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Formation of Bamboo-Like Carbon Nanotubes and Nanofibers Using Co–Si–O and Co–Si Catalysts

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Bamboo-like carbon nanotubes were synthesized by microwave plasma chemical vapor deposition (MPCVD) using CH₄ and N₂ as source gases in various ratios. Two types of catalytic films, namely, a condition 1, Co film/SiO₂/Si substrate, and, a Co film/Si substrate layer with rapid thermal annealing (RTA; condition 2), were used as catalysts to grow carbon nanotubes. The interaction between the catalytic film and the Si substrate or between the catalytic film and the SiO₂ interlayer occurred during the H₂ reduction step before nanotube growth. The chemical compositions of catalytic particles capping the carbon nanotubes were identified by energy-dispersive X-ray spectroscopy (EDS) as Co–Si–O and Co–Si for conditions 1 and 2, respectively. The growth of the base and tip growths was investigated and is suggested to be governed by the capillary effect and the strength of adhesion between the catalytic particles and the underlayer. Transmission electron microscopy (TEM) analysis reveals that the carbon nanotubes and nanofibers have bamboo-like structures with hollow internal compartments. The formation mechanisms of these bamboo-like structures are discussed. © 2010 The Japan Society of Applied Physics

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1. Introduction

Edison's pioneering work on carbon fibers was motivated by the need for materials that could be used in an incandescent light bulb.¹⁾ Following his work, carbon fibers or carbon whiskers were prepared to meet specific requirements, such as stiff composite materials, and high-thermal-conductivity commercial products. Approaches to the catalytic growth of carbon fibers aim to synthesize more crystalline graphites, whose directions are more highly oriented. The approaches also lead to the later work of catalytic growth of carbon nanotubes. Notably, the distinction between carbon nanotubes and nanofibers is very clear and dependent on the grain size in the cross section. The nanotube in the cross section is a single domain or grain characteristic of the cross section. In contrast, nanofibers have a grain size that is small compared with its circumference.²⁾ Thus, the unique single crystal nature of carbon nanotubes permits the use of the Brillouin zone folding approach to predict their electron and phonon dispersion relations.

The growth of catalyst-assisted carbon nanotubes is generally considered to proceed with the decomposition and adsorption of carbonaceous gases on catalytic particles then with the dissolution and diffusion of carbon atoms into the catalysts, and finally with the precipitation of graphite layers to form tube walls.³⁾ A bamboo-like nanotube is a hollow tube with interior compartments. The growth mechanisms of bamboo-like tubes have been proposed^{4,5)} and are identical to the base growth model. The precipitate of graphite sheets is formed as a cap on the surface of a catalytic particle, and then, the growth of graphite sheets follows to form a graphite sheath, which may slide out of the catalytic particle when the accumulated stress reaches a specific value. The above cycle is repeated to yield a series of compartments that form a bamboo like carbon nanotube. One study⁶⁾ reveals the competition between the torn shell from a catalytic particle (V_s) and the growing shell from a catalytic particle (V_p) that indicates whether the tube is formed as a carbon shell, a hollow tube or a bamboo tube.

The bamboo like structure was also considered to be formed by the low surface tension of catalytic particles (such as Ni and Al–Si–Cu),^{7–9)} and thus the catalytic particles wetted the walls poorly. The catalytic particles jumped out from a graphite sheath to release the stress and a hollow compartment was formed.

In some studies, the bamboo like structure obtained using a precursor including N₂ or NH₃ gas was investigated.^{5,10–14)} One study¹⁵⁾ also demonstrated the formation of a CN_x/carbon nanotube junction by varying the type of source gas used. Therefore, varying the composition of a precursor mixture can yield interesting insights. In this study, two types of silicide films, namely, Co and Co silicide films, were prepared to elucidate the behavior of Co-based catalytic materials. The growth mechanisms of nanotube or nanofiber structures are addressed.

