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Multi-Walled Carbon Nanotubes Growing Vertically from Root Particles

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The catalytic growth of multi-walled carbon nanotubes (MWCNTs) was performed on Si substrates with and without interfacial layers, by microwave plasma chemical vapor deposition (MPCVD). Many vertically grown, dense MWCNTs attached to a catalytic film penetrated the root particles. The diameter of root particles, in the order of 100 nm, is larger than the tube diameters of 10–15 nm. Base growth and tip growth are proposed as part of a new CNT growth model. The interaction between catalytic film and the supporting interfacial layer is suggested to determine whether the catalytic particles are driven up or pinned down on the substrate during the growth. © 2010 The Japan Society of Applied Physics

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1. Introduction

Carbon nanotubes (CNTs) that consist of sheet(s) of graphite rolled into a cylinder were observed by Iijima in 1991.¹⁾ They exhibit fascinating properties and promising technological applications. Understanding their mechanism of growth is very important for improving their yield and quality in various applications. However, the growth mechanisms of CNTs are very complicated and are still disputed. They can depend on the method of deposition, the catalysts used and process parameters. Several mechanisms have been proposed for the growth of multi-walled CNTs (MWCNTs). Baker²⁾ adopted the concept of vapor–liquid–solid mechanisms³⁾ to explain Si whisker growth, and suggested the following growth sequence of CNTs: hydrocarbon decomposed into carbon atoms on the catalyst surface and dissolving into the catalyst. Then carbon atoms diffuse through the catalyst particle, and precipitate onto the back surface to form the filament structure. The rate-determining step was carbon diffusion. Oberlin *et al.*⁴⁾ proposed that the surface diffusion of carbon around, rather than through, the catalyst particle, is crucial for the growth. In the arc-discharge method, Endo and Kroto⁵⁾ suggested that tube formation involving the C₂ adsorption process was assisted by the presence of a pentagonal lattice to reconstruct cap morphology. Iijima *et al.*⁶⁾ clarified the open-end growth mechanism, in which carbon atoms are added at the open ends of the tubes. The catalytic growth of single-walled CNTs (SWCNTs) is still a debated issue. Dai *et al.*⁷⁾ proposed the yarmulke mechanism wherein carbon forms a hemispherical graphene cap called a yarmulke, on the catalyst particle, and the nanotubes grow from such yarmulkes. The root growth mechanism for SWCNTs is another mechanism,^{8–12)} wherein a large number of CNTs grow rapidly from the surface of a single catalytic particle, which is much larger than the CNT diameter.

The control of the tube diameter, density and length during growth is important in industrial production. We present a way of growing dense, vertically aligned MWCNTs bundles by applying an interfacial layer (Ti, SiO₂). Vertically, CNTs are either underneath or above the catalytic film. Also, MWCNT growth mechanisms for base growth and tip growth are proposed.

Table I. Sample designation and results.

Sample	Catalyst	Process ambient CH ₄ /H ₂ (sccm)	Deposition time (min)	Buffer layer	Mechanism
1	Fe	10/100	6	None or SiO ₂	Base growth
2	Co	10/100	10	Ti	Base growth
3	Fe	10/100	5	SiO ₂	Tip growth
4	Co	10/100	10	SiO ₂	Tip growth

2. Experimental Procedure

MWCNTs were synthesized by a microwave plasma chemical vapor deposition (MPCVD) system with CH₄+H₂ source gases. An interfacial layer of Ti (75 Å) or SiO₂ (1000 Å) was deposited on the Si substrate before catalytic film deposition. The Ti film and SiO₂ were formed by physical vapor deposition (PVD) and plasma-enhanced chemical vapor deposition (PECVD), respectively. Then, two kinds of catalytic films were deposited on Si before CNTs were synthesized: (1) Fe film (20 Å) and (2) Co film (20 Å). Table I lists the process conditions and the results. CNTs were synthesized as follows. (1) Reduction in H₂ plasma at 0.67 kPa for 10 min, at a microwave power of 500 W; (2) introduction of CH₄/H₂ process gases at a pressure of 2.13 kPa and a microwave power of 800 W. The temperature was 650 °C during the growth of CNTs, as determined by placing a thermocouple under the substrate holder. The morphologies and microstructures of CNTs were identified by scanning electron microscopy (SEM; Hitachi S-4000), transmission electron microscopy (TEM; JEOL 2000 FX); and high-resolution transmission electron microscopy (HRTEM; JEOL 4000FX).

