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Vertical Growth of Individual Single-Walled Carbon Nanotubes on Silicon and SiO\textsubscript{2} Substrates

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Individually isolated single-walled carbon nanotubes (SWNTs) have been successfully grown vertically on a substrate by chemical vapor deposition with methane and Fe or Co catalysts. Vertical growth is obtained when the growth temperature was high, 900–1000 °C, and the tube diameter is large, 2–5 nm. Vertically grown SWNTs are short, ranging from several tens to 300 nm, which are useful for use as tips of a field emission or probe microscope. Fullerene encapsulation has been achieved directly in vertical SWNTs on a substrate. [DOI: 10.1143/JJAP.44.1564]

KEYWORDS: carbon nanotubes, chemical vapor deposition, fullerene encapsulation

1. Introduction

Single-walled carbon nanotubes (SWNTs)\textsuperscript{1} are nanoscale tubular materials with a variety of excellent properties. Expectations of their applications in diverse fields have driven extensive studies in the past decade.\textsuperscript{2} For such applications, the formation of various structures using SWNTs is desirable. These structures involve shapes of a single wire, rope, column, sheet, and wall among others, either sustained in space or placed on a substrate. SWNTs synthesized by a mass production method usually form bundles.\textsuperscript{3} SWNTs can be grown individually isolated on a substrate by chemical vapor deposition (CVD) when the catalyst density is low or the SWNT yield is low.\textsuperscript{4} Long SWNTs on the millimeter scale are aligned on a substrate.\textsuperscript{5} The mechanical strength of SWNT makes it possible for an individual SWNT to be suspended between mesa structures.\textsuperscript{6–8} A bulk sheet made of SWNT bundles (“buckey paper”) has been fabricated and used in photoemission spectroscopy.\textsuperscript{9} These diverse architectures will open up new applications. However, the vertical growth of individual SWNTs was not easy to achieve. When a low density of SWNTs is grown by CVD on a substrate, SWNTs normally lie on the substrate.\textsuperscript{5,8} In the initial stage of growth, a SWNT should be able to grow in any direction, but once a long nanotube touches the substrate surface, it lies on the substrate due to the van der Waals interaction with the substrate. Recently, the vertically aligned growth of SWNTs has been achieved using a CVD method with ethanol.\textsuperscript{10} However, these are bundles of SWNTs and they are highly dense structures. For their applications such as the tips of a field emission or scanning probe microscope, vertically grown SWNTs should be individually isolated. Very recently, such isolated growth has been achieved by plasma CVD.\textsuperscript{11}

Here we report the vertical growth of individually isolated SWNTs on a silicon or silicon oxide substrate by conventional thermal CVD. Vertical growth has been achieved using rather large catalyst particles and a high growth temperature in CVD with methane. Vertically grown SWNTs are typically 300 nm or shorter, which is useful for use as tips of a field emission or scanning probe microscope.

2. Experimental

The substrate was either a silicon wafer or a thermally oxidized silicon wafer. The thickness of the thermal oxide was 100 nm. The furnace for CVD was a cold wall type, which is described in detail elsewhere.\textsuperscript{12} Argon and methane were used as the purge gas and carbon source, respectively. During the heating of the substrate, argon gas flowed, and the gas flowing was changed from argon to methane to start CVD growth after a constant temperature was achieved. The pressure was 66.5 kPa and the flow rate 300 sccm. A Co or Fe thin film as the catalyst was deposited using a conventional vacuum evaporator. Heat treatment of catalyst deposits in argon produced nanoparticles. By changing the catalyst film thickness (or coverage for a sub-monolayer film), we were able to control the size of catalyst nanoparticles and thus the density of the grown nanotubes. With a film thickness of about 1 nm, the nanoparticles were approximately 10 nm diameter, and individual SWNTs were obtained at 800–900 °C in a methane ambient.\textsuperscript{10} On the other hand, with a thin film of about 0.5 nm thickness, the bundles of SWNTs were grown.

3. Results and Discussion

In the present work, we used smaller film thickness to obtain catalyst particle sizes of 2–5 nm. With these particle sizes a mixture of individual and bundle SWNTs were obtained. Scanning electron microscopy (SEM) images of CVD-grown SWNTs on the SiO\textsubscript{2} substrate at three growth temperatures are shown in Fig. 1. SWNTs contacting the SiO\textsubscript{2} surface exhibit a peculiar contrast: the SiO\textsubscript{2} surface nearby the SWNT gives a thick and blurred image caused by an electron-beam-induced current (This is more clearly shown in Fig. 4, which was obtained using a lower-energy electron beam).\textsuperscript{13} For the specimen grown at 850 °C (Fig. 1(a)), many SWNTs lying on the substrate surface are seen. These are observed as gray images in the photograph. Some of them are bundles, which appear as thick wirelike images, showing a three-dimensional top-
ography (i.e., the upper half appears brighter and the lower half darker). Different from these images, very bright structures are recognized in the SEM photograph of the $900^\circ\text{C}/\text{C}$-grown specimen [Fig. 1(b)]. The bright structures have a variety of lengths but are smaller than 300 nm. Their density is higher for the $1000^\circ\text{C}/\text{C}$-grown specimen [Fig. 1(c)]. The bright structure does not show a three-dimensional topography. Note that such an image contrast is obtained by SEM when observing a wire structure comparable to or thinner than the beam diameter and suspended in space. Thus, it is likely that those bright structures are vertically standing nanotubes.