2. Experimental Procedure

Carbon nanotubes and nanofibers were deposited on Si wafers by microwave plasma chemical vapor deposition (MPCVD). Two types of films were employed as catalysts before the growth of nanotubes: (1) a Co film (75 Å)/SiO₂ (1000 Å) on a Si substrate and (2) a Co film (75 Å) on Si substrate followed by two steps of rapid thermal annealing in N₂ ambient at 600 °C, for 60 s, and then at 760 °C for 20 s. The second condition can be defined as the CoSi_x film on the Si substrate, where the Co film was formed by physical vapor deposition (PVD) and the SiO₂ film by plasma-enhanced CVD (PECVD). The synthesis of carbon nanotubes involved the following processes: (1) H₂ reduction for 10 min at a deposition pressure of 16 Torr, and a microwave power of 960 W and (2) the introduction of CH₄/N₂ process gases using the mixture ratios listed in Table I, at a deposition pressure of 16 Torr and a microwave power of 960 W for 3 min.

The Perkin Elmer scanning Auger probe (AES) system was used to obtain the depth profiles of the two types of catalytic films following H₂ reduction. Scanning electron microscopy (SEM) was employed to determine the morphologies of the carbon nanotubes and nanofibers, and X-ray energy dispersive spectroscopy (EDS) was used to determine

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Table I. Sample designations and deposition parameters.

Sample	Catalytic film preparation condition	Catalytic particle composition	Process gases CH ₄ /N ₂ (sccm/sccm)	Morphology
1	Co on Si substrate with RTP	Co-Si	10/100	Bamboo-like nanotubes
2	Co/SiO ₂ on Si substrate	Co-Si-O	10/100	Bamboo-like nanotubes
3	Co/SiO ₂ on Si substrate	Co-Si-O	10/80	Bamboo-like nanotubes
4	Co/SiO ₂ on Si substrate	Co-Si-O	10/50	Bamboo-like nanofibers

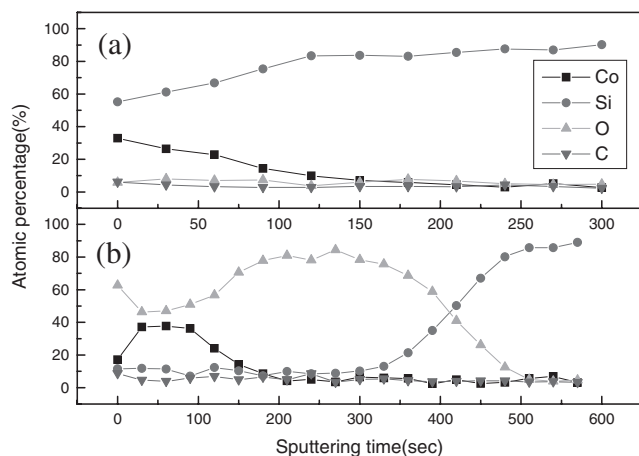


Fig. 1. AES depth profiles of two types of catalyst films on Si substrates following H₂ plasma reduction before the growth of carbon nanotubes. (a) Co film/SiO₂ substrate and (b) Co film/Si substrate layers.

the chemical compositions of catalytic nanoparticles that capped the tubes.

3. Results and Discussion

Figure 1 shows the AES depth profiles of the two types of catalytic films [condition 1: a Co film/SiO₂/Si substrate layer and condition 2: a Co film/Si substrate layer with rapid thermal annealing (RTA) followed by H₂ reduction for 10 min to identify the chemical composition of the film]. In the Co-SiO₂¹⁶⁾ system, CoSiO₄ is formed on the tie line between Co and SiO₂; the existence of this phase shows that Co can react with SiO₂. This finding is consistent with the AES depth profile shown in Fig. 1(a) that indicates that Co can react with SiO₂. In contrast, the composition gradient of CoSi_x across the reacted layer is observed for the film of condition 2. In the Co-Si system,¹⁶⁾ the intermediate phase sequence Co → Co₂Si → CoSi → CoSi₂ occurs in a temperature range from 300 to 800 °C for rapid thermal processing or processing in a furnace. Consequently, the interaction between the catalytic film and the Si substrate or between the catalytic film and the SiO₂ interlayer occurs during the H₂ reduction step before nanotube growth.

