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Synthesis of bamboo-shaped multiwalled carbon nanotubes using thermal chemical vapor deposition

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Abstract

The vertically aligned multiwalled carbon nanotubes (CNT) are synthesized in high density on a large area of cobalt deposited silicon oxide substrate, by thermal chemical vapor deposition using C_2H_2 gas, at 950°C. The diameter of CNTs is distributed in the range of 80–120 nm and the length is about 20 μm. High-resolution transmission electron microscopy analysis reveals that the multiwalled CNTs have the crystalline graphite sheets and the bamboo structure that the tube consists of hollow compartments separated with graphite layers. A possible growth mechanism is suggested to explain the structure of CNTs. The emission current density is 1.1 mA cm^{-2} at 4.5 V μm^{-1}, showing the Fowler–Nordheim behavior.

1. Introduction

Since the first observation of carbon nanotubes (CNT) [1], extensive researches have focused on the synthesis of CNTs with high purity. Various synthetic methods such as arc discharge [2–4], laser vaporization [5,6], pyrolysis [7], and plasma-enhanced or thermal chemical vapor deposition (CVD) [8–15] were employed. Synthesis of well-aligned CNTs on a large area is necessary for one of various applications, electron emitter of field emission displays. The arc discharge and the laser vaporization techniques can produce the large amount of CNTs, but it is very difficult to control the alignment and size [4,5]. These techniques also require purification process to separate pure CNTs from other particles. Many research groups have employed the CVD method for the purpose of large scaled production of CNTs [8–15]. It is shown that the CVD technique can synthesize the CNTs with high purity, high yield, selective growth, and good vertical alignment.

In this Letter, we report the vertically aligned multiwalled CNT growth on a large area of silicon oxide (SiO_2) substrate by using thermal CVD method. The surface of catalytic cobalt (Co) film deposited on the SiO_2 substrate is modified by wet hydrogen fluoride (HF) and/or subsequent ammonia (NH_3) gas etchings. Acetylene (C_2H_2) gas was used to grow CNTs. Our research group has reported the growth of CNTs on cobalt–nickel (Co–Ni) alloy [12,13], Co [14], and Ni [14,15] deposited SiO_2 substrates by using thermal CVD method. Here, we extend the work to synthesize the CNTs on pure Co deposited SiO_2 substrate. Despite many successful syntheses, the growth mechanism is still not com-

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pletely understood. Therefore, we discuss a possible mechanism for the CNT growth.

2. Experimental

The 20×30 mm size p-type Si (100) substrates with a resistivity of 15 Ω cm were thermally oxidized. The thickness of the SiO_2 layer was estimated as approximately 300 nm. The Co metal was thermally deposited on the SiO_2 layers under a vacuum of 10^{-6} Torr. The samples were dipped in a diluted HF solution for 100–200 s, and then loaded on a quartz boat. Argon (Ar) gas was flowed into the quartz CVD reactor in order to prevent the oxidation of catalytic metal while raising the temperature. Samples were pretreated at the temperature range of 750–950°C, by NH_3 gas with a flow rate of 50–200 sccm, for 10–30 min. The CNTs were grown using C_2H_2 gas, with a flow rate of 20–80 sccm, for 10–20 min at the same temperature range. The reactor was cooled down slowly to the room temperature (25°C) under Ar ambient after the growth. The grown CNTs on SiO_2 substrate were examined by a scanning electron microscope (SEM) (Hitachi S-800, 30 kV), to measure the length, the diameter, the alignment, and the uniformity. High-resolution transmission electron microscope (TEM) (Philips, CM20T, 200 kV) was used to determine the wall structure of individual CNT. A Raman spectrometer (Renishaw micro-Raman 2000) was also used to evaluate the structure and crystallinity. Field emission measurement was conducted in a vacuum chamber (1×10^{-6} Torr). A positive voltage was applied to the anode and the emission current was measured with an electrometer (Keithley 619).

3. Results and discussion

Fig. 1a–c are the SEM micrographs of the vertically aligned CNTs grown on a Co deposited SiO_2 substrate. The NH_3 and C_2H_2 gases flow with a rate of 100 sccm for 30 min and 40 sccm for 10 min, respectively, at 950°C. Fig. 1a shows well aligned CNTs on the substrate. The CNTs are oriented vertically to the substrate and in uniform length of about 20 μm. Fig. 1b reveals that the CNTs are grown with high density. Top view of the vertically aligned CNTs is shown in Fig. 1c, showing that their diameters are distributed in the range of 80–120 nm. The CNTs have very clean surface, and most of them have a curved tip. Fig. 1d is the surface morphology of the Co deposited SiO_2 substrate after the NH_3 pretreatment, showing that the diameter of catalytic particles is in similar range as that of CNTs.

TEM analysis was performed on the CNTs to determine the wall structure. Using the ultrasonic treatment in acetone, the CNTs were separated from the substrate, and then dispersed on a carbon TEM microgrid. The TEM image in Fig. 2a shows the multiwalled CNTs in various diameters. An important feature is that the tube consists of the hollow compartments, looking like the bamboo. The inside of CNT is hollowed without any catalytic particles and the root is opened. As the diameter of CNT increases, the separation layers appear at the shorter distance. Fig. 2b is the high-resolution TEM image for a bamboo-shaped CNT. The outer diameter is 80 nm and inner diameter is about 50 nm. The hollowed compartments are spaced at nearly equal separation of 100 nm, with conical shaped graphite layers whose curvature is directed to the root of CNT. Fig. 2c is high-resolution TEM image for tip part of a narrow bamboo-shaped CNT. The sharp fringe of the walls indicates good crystallinity of graphite sheets. However, the inner and outer walls are in defective crystalline structure. Fig. 2d shows high-resolution TEM image for the joint part of graphite sheets in a bamboo-shaped CNT. Noticed that the multiwalls are curved, which is different from those of Fig. 2b,c. The defects of crystallinity can be seen at the joint area of graphite sheets.