3. Results

Figures 1(a) to 1(f) show the SEM images of samples 1 to 4, and reveal vertically grown, dense CNTs. The top view of SEM images of samples 1 and 2 indicate a high density of CNTs, the catalytic films still remain on the substrate. In contrast, CNTs covered with a top thin layer and embedded with nanoparticles were obtained for samples 3 and 4, as shown in Figs. 1(c) to 1(f). The lack of an interfacial layer or the presence of a Ti interfacial layer can promote the bonding of Fe or Co catalysts with the

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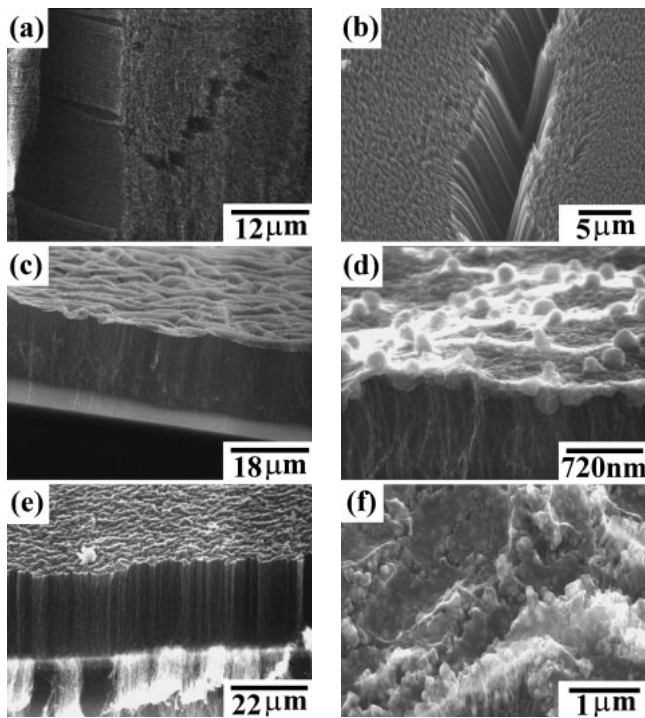


Fig. 1. SEM images: (a) sample 1, (b) sample 2, (c) sample 3, (d) corresponding close-up view of (c), (e) sample 4, and (f) corresponding close-up view of (e).

supporting media, forming the silicide or Co–Ti–Si compounds. The CNT growth is thus governed by base growth. The presence of the SiO₂ interfacial layer effectively blocks the Co from interacting with the Si substrate. The Co catalysts are driven upwards during growth, inducing the tip growth of CNTs. However, using Fe catalysts with the SiO₂ interfacial layer causes Fe catalyst to be present at the top of the tubes with only a brief deposition time. A longer deposition time is suggested to cause bonding between Fe and the SiO₂ film, resulting in the base growth of CNTs. According to the Fe–Si phase diagram, two phases, FeSi and FeSi₂, are present at process temperature. In the Co–Si system, the intermediate phase sequence Co → Co₂Si → CoSi → CoSi₂ occurs in the temperature range 300–800 °C. The metal silicide thus formed is bound tightly to the substrate, resulting in base growth.

Consequently, the interfacial layer may determine the catalyst film location in relation to the substrate. Figures 2(a) to 2(c) show the TEM images of CNTs the samples for TEM investigation were prepared by ultrasonic dispersion and were dropped to a carbon-copper grid. Notably, for each sample with a different interfacial layer or catalytic material (Fe or Co), the basic result was the same: MWCNT bundles have one free end and the other end in linked to the catalyst film and embedded with nanoparticles. Figure 2(a) shows the typical microstructure obtained by TEM. The diameter of nanoparticles (100–150 nm) exceeds the tube diameter of CNTs (10–15 nm), and multiple CNTs grow out from a single nanoparticle. This phenomenon is similar to the root-growth mechanism for SWNTs, first proposed by Saito *et al.*⁸⁾ to explain the sea-urchin-like structures. The process that results in a

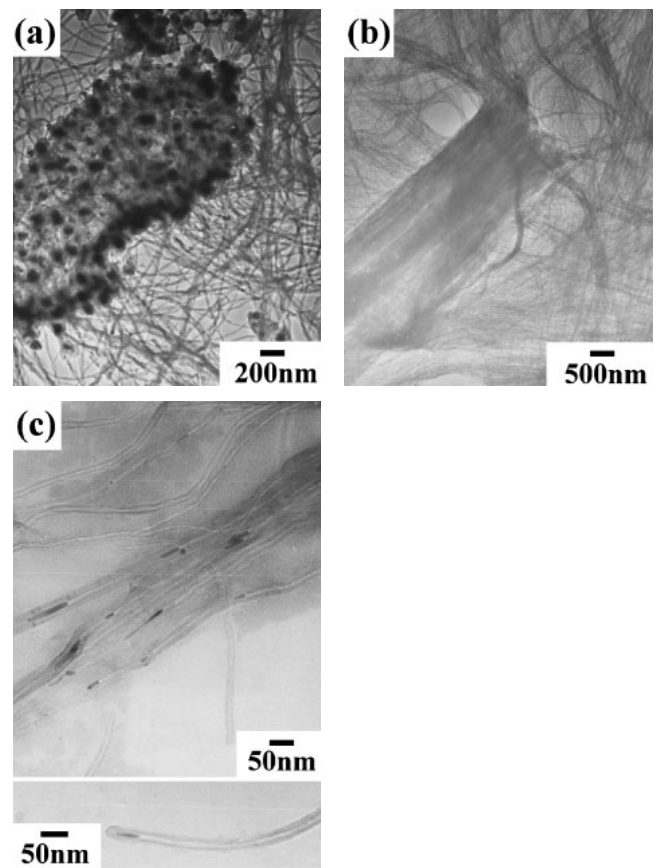


Fig. 2. TEM images: (a) MWCNTs attached to the catalytic particles, (b) dense MWCNT bundles, (c) ends and stems of CNTs, showing split particles.