The chemical compositions of catalytic particles capping the carbon nanotubes are examined spectroscopy EDS with a transmission electron microscopy (TEM) instrument. Co and Si signals are detected for the catalytic particle under the film of condition 1. Under condition 2, Co, Si and O signals are detected. These results agree with those of AES chemical analysis. Other Cu and C signals are considered to originate from either the carbon TEM ring or the carbon atoms dissolved in the catalytic particles.

Figures 2(a) and 2(b) show SEM morphologies of carbon nanotubes of samples 1 and 2. Table I shows the detailed descriptions of each sample. Obviously, for sample 1, the conical CoSi_x particles still remain on the substrate. In contrast, for sample 2, the cork-shaped Co-Si-O particles are located at the tip of the nanotubes. Whether carbon nanotubes grow by either “tip growth” or “base growth” is an interesting subject for research. Baker¹⁷⁾ established that the interaction between metal catalytic particles and the supporting medium dominates the growth. Therefore, the adhesion between catalytic particles and the interlayer crucially governs the favored growth mechanism. CoSi₂ has an fcc CaF₂ structure with only 1.2% lattice mismatch with Si.¹⁹⁾ Epitaxial CoSi₂ is formed on the interface surface of the Si substrate. The other intermediate phase is formed on top of the CoSi₂ phase, suggesting that the CoSi_x nanoparticles strongly adhere to the CoSi₂ film. Therefore, the growth of carbon nanotubes is dominated by base growth using the CoSi_x catalyst. For catalytic nanoparticles of Co-Si-O, the Co-Si-O phase is unstable and dissociates at 900 °C. Co-rich Co-Si-O nanoparticles may have loosely bonded to the SiO₂ interlayer. Thus, the contact angle between the nanoparticles and the substrate may help the carbon atoms to precipitate on the backsurface of a catalyst droplet, which is pushed upward by growing nanotubes; tip growth therefore dominates. Figures 2(c) and 2(d) show the SEM morphologies of carbon nanotubes and nanofibers obtained using Co-Si-O catalysts for samples 3 and 4, respectively. Notably, the catalytic particles shown in Fig. 2(c) can also be seen on top of the fibers, which are quasi-aligned. Carbon nanofibers of sample 4 are randomly oriented, as shown in Fig. 2(d), where the inset graph in the upper corner shows that the curly catalyst materials fill the fibers.

Figures 3(a)–3(c) show TEM images of samples 2–4, respectively, indicating the effect of CH₄/N₂ ratio on the structure of carbon nanotubes or nanofibers. For sample 2, CH₄/N₂ = 0.1 and both hollow carbon nanotubes and nanotubes with interior compartments are observed. The formation mechanism of the bamboo like structure is considered to be the precipitation of carbon atoms on the surface of the catalytic particle to form graphite sheets, and therefore, the curvature of the catalytic particle is very large, such that the surface is flat and the bamboo-like structure cannot be generated. The main differences between the bamboo growth models used in this study and in previous one^{1–5)} are the catalyst shape and the introduction of the N₂ precursor. The inset in Fig. 3(b) shows such a situation. Restated, only the formation of catalytic particles with sharp tips can promote the formation of the bamboo like structure. The precursor in the presence of N₂ gas is also beneficial

