Dependence of the Vertically Aligned Growth of Carbon Nanotubes on the Catalysts

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Multiwalled carbon nanotubes were grown vertically aligned on the iron, cobalt, and nickel catalytic nanoparticles deposited on alumina substrates by thermal chemical vapor deposition of acetylene in the temperature range 900−1000 °C. The growth rate of carbon nanotubes on the iron catalyst is about 2 times higher than those on the cobalt and nickel catalysts over the temperature range. The growth rate enhances approximately by a factor of 2 for the temperature increase from 900 to 1000 °C, irrespective of the catalysts. The degree of crystalline perfection of the graphitic sheets also depends on the catalysts, which has a good correlation with the growth rates. The results suggest that the bulk diffusion of carbons would play a major role in determining the growth rate as well as the crystallinity of carbon nanotubes.

1. Introduction

Synthesis of carbon nanotubes (CNTs) has been extensively investigated by a number of research groups, since the first observation in 1991.[1] Various methods, e.g., arc-discharge,[2,3] laser ablation,[4] pyrolysis,[5] and chemical vapor deposition (CVD),[6−8] have been developed for the production of CNTs. The catalysts of CNT growth are usually the transition metal particles in nanometer size. The use of transition metal particles as catalysts had been early recognized in the synthesis of carbon nanofibers.[9−11] The catalytic activity certainly relates to the decomposition of carbon precursors, the formation of metastable carbides, the diffusion of carbons, the formation of graphitic sheets, etc. For the growth process of single-walled and multiwalled CNTs, the roles of the catalysts were investigated theoretically and experimentally by a number of research groups.[12−15] Understanding the catalytic activity would lead eventually to a controlled growth of CNTs, which is prerequisite for various potential applications.

In the present work, we have investigated the effects of catalyst on the growth properties of vertically aligned multiwalled CNTs. Iron (Fe), cobalt (Co), and nickel (Ni), which are known as the most effective catalysts for the growth of multiwalled CNTs, are chosen. The catalytic nanoparticles were formed using a simple method: a thin film of metal salt is deposited on the alumina substrates, followed by the ammonia (NH₃) pretreatment at the growth temperature of CNTs. The CNTs were synthesized vertically aligned on the Fe, Co, and Ni nanoparticles deposited on the alumina substrates using thermal CVD of acetylene (C₂H₂) at three temperatures, 900, 950, and 1000 °C. The growth rate of CNTs and the crystallinity of graphitic sheets were compared for three catalysts, providing an insight into the growth mechanism of CNTs.

2. Experimental Section

The 0.01−1 M ethanol solution of metal salts, i.e., FeCl₂·4H₂O (Aldrich, 99.995%), CoCl₂·*x*H₂O (Aldrich, 99.999%), and NiCl₂·6H₂O (Aldrich, 99.9999%), has been prepared in an argon (Ar)-filled glovebox. A 10 mm × 20 mm size alumina substrate was coated with a drop of metal chloride solution and dried by Ar. The thickness of metal chloride film was 300 nm to 1 μm. The coated substrates were loaded on a quartz boat placed in a quartz tube reactor. The reactor was heated to the growth temperature (900−1000 °C) under Ar flow. X-ray diffraction (XRD, Philips X'PERT MPD) analysis and scanning electron microscopy (SEM, Hitachi S-4300) images revealed that the metal chloride film is reduced to the microsized metal particles at the growth temperature. The substrates were pretreated by NH₃ with a flow rate of 10−50 sccm for 5−20 min, forming the nanosized catalytic particles. The CNTs were grown using C₂H₂ with a flow rate of 10 sccm for 5 min. The reactor was cooled to room temperature under Ar flow. The configuration and structure of the products were examined by SEM, transmission electron microscopy (TEM, Hitachi H9000-NAR, 300 kV), and Raman spectroscopy (Renishaw RM1000) using the 514.5 nm line from an argon ion laser.