large number of nanotubes growing radially from a single catalytic particle is suggested to involve carbon segregation and nucleation on the metal surface. In this experiment, the presence of catalyst on the base for samples 1 and 2, is evidence of base growth. In contrast, samples 3 and 4 exhibit tip growth. Figure 2(b) shows MWCNT bundles. Large ropes of MWCNTs have similar diameters and lengths, indicating that the tubes grow cooperatively. The catalysts split from the root particle can be found on the other end of CNTs, or they remain in the tube stems, as shown in Fig. 2(c). Accordingly, Fig. 3 schematically depicts the growth models of CNT film, with a low H₂ reduction temperature (~590 °C). Under such conditions, the system energy and surface energy for forming new particles favor the formation of large particles (100–150 nm). The liquid state of the catalytic particles allows carbon atoms to be dissolved to supersaturation. The introduction of many carbon atoms into the liquid state of nanoparticles may cause the surface instabilities. These surface instabilities induce the formation of small protrusions that act as nuclei embryos for the subsequent growth of MWCNTs. Notably, vertically, CNTs are clearly either underneath the or above the catalytic film, indicating that the growth involves bulk diffusion of carbon atoms through the catalytic particles. When the carbon atoms are segregated and diffused around the surface of the nanoparticles, CNTs grow rapidly rather than on one side of the nanoparticles. The growth of CNTs proceeds through

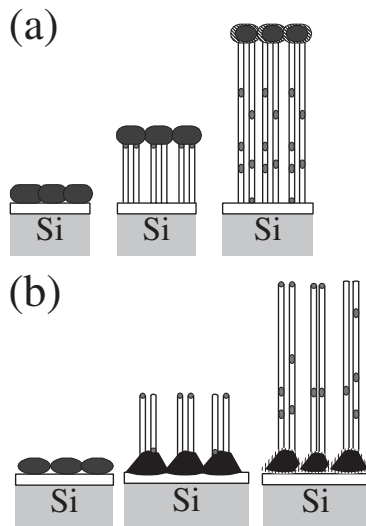


Fig. 3. Schematic diagrams of growth mechanisms of (a) tip growth of MWCNTs and (b) base growth of MWCNTs. The black particles represent the catalysts.

further incorporation of carbon atoms into root particles. During synthesis, some small nanoparticles split off from root particles because of capillary suction, revealing the liquid state of the particles and surface instability. The processes continue until the catalytic particle is made inactive by the surrounding graphite sheets. Figure 4 shows the HRTEM image of MWCNTs and reveals that the root particle is surrounded by multi shell graphite sheets and protruding MWCNTs [Fig. 4(a)]. The nanoparticle, encapsulated in the inner tube, is observed [Fig. 4(b)]. The growth mechanism, tip growth or base growth, depends on the catalyst film rather than on the catalyst particle.^{3–5)} Vertical CNTs of uniform diameter and growth are formed simultaneously.

4. Conclusions

We investigated the mechanisms of base growth and tip growth for MWCNTs. Vertically grown, dense MWCNTs attached to a catalytic film reveal that many MWCNTs penetrate the root particles. This result offers a different perspective catalyst-assisted growth of MWCNTs, and supports a similarity between the root growths of SWCNTs and that of MWCNTs. The presence of the catalytic film, either on the base or the top of CNTs, as governed by the interfacial layer, may satisfy the possible requirements for further application. The growth rate of

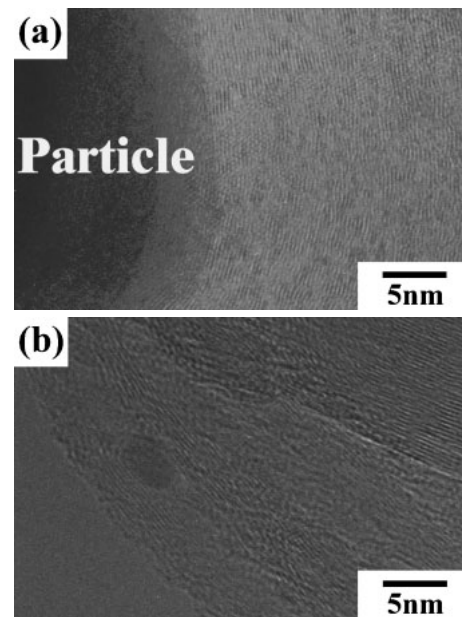


Fig. 4. HRTEM image of MWCNTs: (a) particles are surrounded by multiple graphite sheets, and MWCNTs penetrate the root particle; and (b) a nanoparticle splits off from a root particle.

CNTs using Fe catalyst exceeds that when using Co catalysts. The Co film is better than the Fe film for controlling both tip growth and base growth, since the Fe can interact with SiO₂ for a longer deposition time. Inserting a SiO₂ layer prevents interaction between Co film and Si.

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