Controlled growth of Carbon Nanotubes using thermal CVD

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Abstract

Vertically aligned CNTs were grown on Fe-deposited SiO_2 substrates using thermal CVD of acetylene gas. The size of Fe particle is controlled by the flow rate of NH_3 and pretreatment time, which leads to control the diameter of CNTs. As the diameter of CNTs decreases, the growth rate is enhanced with an inverse dependence of the CNT diameter. The growth rate of CNTs increases linearly as the growth time increases until 30 min but is rapidly decreased over 40 min. We found an inverse relation between the diameter and growth rate of carbon nanotubes. As the diameter of CNTs increases, the compartment layers of bamboo-shaped CNTs appear more frequently. A base-growth model is suitable to explain the dependence of growth rate and structure of CNTs on the diameter size of catalytic particles.

1. Introduction

Carbon nanotubes (CNTs), since its first discovery in 1991 [1], have been considered for many potential technological applications because of its extraordinary electrical and mechanical properties. The CVD method has attracted much attention because of the advantage that the growth of CNTs can be achieved with high purity, high yield, and vertical alignment. The growth of vertically aligned CNTs in a controlled manner is necessary for many applications. A number of research groups reported that the diameter of CNTs is controllable by the size of catalytic particle which can be varied with the growth parameters of CVD, *i. e.* plasma intensity, thickness of catalyst film, composition of precursors, *etc* [2-6]. Ren *et al.* announced that the diameter of CNTs depends on the catalyst particle size [7]. They controlled the catalyst particle size by changing the thickness of stainless steel film. However, not much systematic diameter-control has been demonstrated for thermal CVD growth of CNTs.

In this work, we report a controlled growth of vertically aligned CNTs using thermal CVD of acetylene (C_2H_2) gas at 950 °C. We suggest that the diameter, growth rate, and structure of CNTs can be easily controlled by changing the diameter of catalyst particles.

2. Experimental

A 50 nm-thick Fe film was thermally deposited on a SiO_2 layer using a thermal evaporator under a pressure of 10^{-6} Torr. The Fe-deposited SiO_2 substrates were loaded with face down direction on a quartz boat in CVD reactor. Argon (Ar) gas was flowed into the CVD reactor in order to prevent the oxidation of Fe while raising the temperature. The Fe-deposited SiO_2 substrates were pretreated by NH_3 gas with a flow rate in the range 100-300 sccm for 20-240 min at 950 °C, in order to form the Fe particles in nanometer size [8]. C_2H_2 gas was supplied with a flow rate of 30 sccm for 3-30 min at 950 °C to grow the CNTs. The Fe particles and CNTs were examined by a scanning electron microscope (SEM) (Hitachi S-800, 30 kV). A transmission electron microscope (TEM) (Philips, CM20T, 200kV) was used to investigate the structure of CNTs.

3. Results and Discussion

Fig. 1 shows SEM micrographs for vertically aligned CNTs grown on Fe-deposited SiO_2 substrate. The C_2H_2 gas for CNT growth is fixed to the flow rate of 30 sccm for 10 min at 950 °C but the NH_3 pretreatment condition is changed to manipulate the size of Fe catalytic particles. Fig. 1(a) and Fig. 1(d) are SEM micrographs of vertically aligned CNTs grown on the Fe particles. The flow rate of NH_3 gas is 100 sccm for 20 min. We measured the size and the