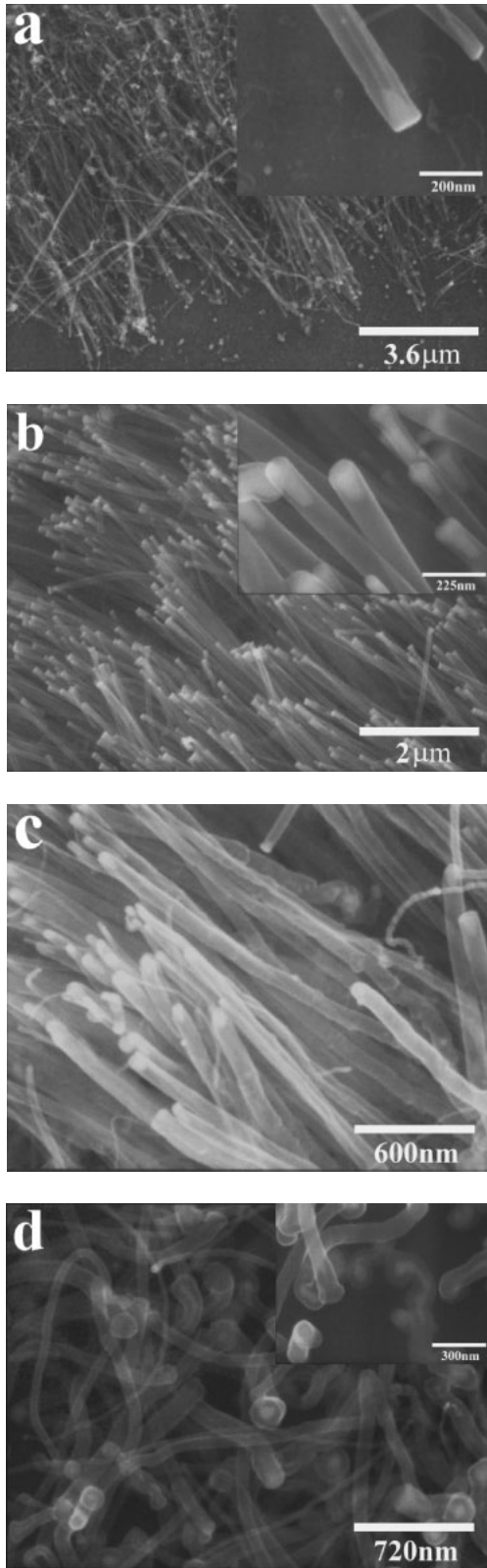


Fig. 2. SEM morphologies of carbon nanotubes and nanofibers: (a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4.

for forming the C–N bond in sp^3 hybridization. This can form the curvature of the compartment layer. For sample 3, $CH_4/N_2 = 0.125$ and the bamboo-like carbon nanotubes are observed; some nanoparticles splitting from the original particles are encapsulated in the inner tube, as indicated by arrows. The split catalytic particles are observed at

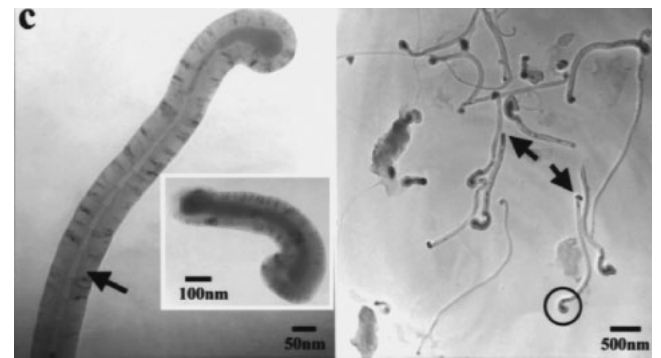
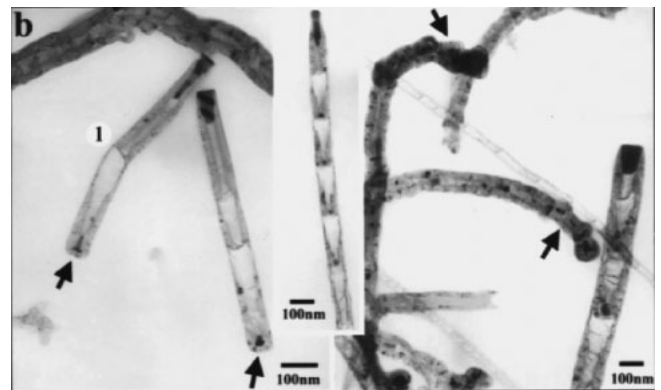
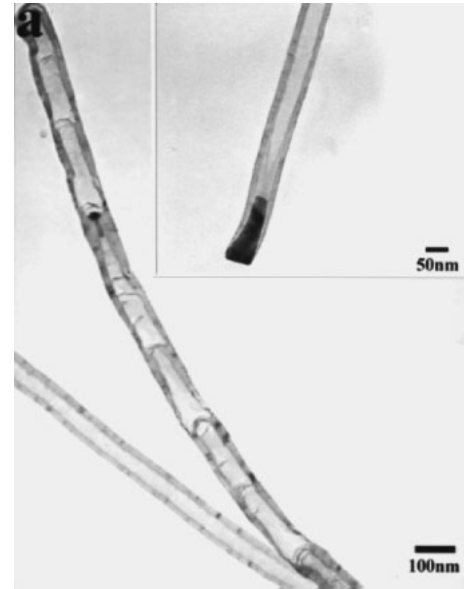


