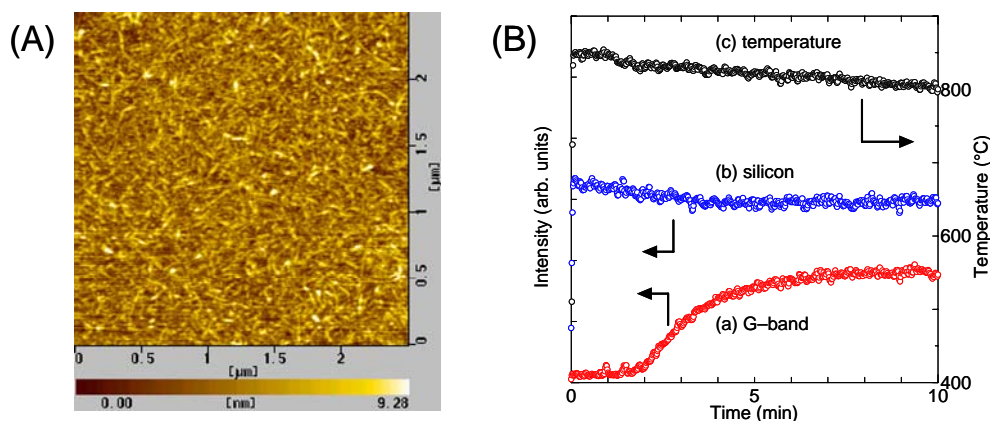


Fig. 4. (A) AFM image of SWNTs generated from Co/Mo catalyst particles by the laser heating CVD method. SWNTs on the silicon surface were tangled, like the SEM image in Fig. 3(B). (B) Time variation of the silicon and the G-band peak intensities during the entire laser heating CVD process. While the silicon peak intensity (b) was almost constant, the intensity of the G-band (a) appeared after the supply of ethanol gas (at 1 min) and increased with time.

during the whole CVD process. The intensity curve of the G-band in Fig. 4(B) shows the SWNT growth, which is very similar to *in situ* absorbance measurement results reported in Ref. [11].

4. Conclusion

We succeeded in synthesizing SWNTs from 2 kinds of metal catalysts using a laser heating CVD method. In the case of Fe/Co catalyst particles supported with zeolites, high-quality SWNTs were locally generated within a 30- μm diameter spot. SWNTs were also synthesized directly on a silicon substrate from Mo/Co metal particles using laser heating CVD. Raman scattering, FE-SEM and AFM observations revealed that these synthesized SWNTs were high quality, while their growth was not localized by the laser spot because of the high thermal conductivity of the silicon substrate. Moreover, *in situ* Raman scattering measurements were performed.

Acknowledgement

The authors thank E. Einarsson (The University of Tokyo) for discussions.

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