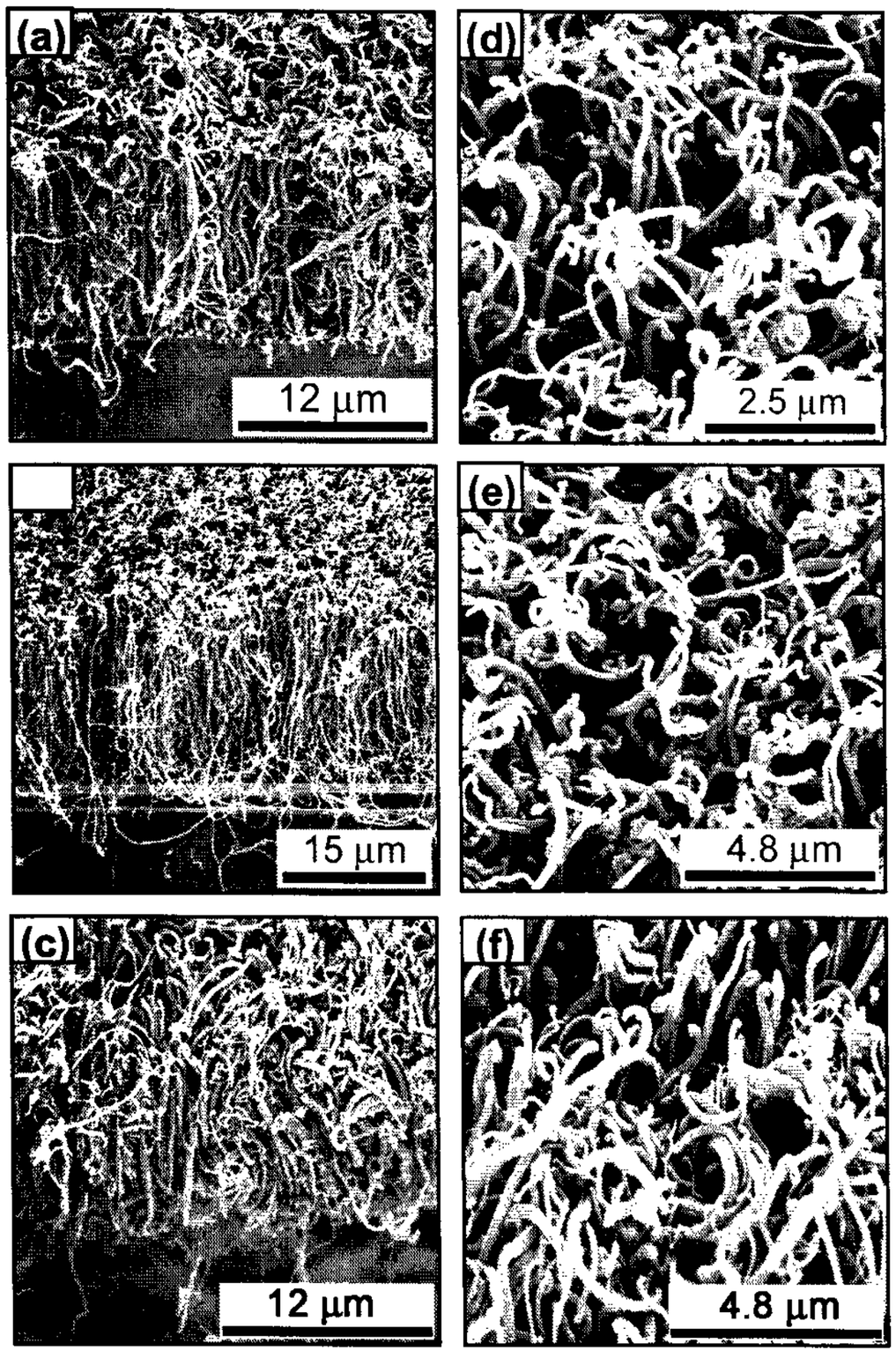

Figure 1 SEM micrographs for vertically aligned CNTs grown on Fe-deposited SiO_2 substrate. The C_2H_2 gas for CNT growth is fixed to the flow rate of 30 sccm for 10 min. The flow rate of NH3 gas is (a) 100 sccm for 20 min, (b) 300 sccm for 120 min, (c) 300 sccm for 240 min, and (d), (e), (f) are the top view of (a), (b), (c) respectively

density of catalytic particles before the CNT growth.

