Carbon-nanopillar tubulization caused by liquidlike iron catalyst nanoparticles

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Amorphous carbon nanoparticles that we fabricated with electron-beam induced chemical vapor deposition were tubulized by heating at 600°C-650°C in the presence of iron nanoparticles. The tubulization process of the amorphous carbon nanopillar was observed in situ by using transmission electron microscopy and scanning transmission electron microscopy. A molten catalyst nanoparticle penetrated the amorphous carbon nanopillar, dissolving it and leaving a graphite track behind. The nanoparticle moved with its shape changing like the movement of an earthworm. Z-contrast images of the molten catalyst nanoparticle revealed that dissolved carbon atoms were diffused through its outer layer. The tubulization mechanism is a solid-quasiliquid-solid mechanism in which the carbon phase transformation is a kind of liquid phase graphitization of amorphous carbon catalyzed by liquefied metal-carbon alloy nanoparticles. [DOI: 10.1380/ejssnt.2006.401]

Keywords: Carbon nanotube; Iron catalyst; In situ Transmission Electron Microscopy

I. INTRODUCTION

Carbon nanotubes [1–3] are currently the focus of intense research because of their remarkable properties and their potential to impact broad areas of science and technology. To clarify the role of metal catalysts in carbon nanotube synthesis is important to enable understanding of the carbon nanotube growth mechanisms. Understanding these mechanisms is of great value for controlling their structure and properties. However, despite the enormous progress in nanotube synthesis [4–6], their growth mechanisms are still being sought because only a few direct observations of the carbon nanotube growth process have been reported [7, 8].

Fujita, et al. reported the graphitization of iron doped carbon pillars fabricated with a beam-induced chemical vapor deposition (CVD) technique, by annealing them at about 800°C for 30 min in vacuum [9, 10]. Therefore, we have tried to synthesize carbon nanotube from amorphous carbon nanopillars with a heat treatment and to observe their formation in situ by using transmission electron microscopy (TEM) [11] and scanning transmission electron microscopy (STEM).

In this paper, we present some results of in situ TEM and STEM observation of the amorphous carbon-nanopillar tubulization process. In conventional gas CVD of carbon nanotubes, carbon atoms to form nanotube were supplied by gas. However, in our work, the carbon atoms to form nanotubes were supplied by a solid. We assume that the role of the metal catalyst particle should be the same in both these methods.

II. EXPERIMENTAL

Our sample preparation is illustrated in Fig. 1. First, we deposited an iron-doped amorphous carbon foundation on the side of a molybdenum grid for the TEM by using focused-ion-beam-induced CVD (FIB-CVD) [12] with a ferrocene (FeC10H10) gas source [9] injected through a nozzle. The nozzle was located near the specimen. The size of the foundation was about 1 µm×1 µm×1 µm. The FIB system we used was the SEIKO SMI-2050. Next, we grew amorphous carbon nanopillars, which were 10-100 nm in diameter and 100-500 nm long, on the foundation by using electron-beam-induced CVD (EB-CVD) [13] in a phenanthrene (C14H10) gas atmosphere [10]. The electron beam system we used was a conventional high-resolution scanning electron microscope (Hitachi S5000). A scanning electron micrograph of as-deposited nanopillars is presented in Fig. 2.

The molybdenum grid, on which the iron-doped carbon foundation with the amorphous carbon nanopillars was grown, was loaded on a specimen heating holder of an ultra-high-vacuum (UHV) TEM (JEOL 2000FXVII). The UHV-TEM was equipped with a video camera [14]. The tubulization process of the amorphous carbon nanopillars was observed in situ by using UHV-TEM operated at 200 keV and was recorded on videotape at a TV-rate time resolution.

For STEM (Hitachi HD-2300) observation, we grew the iron-doped carbon foundation with the amorphous carbon nanopillars directly on a tungsten heater of a specimen heating holder for STEM.
FIG. 1: Images illustrate the sample preparation method. (a) An amorphous carbon foundation containing iron was deposited on a molybdenum grid for the TEM with focused-ion-beam-induced chemical vapor deposition by using a ferrocene (FeC_{10}H_{10}) gas source injected through a nozzle. (b) Amorphous carbon nanopillars were grown on the foundation with electron-beam-induced chemical vapor deposition in a phenanthrene (C_{14}H_{10}) gas atmosphere.