To observe the bright structures directly by transmission electron microscopy (TEM), a thin piece of specimen was set perpendicular to a microgrid for TEM observation. Thus, the electron beam hits the specimen surface at a grazing angle, enabling the imaging of nanotubes standing on the substrate. TEM photographs are shown in Fig. 2 for $1000^\circ\text{C}$-grown specimens. In the low-magnification image [Fig. 2(a)], vertically grown nanotubes are seen. Some of them are literally vertical to the substrate and others are inclined. A high-magnification image of the root part shows that the nanotube is single-walled [Fig. 2(b)]. Because of vibration, an atomic layer image could not be obtained for the tip of a long nanotube. For shorter nanotubes, the tip as well as the root could be observed simultaneously as shown in Fig. 2(c). This shows that catalyst particles are absent at the tip, indicating the root growth of nanotubes. Catalyst particles are observed on the substrate surface.

The diameter of vertically grown SWNTs is rather large. In Fig. 2(b), the diameter is as large as 5 nm. The diameter distribution obtained from several TEM photographs such as that shown in Fig. 2(c) is presented in Fig. 3 together with the Co catalyst particle size. Note that we measured the sizes of nanotubes and catalysts independently, because a one-to-one correlation between the nanotube and catalyst was difficult to observe in the TEM images. The diameter of vertically grown SWNTs ranges from 3–5 nm. Horizontally grown SWNTs were difficult to observe by TEM, but their diameters evaluated using Raman spectroscopy were 1–2 nm. In Raman spectroscopy, only nanotubes whose diameter resonates with the excitation wavelength are detected. So nanotubes thicker than 2 nm were not

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Fig. 1. Temperature dependence of SEM images of SWNTs grown on $\text{SiO}_2$ substrate using Co catalyst. These SWNTs were grown at (a) $850^\circ\text{C}$, (b) $900^\circ\text{C}$, and (c) $1000^\circ\text{C}$. The electron beam energy for SEM was 30 keV.

Fig. 2. TEM images of SWNTs grown on $\text{SiO}_2$ substrate at $1000^\circ\text{C}$ using Co catalyst. (a) Low-magnification image of vertically grown SWNTs. (b) High-magnification image of the root of vertically grown SWNT. (c) Image of vertically grown SWNTs together with catalyst particles. The electron beam energy for TEM was 100 keV.
detected by Raman spectroscopy in our measurement, even when thicker nanotubes existed. Thus, we can say that small-diameter nanotubes, 1–2 nm, exist in horizontally grown SWNTs, while such small-diameter nanotubes were not found by TEM in the vertically grown SWNTs. Interestingly, the catalyst has a similar size distribution. It is likely that a vertically grown SWNT has almost the same diameter as the catalyst particle.

In addition to the difference in diameter between the horizontally and vertically grown SWNTs, these two kinds of nanotube grow at different periods of the CVD process. SEM images for two different growth durations using the Co catalyst are shown in Fig. 4. After 30 s growth at 1000°C, only horizontally grown nanotubes are seen [Fig. 4(a)]. In contrast, vertically grown SWNTs are noted after 120 s growth. This result clearly shows that SWNTs grow horizontally in the very initial stage of methane supply, after which they grow vertically. However, we did not observe a substantial change for a longer growth time. Thus, the growth is almost saturated in 2 min.

Here, we mainly show the case of using the Co catalyst on the SiO\(_2\) substrate, but the results were similar to that using the Fe catalyst on the SiO\(_2\) substrate. Concerning the substrate, the vertical growth could be obtained both on the Si and SiO\(_2\) substrates at 900–950°C with the Fe catalyst. However, on the Si substrate surface, the silicidation of a metal catalyst can occur, resulting in the poisoning of the catalyst.\(^{16}\) For the Co catalyst, silicidation occurs at 850°C or higher, at which the native oxide of Si desorbs. Thus, vertical growth could not be obtained on the Si substrate with the Co catalyst. On the other hand, SiO\(_2\) base is selectively formed beneath an Fe particle on the Si surface by heating at 850–900°C.\(^{15}\) The SiO\(_2\) base prevents the silicidation of Fe up to 950°C. However, the SiO\(_2\) base desorbs at temperatures higher than 950°C, thus nanotubes barely grow on Si at this temperature range. On the SiO\(_2\) substrate surface, silicidation is not significant at least up to 1000°C. Thus, the SiO\(_2\) substrate is preferable for vertical growth.