3. Results

Figure 1 shows SEM images for the vertically aligned CNTs grown on the catalytic particles deposited on alumina substrates at 900 and 1000 °C. Parts a and b of Figure 1 show the CNTs grown on the Fe-deposited substrates, respectively, at 900 and 1000 °C. The respective lengths are 35 and 55 μm. Parts c and d of Figure 1 show the CNTs grown on the Co-deposited substrates. The lengths are 15 and 30 μm, respectively, at 900 and 1000 °C. Figure 1e shows 17 μm long CNTs grown at 900 °C, and Figure 1f shows 30 μm long CNTs grown at 1000 °C,

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Carbon Nanotube Growth Dependence on Catalysts

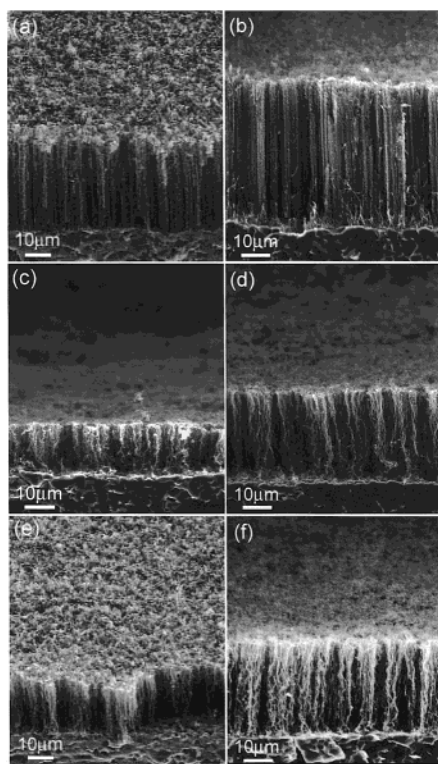*J. Phys. Chem. B, Vol. 106, No. 36, 2002* **9287**

Figure 1. SEM micrographs of the vertically aligned CNTs grown on a large area of the alumina substrates, using the catalysts (a) Fe at 900 °C, (b) Fe at 1000 °C, (c) Co at 900 °C, (d) Co at 1000 °C, (e) Ni at 900 °C, and (f) Ni at 1000 °C.

on the Ni-deposited substrates. From the many experimental runs, it is found that the average lengths of CNTs grown on the Fe, Co, and Ni catalysts at 900 °C are 30 ± 5, 15 ± 5, and 15 ± 5 μm, respectively. The respective average lengths of CNTs grown at 1000 °C are 65 ± 15, 30 ± 5, and 30 ± 5 μm, respectively. The density of CNTs is ∼10^{10}/cm². Dividing the length by the growth time (5 min) yields the average growth rate of CNTs in a unit of μm/min. The growth rate is constant during the first 10 min, but after that the growth rate decreases as the carbonaceous particles cover the surface of the substrate. Thus the growth rates of CNTs were obtained within the time regime that the constant growth rate is maintained. The growth rates of CNTs are summarized in Table 1. As the temperature increases from 900 to 1000 °C, the growth rates are enhanced approximately by a factor of 2 for all catalysts. The growth rate of CNTs grown on the Fe catalyst is about 2 times higher than the case of Co and Ni catalysts.

The vertically aligned CNTs were grown under a restricted growth condition that the metal nanoparticles were formed with a size in the range of 30−150 nm and a density as high as 10^9−10^{10}/cm² on the substrates. Such conditions were achieved when the flow rate of NH₃ was 30−50 sccm and the pretreatment time was 5−20 min at 900 °C for all catalysts. As the growth temperature increases to 1000 °C, the flow rate and pretreatment time are down to 10−20 sccm and 5−10 min, respectively. At the higher temperatures, the average size of catalytic nanoparticles increases and the distribution becomes broader, which is due to the more efficient agglomeration of the nanoparticles. Thus the particle density tends to decrease at the higher temperature. The similar average sizes of Fe, Co, and Ni nanoparticles were made at the same growth temperature, by adjusting the thickness of the metal chloride film. The flow rate of C₂H₂ was 10 sccm, to supply enough carbons to grow the CNTs without depositing carbonaceous particles. The growth

rate was reproducible for each catalyst and temperature within the experimental errors. The experiments were carried out many times to derive the accurate numbers.