The average size of Fe particles is about 200 nm and their density is about $2\times10^9/cm^2$. As shown in Fig. 1(a), the high density CNTs with a length about 12 μm are vertically grown on a large area substrate. Fig. 1(d) shows that the average diameter of CNTs is 130 nm, which is in a narrower range than that of catalytic particles. Fig. 1(b) and Fig. 1(e) are SEM micrographs for the vertically aligned CNTs grown on the Fe particles in which the flow rate of NH_3 gas is 300 sccm for 120 min. In this condition, the Fe particles with an average diameter of 130 nm are formed with a density of $\sim4\times10^9/cm^2$. The NH_3 pretreatment with a higher flow rate and a longer time etches efficiently

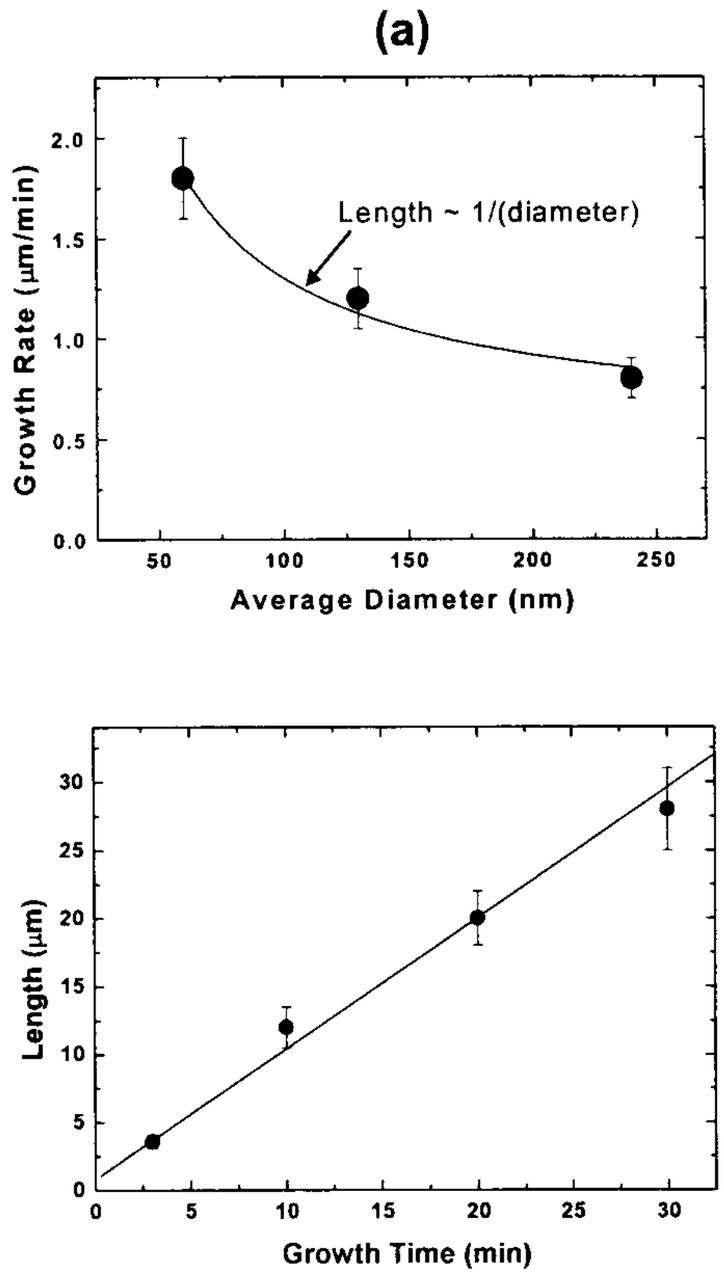

Figure 2 Dependence of CNT growth on the average diameters and growth time. (a) The growth rate of CNTs as a function of average diameter. The data points are fitted by an inverse function of average diameter as shown as a curve. (b) The length vs. the growth time for the CNTs with a diameter of 130 nm.