Fig. 3. TEM micrographs of carbon nanotubes and nanofibers: (a) sample 2, (b) sample 3, and (c) sample 4.

uncertain positions such as at the end of a tube or on the compartment layers. The left-hand side of Fig. 3(b) indicates the original and split catalytic particles on top and at the root, respectively, and the number ① signifies a compartment layer. Interestingly, the upper and bottom walls differ in wall thickness. The growth can be considered to proceed with the original and split catalytic particles. The carbon atoms can diffuse through both catalytic particles (top and root) to precipitate to form graphite sheets that form fibers walls. Notably, the growth mechanisms are the growth of the base and the growth of the tip growth. As growth continues, the compartment layers are formed by the catalytic particles and thus compartments of various sizes are formed. For

sample 4, $\text{CH}_4/\text{N}_2 = 0.2$ and bamboo-like fibers are observed. Interestingly, the catalytic particles are also found at both tube ends. The growth sequences are as follows. Initially, carbon atoms diffuse around the surfaces of catalytic particles, as shown in the insets in Figs. 2(d) and 3(c). Furthermore, the catalytic particles are elongated and thus broken by the growing tubes. Only the split catalytic particle at the root contributes to fiber growth, as proved by the fact that curvatures of the compartment layers are similar to the curvature of the split catalytic particle rather than to that of the curved catalytic particle. In other words, the growth of nanofibers is dominated by base growth. The curved catalytic particles highlighted by a circle on the right-hand side of Fig. 3(c) have complex geometries and do not support the dissolution and diffusion of carbon atoms; therefore they are inactive in nanotube growth.

The CH_4/N_2 ratio is an important factor in the growth of nanotubes or nanofibers. The diffusion of carbon atoms through the catalytic particles can be considered to lengthen the tube walls of the growing tubes, while the diffusion of carbon atoms around the catalytic particles can be considered to thicken the walls of the growing tubes. This growth mechanism is similar to that of arc discharge.¹⁹⁾ Fast, directed carbon ions favor the creation of tubelike structures, while the isotropic Maxwellian distribution tends to thicken the tubes and promote the formation of multishell nanotubes. For sample 2, a higher N_2 to CH_4/N_2 ratio favors carbon nanotube formation since N^+ and NH^+ are etching ions that are effective for removing amorphous carbon. The partial pressure of CH_4 for sample 4 is higher than that for sample 2; therefore, more neutral carbon atoms accumulate on the nanofiber walls laterally, thickening them and resulting in a narrower inner fiber. This action enhances the capillary effect, since the capillary force is inversely proportion to the radius of the tube. Liquid catalytic particles are thus elongated and then split. The splitting of these catalytic particles contributes to the growth, causing the formation of variously oriented graphite sheets, and thereby, carbon fibers.

In this study, the CH_4/N_2 ratio is adjusted to form carbon nanotubes or nanofibers at a growth temperature of 1000 °C. The formation of bamboo-like carbon nanotubes and nanofibers is related to the presence of N_2 gas and to the CH_4/N_2 ratio. Increasing the CH_4/N_2 ratio causes nanofibers to form

rather than nanotubes. The nanofiber definition is based on fiber diameter (>100 nm) and the ratio of the diameter of the hollow fiber to the thickness of the wall (<1).

4. Conclusions

Carbon nanotubes and nanofibers were successfully deposited on Si wafers by the MPCVD method. For a specific CH_4/N_2 ratio, the growth of carbon nanotubes assisted by CoSi_x catalysts is governed by base growth. Growth assisted by a Co–Si–O catalyst is governed by tip growth. This difference is due to the stronger adhesion between the catalyst and the underlayer in the former case. At higher CH_4/N_2 ratios, carbon nanofibers are formed in preference to carbon nanotubes, which are formed at lower CH_4/N_2 ratios. A higher CH_4/N_2 ratio can cause the splitting of the catalyst due to the capillary effect. The split catalytic particles contribute to fiber growth.

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