FIG. 2: A scanning electron micrograph of as-deposited nanopillars.

III. RESULTS AND DISCUSSION

Figure 3 is an illustration of the pillar at each annealing stage. Figure 3a shows an as-deposited amorphous carbon nanopillar. The specimen was heated and kept at 600°C until the drift of the specimen caused by the expansion with temperature of the stage and specimen holder stopped (about 2 hours for TEM observation). During this process, the electron beam intensity was decreased to about 0.1 A/cm² (about 1/1000 of the high-resolution TEM observation condition) to avoid electron beam damage to the carbon nanopillars. When the temperature of the specimen reached about 600°C, iron particles of about 2 nm in size appeared immediately in the iron-doped carbon foundation.

Due to particle coalescence, the iron particles grew to the size of about 10 nm in a few minutes (Fig. 3b). When the drift of the specimen stopped, we raised its temperature from 600°C to 650°C. Though the specimen began to drift slowly, we could still monitor its image with the video camera attached to the UHV-TEM. An iron particle moved toward the bottom of a nanopillar and sintered into it (Fig. 3c). The iron particle changed its shape and size much like a liquid while moving inside the nanopillar. This liquidlike particle moved through the inside of the carbon nanopillar, and left behind a graphitic track.

Figure 4(a, b, and c) is a series of transmission electron micrographs reproduced from videotape of a 10-nm-diameter carbon nanopillar at about 650°C at 10-s time intervals. The iron-carbon alloy particle moved from the bottom toward the top of the nanopillar. Once it reached the top of the nanopillar, the particle did not turn back to the bottom. An electron diffraction pattern (Fig. 4d), taken from the nanopillar corresponding to Fig. 4(c) revealed that the carbon nanopillar had a graphitic structure. This pillar was transformed into a multiwalled (about 10 layers) carbon nanotube by the heating process.

However, the nanotube was not straight, and it contained some defects. We propose that these defects were caused by fluctuation in the moving speed of the iron-carbon alloy particle and in the particle diameter. A molten catalyst nanoparticle penetrated the amorphous carbon nanopillar, dissolving it and precipitating carbon atoms at the tail of the nanoparticle. These atoms arranged themselves into a graphene sheet. Sometimes TEM images of the moving catalyst particle showed diffraction contrast (indicated by an arrowhead) revealing that it had a crystalline nature. Iijima, et al. proposed the concept of the quesisolid state, which is neither solid nor liquid, for nanometer-sized particles [15]. These catalyst particles are considered quasisolid particles.

The equilibrium eutectic temperature of the corresponding iron-carbon alloy is 1150°C. The temperature of 650°C at which the catalyst particles acted as a liquid in this experiment was extremely low by comparison. As it is well known, the melting points of nanometer-sized particles are much lower than those of the correspond-
FIG. 3: Illustrations of the nanopillar at each annealing stage: (a) As-deposited. (b) Heated at 600°C. Iron-carbon alloy particles appeared in the foundation within a few minutes. (c) Heated at 650°C. An iron-carbon alloy particle penetrated an amorphous carbon nanopillar and graphitization started from the bottom of the pillar.

FIG. 4: A series of transmission electron micrographs, reproduced from videotape, showing the graphitization process of an amorphous carbon nanopillar about 10 nm in diameter at about 650°C. An electron diffraction pattern (d), taken from the pillar corresponding to (c), shows that the pillar had a graphitic structure.

FIG. 5: A series of electron micrographs, reproduced from videotape, of a 10-nm-diameter carbon nanopillar at about 650°C. Arrowheads indicate the precipitation interface between the catalyst nanoparticle and the graphitic tube. Arrows indicate the bamboo-like structure.

shape changes, between the shrunken shape of the tail and elongated shape of the top, are repeated like the movement of an earthworm. When the tail of the catalyst particle moved at constant speed, the graphitic tube structure was formed. If the tail of the particle stayed at the same place for a few hundred milliseconds, the graphene sheet closed to make a cap within the nanotube (indicated by arrows). The interface between the catalyst nanoparticle and the graphitic tube (indicated by arrowheads) had a
flat shape and played a key role in nucleation and growth of graphene sheet.