Fe catalyst, resulting in the smaller size Fe particles. Highly purified CNTs with a length about 18 μm are distributed on the substrate and the average diameter of CNTs is about 60 nm. Fig. 1(c) and 1(f) are SEM micrographs for the vertically aligned CNTs grown on the Fe particles. The flow rate of NH_3 gas is of 300 sccm for 240 min. When the NH_3 pretreatment is carries out using a flow rate of 300 sccm for 240 min, the average size of Fe particles becomes approximately 400 nm and the density is about $1\times10^9/cm^2$. The longer pretreatment time results in the larger catalytic particles due to the agglomeration of catalytic particles. The length of CNTs is 8 μm and the average diameter of CNTs is about 240 nm. The growth conditions of CNTs and the results are listed in Table 1. It shows that the size of Fe particles is controlled by the NH_3 flow rate and pretreatment time, which determines the diameter of CNTs. As the average diameter of CNTs increases from 60 nm to 240 nm, the length decreases from 18 μm to 8 μm, corresponding to 2.3 times decrease.

Number of experimental runs	NH_3		C_2H_2		Average Fe particle diameter (nm)	Average CNT diameter (nm)	CNT length (μm)	Growth rate (μm/min)
	Flow rate (sccm)	Time (min)	Flow rate (sccm)	Time (min)				
4	100	20	30	10	200	130	12	1.2
3	300	120	30	10	130	60	18	1.8
2	300	240	30	10	400	240	8	0.8
2	100	20	30	3	200	130	3.6	1.2
2	100	20	30	20	200	130	20	1
2	100	20	30	30	200	130	28	0.9

Table 1 The average diameter and growth rate of CNTs depending on the growth condition.

Fig. 2(a) is a plot of the growth rate of CNTs as a function of average diameter. The average growth rates are 1.8, 1.2, and 0.8 μm/min for the average diameters 60, 130, and 240 nm, respectively. The growth rate can be fitted by an inverse function of average diameter as shown as a curve. Recently, Bower *et al.* reported that the growth rate is inversely proportional to the nanotube diameter for the CNTs grown on cobalt (Co) catalyst using microwave plasma-enhanced CVD [4], which is consistent with our results. Choi *et al.* showed that the growth rate of CNTs increases with decreasing the size of catalytic particles for microwave plasma-enhanced CVD [3]. Baker reported that the growth rate of carbon filaments has an inverse of square root dependence with particle size [9]. As some of workers pointed out [3,9], it could imply that the diffusion of carbons is mainly operative in the growth of CNTs. As the size of particles decreases, the diffusion time for carbons to arrive at the growth site would become short, resulting in an accelerating the growth rate of CNTs. We measured the length of CNTs as a function of growth time. The experimental data are listed in Table 1 for the CNTs with an averaged diameter of 130 nm. Fig. 2(b) displays the length vs. the growth time for the CNTs with a diameter of 130 nm. The length of CNTs increases linearly with the growth time during 30 min, indicating that the growth rate is about constant. We observed that the growth rate decreases significantly over 40 min because carbon atoms can not be adsorbed to the surface of Fe particles due to the carbonaceous particles covering the surface of Fe particles.

Fig. 3(a) is the TEM image showing that all CNTs have bamboo-like structure. The tip of CNTs are closed and free of the encapsulated catalytic particles and compartment layers are directed toward the tips. Catalytic particles which are attached to the root of CNTs are separated during the ultrasonic treatment in acetone. The inset in Fig. 3(a) shows that high-resolution TEM image, revealing that graphite sheets have a good crystallinity without defects. We also found that the diameter of CNTs is strongly correlated to the size of Fe catalytic particle. Fig. 3(b) shows that the compartment layers of bamboo-shaped CNTs appear at a longer distance as the diameter of CNT decreases (see arrows ① and ②). The base-growth mechanism can be adopted to explain our experimental results in which the growth of CNTs depend on the diameter of catalytic particles [10-12]. Carbons generated from the decomposition of C_2H_2 diffuse into the catalytic particles and then form the graphitic sheets on the surface of catalytic particle. The accumulation of carbons at the inside surface of catalytic particle occurs probably mainly via bulk diffusion, which produces a compartment layer. If the carbons are regularly supplied to the catalytic particles, the growth rate would be constant and thus the compartment layers of CNTs can also appear periodically. The size of catalytic particle limits the diameter of growing tube. When the size of catalytic particles is smaller, the diameter of CNTs becomes narrower and the growth rate increases proportional to the inverse of CNT diameter. The increased growth rate of CNTs on the smaller catalytic particle may be due to a reduced arrival time of carbons at the growth site. As the growth rate increases, the compartment layers of CNTs would take place less frequently.