We measured the TEM images for the CNTs grown on three catalysts. The CNTs were taken off from the substrate by a razor and dispersed in ethanol to load homogeneously on the TEM grid. Parts a−c of Figure 2 show the CNTs grown on the Fe, Co, and Ni catalysts, respectively, at 950 °C. The CNTs exhibit exclusively a multiwalled bamboo-like structure irrespective of the catalyst. The closed tips are free of the encapsulated catalytic particles. The average diameters of CNTs are about 60 nm for three catalysts. The diameter distribution and the average diameters of the CNTs are summarized in Table 1, showing the nearly same value for three catalysts at a given temperature. The average diameter of CNTs increases as the temperature increases.

Figure 3 shows HRTEM images for the typical CNTs grown using Fe, Co, and Ni catalysts at 950 °C. The right side of the images corresponds to the outside of the wall in a nanotube. The graphitic sheets are separated by ∼0.34 nm. The outer graphitic sheets are usually less crystalline than the inner graphitic sheets. As shown in Figure 3a, the graphitic sheets of the CNT grown using the Fe catalyst are in a highly ordered crystalline structure. Figure 3b is for a CNT grown on the Co catalyst, showing that the graphitic sheets are waved over a short range and thus are more defective than those of CNTs grown on the Fe catalyst. Figure 3c is for a CNT grown on the Ni catalyst, showing less crystallinity than that grown on the Fe catalyst. The HRTEM images reveal that the CNTs grown on the Fe catalyst exhibit a higher degree of crystalline perfection than those grown on Co and Ni catalysts at three temperatures.

To obtain the information about the crystallinity of entire CNTs, Raman spectroscopy was used. First-order Raman spectra for the CNTs grown on the Fe, Co, and Ni catalysts at 950 °C are displayed in Figure 4a. All spectra show mainly two Raman bands at ∼1580 cm⁻¹ (G band) and ∼1350 cm⁻¹ (D band). In the spectrum of the CNTs grown on the Fe catalyst, a band at ∼1600 cm⁻¹ (D′ band) appears as a bump of the G band. The G band is originated from the Raman active E_{2g} mode due to in-plane atomic displacements. The origin of D and D′ bands has been explained as disorder-induced features due to the finite particle size effect or lattice distortion.[16,17] For the CNTs grown on the Co and Ni catalysts, the D and D′ band becomes stronger and broader. The D′ band is therefore overlapped with the G band, resulting in a converged peak whose position shifts to a higher wavenumber from that of G band by ∼10 cm⁻¹. It was noted that the intensity ratio of the D band to the G band (I_D/I_G) has a linear relation with the inverse of the in-plane crystallite dimension.[16] The value of I_D/I_G is 0.60, 0.72, and 0.75, respectively, for the CNTs grown on the Fe, Co, and Ni catalysts. It indicates that the degree of long-range ordered crystalline perfection would be higher for the CNTs grown on the Fe catalyst compared to those grown on the Co and Ni catalysts, which is consistent with the result of HRTEM. The values of I_D/I_G versus the growth temperatures have been plotted in Figure 4b, showing a decrease of I_D/I_G with the temperature increase. Over the temperature range, the crystallinity of graphitic sheets is better for the CNTs grown on the Fe catalyst than those grown on the Co and Ni catalysts.

4. Discussion

The present results show that the growth rate and the crystallinity of graphitic sheets depend on the catalyst and the growth temperature. Because it is generally agreed that the

TABLE 1: Growth Rate, Diameter, and Degree of Crystallinity of CNTs Grown on Fe, Co, and Ni Catalysts Using Thermal CVD of C_2H_2 at 900, 950, and 1000 °C

	900 °C			950 °C			1000 °C		
catalysts	Fe	Co	Ni	Fe	Co	Ni	Fe	Co	Ni
growth rate (μm/min)	6 ± 1	3 ± 1	3 ± 1	9 ± 1	4 ± 1	5 ± 1	13 ± 3	6 ± 1	6 ± 1
diameter range (nm)	30−100	20−40	30−70	30−150	30−80	30−90	50−180	40−100	50−100
average diameter (nm)	50	30	40	60	60	60	80	80	80
$I_D/I_G{}^a$	0.72	0.79	0.78	0.60	0.72	0.75	0.51	0.53	0.54