Summarizing the experimental results, the vertically grown SWNTs have the following features. (i) They grow at high temperatures, 900°C or higher, and the yield increases with increasing temperature up to 1000°C. (ii) They have a large diameter, typically 3–5 nm. The diameter is thought to be comparable to the catalyst particle size. (iii) The length is small, ranging from several tens to 300 nm. (iv) They show root growth. (v) They appear after the initial horizontal growth of SWNTs.

The mechanism which differentiates vertical growth from horizontal growth is not clear yet. What follows is speculative discussion and should be examined through further studies. The transition of a growth mode from the initial horizontal growth to vertical growth is interesting. Since the density of the horizontally grown SWNTs is not high, the existing nanotubes may not affect new nanotube growth. One possible explanation for the growth mode change is the alternation of catalyst particles in the methane ambience. The melting points of Fe and Co are lower in methane ambience than in argon ambience.\(^{16}\) Thus, the surface diffusion of catalyst elements may change after methane feeding, resulting in the change of particle size. If the catalyst particles become large after the initial horizontal growth, newly grown nanotubes originate from large particles compared to the horizontally grown nanotubes. Since the surface diffusion of catalyst elements should be enhanced causing a large catalyst particle size at a high temperature, the increase in vertically grown nanotube yield with increasing temperature is consistent with the above interpretation. Then, why can large-diameter nanotubes grow vertically? Tentatively, we consider that a SWNT with the same diameter as that of the catalyst particle and with a small length can retain initial growth direction, while
a thin and long SWNT falls on the substrate during extension. This is based on our observation that catalyst particles melt during nanotube growth.\(^{16}\) A thin SWNT approximately 1 nm diameter can grow from a large catalyst particle, e.g., 3–10 nm, but the root of the SWNT must not be fixed on the molten catalyst particle. Thus, the root of the SWNT can move around during growth. On the other hand, if the SWNT diameter is comparable to the catalyst particle size, the root of the SWNT can touch partially the substrate surface. So the contacting part is fixed to the substrate. Still, the reason for the small length of vertically grown SWNTs remains unresolved. The vertical growth seems to be terminated immediately after the initiation of growth. This might be related to the delay of the initiation of vertical growth. In methane ambience a metal catalyst has a finite life time.\(^{17}\) In our experiment, SWNTs kept growing within 2–3 min, but the majority seemed to stop growing in 1 min. Thus, the delayed growth initiation may cause the short growth duration of vertical growth.

Vertically grown individual SWNTs are interesting from the viewpoints of applications. Those nanotubes are short. Since the vibration of the tip is small, they can be used as field emitters. The electric field strongly concentrates on the individual SWNT tips. A small vibration of the tip makes it useful as a probe of a scanning probe microscope, too. They may also be used for elements of nanodevices as a vertical transistor or vertical wiring. For vertical device applications, the encapsulation of fullerene-based molecules is an important technique to modify the electric properties of nanotubes.\(^{18,19}\) Here, we will show the direct encapsulation of fullerene in vertically grown individual SWNTs.

The substrate with vertically grown SWNTs was heated to 420°C in air for 30 min to remove the cap of SWNTs. Then, the substrate with cap-opened SWNTs was exposed to fullerene vapor at 450°C for 36 hours in a quartz capsule. After the fullerene exposure process, roughly one-half of vertically grown SWNTs disappeared probably due to oxidation in the capsule. The sample was observed by TEM in the same way as in the case of SWNTs shown in Fig. 2. A TEM photograph of fullerene encapsulation in vertically grown SWNTs is shown in Fig. 5. There are a bundle with three SWNTs and a short isolated SWNT. All of them are filled with fullerene. Since these SWNTs have a large diameter, about 3 nm, fullerene align in two or three rows. This result demonstrates that fullerene encapsulation is possible for SWNTs on the substrate.

4. Conclusions

We have succeeded in growing individual SWNTs vertically standing on the substrate by chemical vapor deposition with methane. The key for obtaining vertical growth is to use large catalyst particles, 2–5 nm diameter, and higher growth temperatures, 900–1000°C. The vertically grown SWNTs have diameters comparable to those of catalyst particles. The length of the vertically grown SWNTs is small, ranging from several tens to 300 nm. The large diameter and small length should be responsible for preventing the individual SWNTs falling on the substrate surface. Vertical growth occurs following the initial horizontal growth of SWNTs, probably 30–60 s after flowing methane. The alternation of catalyst particles in methane ambience might cause the growth mode transition from horizontal growth to vertical growth. We have demonstrated that fullerene encapsulation is possible directly in vertical SWNTs on the substrate.

Currently, the angle and the density of vertically grown nanotubes are not controlled. For some applications, the controls of growth direction, density and even growth position are crucial. Lithographically patterned catalyst dots can be used for the growth density and position control. As for the angle control, the application of electric\(^{20}\) or magnetic\(^{21}\) fields vertically to the substrate surface might be effective for precise vertical alignment.

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