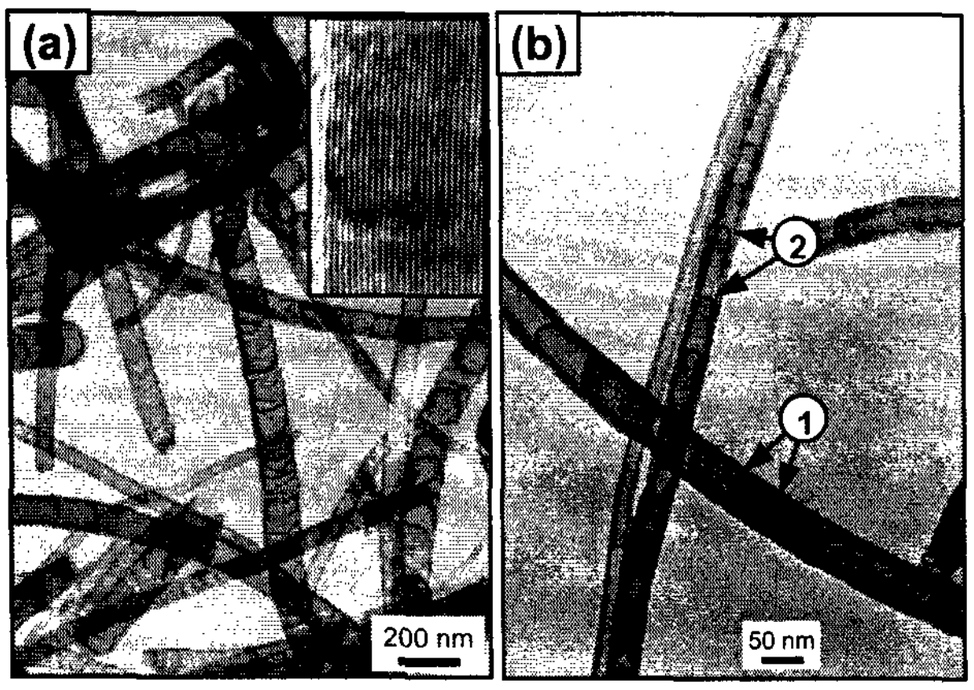

Figure 3 TEM images showing that all CNTs have bamboo-shaped structure. (a) TEM image for bamboo-like structured CNTs, revealing the closed tips without encapsulated Fe particles and compartment layers with a curvature directed toward the tip. The inset in

4. Conclusion

we have grown the vertically aligned CNTs on Fe-deposited SiO_2 substrates using thermal CVD of acetylene gas at 950 °C. The size of Fe particle is controlled by the flow rate of NH_3 gas and pretreatment time, which leads to control the diameter of CNTs. The size of catalytic particle limits the diameter of CNTs. As the diameter of CNTs decreases, the growth rate is enhanced with an inverse dependence of CNT diameter. The growth rate of CNTs increases linearly as the growth time increases until 30 min but rapidly decreased over 40 min. As the diameter of CNTs increases, the compartment layers of bamboo-shaped CNTs appear in more frequent period. Base-growth model is suitable to explain the dependence of growth rate and structure of CNTs on the diameter size of catalytic particles.

5. Acknowledgnents

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