^{a} The intensity ratio of D band relative to G band, with an error of 5%.
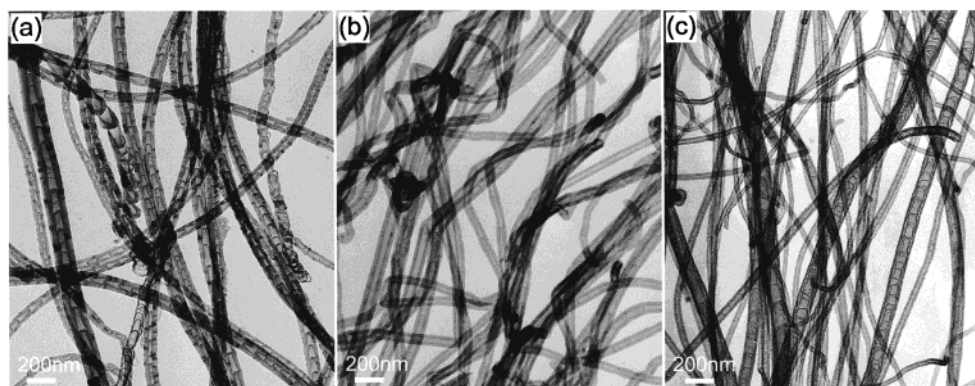
Figure 2. TEM image for the bamboo-like structured CNTs grown on the (a) Fe, (b) Co, and (c) Ni catalysts at 950 °C. The average diameter is about 60 nm.
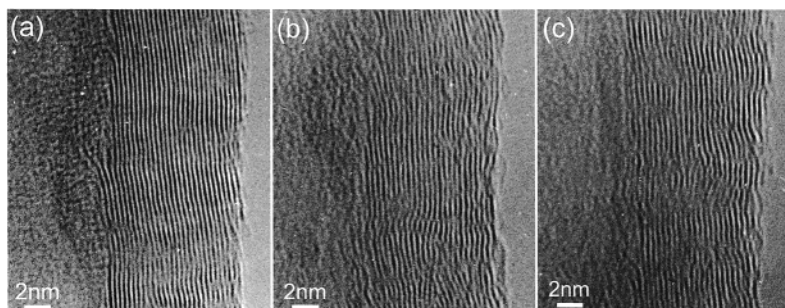
Figure 3. HRTEM images for the typical CNTs grown on the (a) Fe, (b) Co, and (c) Ni catalysts at 950 °C. The CNTs grown on the Fe catalyst exhibit a higher degree of crystallinity compared to those grown on the Co and Ni catalysts.

diffusion of carbons is the rate-determining step in the growth of carbon nanostructures, let us assume that the growth reaction of CNTs is simply a diffusion-controlled reaction. The growth rate of CNTs would be governed by the rate at which the reactants diffuse through the metal. If the growth rate is a pseudo-first-order reaction, the growth rate (v) can be defined as $v = k_d[C]$, where k_d is proportional to the diffusion coefficient of carbons and [C] is the concentration of carbons in bulk metal. The diffusion coefficients of carbons in bulk γ-Fe, Co, and Ni, respectively, are 6.0×10^{-8}, 4.4×10^{-8}, and 9.5×10^{-8} cm^2 s^{-1}, at 900 °C.[18] They increase to 2.0×10^{-7}, 1.5×10^{-7}, and 2.9×10^{-7} cm^2 s^{-1}, respectively, at 1000 °C, by a factor of ~3. The respective diffusion energy of carbon is 35, 37, and 33 kcal/mol. The carbons can be saturated into bulk γ-Fe, Co, and Ni, by an extent of 1.2−1.5, 0.2−0.3, and 0.2−0.3 wt % in the temperature range 900−1000 °C.[19] Fe is a more efficient metal for the carbon saturation than Co and Ni. Suppose that the carbons are saturated in the catalytic particles, the relative ratio of the growth rates would be 8:1:2 at 900 °C and 7:1:2 at 1000 °C, respectively, for Fe, Co, and Ni. Remarkably, Fe exhibits the highest growth rate and Co and Ni show a comparable growth rate relative to Fe, which are consistent with the present result. Furthermore, the growth rate is predicted to enhance approximately by 3−4 times for the temperature

increase from 900 to 1000 °C, which is close to that of the present CNTs. Therefore, it suggests that the growth of CNTs may follow a diffusion-controlled first-order reaction whose rate is proportional to the diffusion coefficient and saturated concentration of carbons in bulk metal.