Based on molecular dynamics simulations, Raty, et al. reported that the presence of a solid iron-carbon solution and hence supersaturation-segregation processes are not needed for the growth process on small metal nanoparticles, and most likely they do not occur [19]. Therefore, we tried to observe Z-contrast images of the catalyst particle by using STEM and to clarify the path of the dissolved carbon atoms diffused. The Z-contrast images and corresponding electron diffraction patterns of the catalyst iron nanoparticle at $600^\circ$C are shown in Fig. 6.

Because the specimen was in direct contact with the heating element, the temperature was lower than for TEM experiments. The Z-contrast image of the outer part of the catalyst nanoparticle was darker than its inner part. This Z-contrast image of the catalyst nanoparticle was due to the carbon-iron ratio difference or to a thickness difference was unclear. Considering the liquidlike behavior of the nanoparticle and the existence of the interface between the nanoparticle and the graphitic tube, we supposed that the dissolved carbon atoms diffused through the outer part of the catalyst nanoparticle. The electron diffraction pattern (Figs. 6 a2 and b2) revealed that the catalyst particle had a crystalline nature.

Figure 7 offers corresponding models of this carbon nanotube growth mechanism. Dissolved carbon atoms were diffused through the outer part of the catalyst iron nanoparticle. When the tail of the catalyst particle moves smoothly (Fig. 7a), precipitating carbon incorporates at the edges of the growing nanotube. When the moving speed of the catalyst particle tail is 0 for a few hundred milliseconds, the precipitating carbon incorporates into a graphene cap and a bamboo-like structure forms [18]. We propose that the motive force of the catalyst particle is the difference between the solubility of amorphous carbon in iron and that of graphite carbon in iron. Another possible motive force is that there are temperature gradients in the nanopillar and nanoparticle.

IV. CONCLUSIONS

We have described how amorphous carbon nanopillars that we fabricated by using EB-CVD were tubulized by heating them at $600^\circ$C - $650^\circ$C in the presence of iron nanoparticles with in situ TEM and STEM. Our observations indicate that the tubulization mechanism is a solid-quasiliquid-solid mechanism in which the carbon phase transformation is a kind of liquid phase graphitization of amorphous carbon catalyzed by liquefied metal-carbon alloy nanoparticles [20, 21]. Though we need to conduct further experiments to confirm that the iron-carbon ratio difference of the catalyst nanoparticle provided the Z-contrast images, we suppose that dissolved carbon atoms diffused through the outer part of the nanoparticle. The low-temperature liquefaction of catalyst particles causes the principal difference as compared to the synthesis of carbon nanofibers that are usually catalyzed by solid cat-

![FIG. 6: A series of Z-contrast images and these corresponding electron diffraction patterns of the catalyst iron nanoparticle. The outer part of the particle shows darker contrast than its inner part. Dissolved carbon atoms diffused through the outer part of the catalyst particle.](image)

![FIG. 7: A model of the carbon nanotube growth process. Dissolved carbon atoms diffused through the outer part of the catalyst iron nanoparticle. (a) When the tail of the catalyst particle moves smoothly, precipitating carbon incorporates at the edges of the growing nanotube. (b) When the moving speed of the catalyst particle tail is 0 for a few hundred milliseconds, the precipitating carbon incorporates into a graphene cap and a bamboo-like structure forms.](image)
alysts of similar composition in a related graphitization process. We believe that by using this technique single-walled carbon nanotubes can be synthesized with very thin (about 1-2 nm in diameter) carbon nanopillars and very small catalytic particles (about 1-2 nm in size).

Carbon and metal catalyst composite nanopillars can thus be fabricated at any place, in any direction, at any length and any thickness by using nanofabrication and heat treatment at a temperature below the equilibrium eutectic temperature of the corresponding iron-carbon alloy (1150°C). Therefore, we should be able to synthesize carbon nanotubes of any desired size at any desired location. This graphitic nanotube synthesis technique of nanofabrication promises to bring about a great advance in nanotube electric devices.

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