We assumed that the Fe nanoparticles are in the γ-phase. The γ-phase is thermodynamically more stable than the α-phase at temperatures 900−1000 °C with the dissolved carbons up to 1.2−1.5 wt %.[19] Even if the Fe nanoparticles before the CNT growth were identified as α-Fe using X-ray diffraction analysis, there is a great possibility that the Fe nanoparticles would undergo fast phase transformation into γ-phase during the growth of CNTs. If the Fe nanoparticles were in the α-phase during the CNT growth, the relative growth rates of CNTs grown on Fe, Co, and Ni would be 40:1:2 and 20:1:2 at 900 and 1000 °C, respectively. The diffusion energy of carbons in α-Fe is 19 kcal/mol and the diffusion coefficients are 1.6×10^{-6} and 3.1×10^{-6} cm^2 s^{-1}, at 900 and 1000 °C, respectively.[19] The carbon concentration is assumed to be 0.2−0.3 wt %, which is the same as that of Co and Ni. The relative growth rates are less appropriate to explain the experimental results, compared to those estimated using the α-phase assumption.

It was reported that the growth rate of carbon nanofibers or CNTs has an inverse dependence on the size of catalytic

Carbon Nanotube Growth Dependence on Catalysts

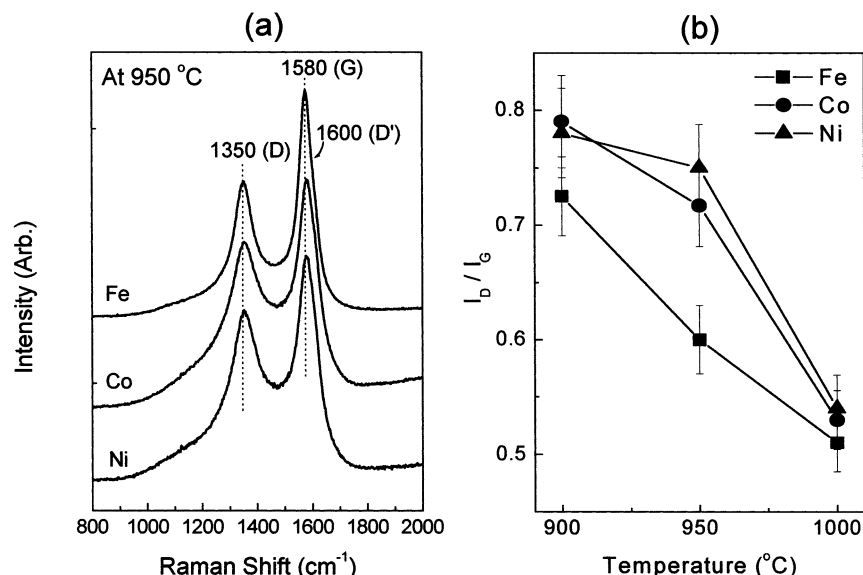*J. Phys. Chem. B, Vol. 106, No. 36, 2002* **9289**

Figure 4. (a) Raman spectrum of the CNTs grown on the Fe, Co, and Ni catalysts at 950 °C. (b) A plot of the I_D/I_G values at three temperatures.

particles.[10,20,21] Because the size of catalytic particles limits the diameter of CNTs, the growth rate may decrease with increasing the diameter of CNTs. Though the average diameters of CNTs are about the same for all three catalysts at a given growth temperature, they increase with the temperature by a factor of 2. If all CNTs were in the same diameter for three temperatures, the enhancement factor of the growth rate for the temperature rise would be higher than 2, which is even closer to the predicted value.

The crystallinity of graphitic sheets has a good correlation with the growth rate, suggesting that the bulk diffusion of carbons also plays an important role in determining the crystallinity of CNTs. As the bulk diffusion rate of carbons increases, the buildup of graphitic sheets would be more successful with less stacking faults, producing a higher degree of crystalline perfection. Here we adopt a base-growth model of the bamboo-like structured CNTs to explain how the growth rate and the crystallinity of graphitic sheets can be established by the bulk diffusion of carbons. The growth mechanism is illustrated in detail elsewhere.[22] The growth process can be basically separated into five steps as follows.

The first step (step 1) is *the formation of the closed tip.* Carbons produced from the decomposition of C_2H_2 adsorb on the catalytic metal particle. Then they diffuse via the surface and bulk of the metal particle to form the multilayered graphitic sheets as a cap on the catalytic particle. As the cap lifts off the catalytic particle, a closed tip with inside hollow is produced. The motive force departing from the catalytic particle may be the stress accumulated under the graphitic cap.[23] The size of catalytic particles confines the diameter of the growing tube. The second step (step 2) is *the growth of the wall.* The multilayered graphitic sheets are now continuously grown toward the vertical direction, forming the wall. All multilayers of graphitic sheets would grow simultaneously. The inside graphitic sheets can be formed mainly by the supply of carbons from the bulk. The third step (step 3) is *the production of the compartment layer.* The carbons accumulated at the inside surface of the catalytic particle, probably mainly via bulk diffusion, can form the graphitic sheets on the catalytic particles as in the step 1. The fourth step (step 4) is *the formation of the joint between compartment layer and wall.* When the compartment graphitic sheets are grown fully under the hollow cap, they join with the graphitic sheets of the wall. The wall and

compartment layers would grow at the same rate and eventually depart from the catalytic particle due to the stress. The fifth step (step 5) is *the production of bamboo-like structure owing to the compartment layers.* Whereas the wall grows upward, the next compartment layer is produced on the catalytic particle and will be combined again with the wall. The periodic connection of the compartment layers with the wall yields the bamboo-like structure.

If the bulk diffusion rate of carbons were lower than that of surface diffusion, the rate-determining step involves the formation of graphitic sheets via the carbon supply from the bulk. Because the multilayers of graphitic sheets probably grow simultaneously, the growth rate of the inside graphitic sheets of the wall (in step 2) and that of the compartment layers (in step 4) would determine the growth rate of the wall toward the vertical direction. This rate-determining step would be the diffusion-controlled first-order reaction, as we assumed above.

Recently, Anderson and Rodriguez reported that the carbon nanofibers generated from a silica-supported Fe catalyst with an ethylene:hydrogen 4:1 mixture at 600 °C exhibit a high degree of crystalline perfection whereas the structure of those grown from the Co catalyst system were almost amorphous.[24] Their result agrees with the present work. It was proposed that the crystallographic features of catalytic metal faces would determine the stacking arrangement of graphitic sheets and the crystallinity of carbon nanofibers.[25] The SEM images were measured for the crystallographic feature of the nanoparticles after the NH_3 pretreatments, showing all smooth polygonal faces without any particular difference for the three catalysts. All CNTs are vertically aligned and exhibit the bamboo-like structure irrespective of the catalysts. Further studies may be therefore necessary to find a possibility that the crystallographic characteristics of catalytic particles influence the structure and crystallinity of CNTs.

5. Conclusion

We have examined the growth properties of vertically aligned multiwalled CNTs grown on the alumina substrates for three catalysts, i.e., Fe, Co, and Ni nanoparticles. The catalytic nanoparticles were formed by the coating of the substrates with metal chloride film, followed by NH_3 pretreatment. The CNTs were synthesized using thermal CVD of C_2H_2 at 900, 950, and

Kim et al.

1000 °C. The growth rate of CNTs on the Fe catalyst is about 2 times higher than those grown on the Co and Ni catalysts over the temperature range 900−1000 °C. As the temperature increases from 900 to 1000 °C, the growth rate enhances approximately by a factor of 2 for all catalysts. The bamboo-like structured multiwalled CNTs are exclusively produced irrespective to the catalyst. The HRTEM images and Raman spectra reveal consistently that the crystallinity of CNTs grown on the Fe catalyst is better than that of the CNTs grown on the Co and Ni catalysts. The growth rate and the degree of the crystalline perfection of graphitic sheets are in good correlation. The results can be suitably explained by the assumption that the rate-determining step of the CNT growth is a diffusion-controlled first-order reaction whose rate is proportional to the diffusion coefficient and saturated concentration of carbons in bulk metal. We explained how the bulk diffusion rate of carbons would determine the growth rate and crystallinity of the bamboo-like structured CNTs by adopting the base-growth model.

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