Fig. 3 is the micro-Raman spectrum for the CNTs grown on SiO_2 substrate. The excitation laser is a 632.8 nm He–Ne laser. The multiwall structure of CNTs is identified by a clear G-line at 1571.9 cm^{-1} with a small bump at 1604.2 cm^{-1} [16,17]. There is no second order peak at ~ 1720 cm^{-1}. The breathing mode peak at 190.5 cm^{-1} [18] is significantly diminished, confirming the multiwall structure of CNTs. The peak at 1318.0 cm^{-1} could be resulted from the defective outer graphite sheets of multiwalled CNTs [19]. We noticed that the relative intensity of 1571.9 cm^{-1} peak (G-line) to 1318.0 cm^{-1} peak is larger than that of the previous work [12,14],

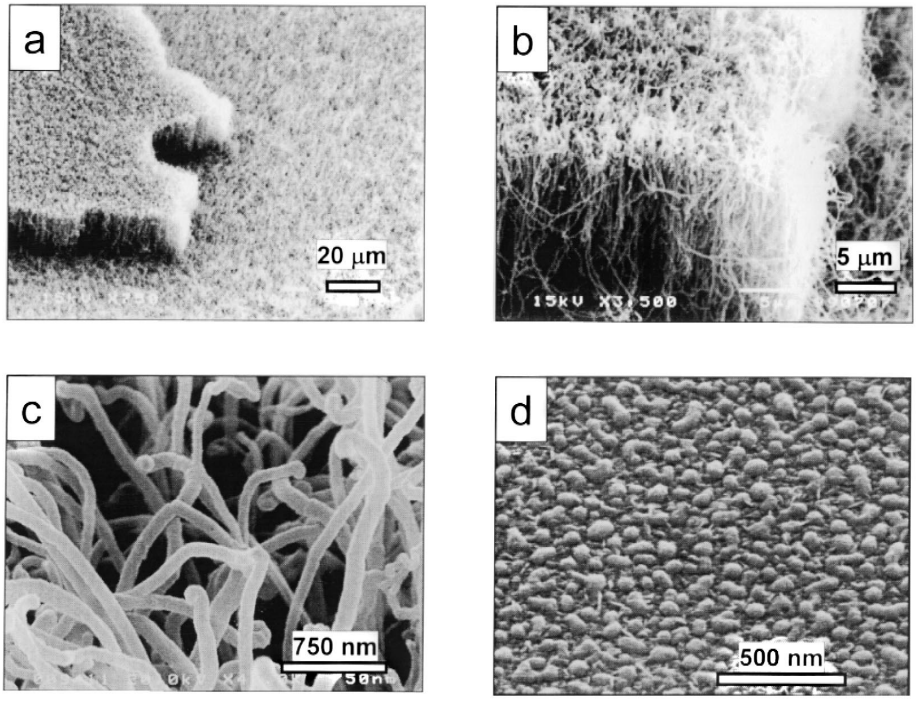

Fig. 1. SEM micrographs of well aligned CNTs grown on a large area (20×30 mm) of Co deposited SiO_2 substrate, under the condition that the C_2H_2 gas flows with the rate 40 sccm for 10 min at 950°C. The Co metal layers were pretreated at 950°C, by NH_3 gas with a flow rate of 200 sccm, for 30 min. The edges are peeled off in order to visualize the alignment of CNTs. (a) Uniformly distributed morphology of vertically aligned CNTs with the length of about 20 μm. (b) The magnified side view of (a), showing high density. (c) Top view of the vertically aligned CNTs, showing that the diameter is in the range of 80–120 nm. (d) The surface morphology of the Co deposited SiO_2 substrate after the NH_3 pretreatment, showing that the diameter of catalytic particles is in similar range as that of CNTs.

indicating that the crystallinity of the graphite sheets increases. Therefore, the Raman spectrum analysis provides definite evidence that the CNTs have multiwalls with good crystallinity and there are some defects on the wall surface.

We have already reported that the NH_3 pretreatment is very crucial step to obtain high density of nucleation sites [12–15]. The NH_3 pretreatment etches the surface of catalytic metal, which results in catalytic metal particles acting as the nucleation seeds for the growth of CNTs. The size of catalytic particle determines the diameter of CNTs [9–15], which is confirmed by the SEM micrographs of Fig. 1c,d.

In this work, we have successfully synthesized the vertically well-aligned CNTs on pure Co deposited SiO_2 substrate. The diameter of CNTs is distributed in the range of 80–120 nm and the length is about 20 μm. The multiwalled CNTs have the bamboo structure with good crystalline graphite sheets, which the hollow compartments are separated with the graphite layers. It has been known that Co–Ni bimetal catalyst is more efficient than monometal catalyst in arc discharge synthesis of CNTs [6]. This work shows that the thermal CVD synthesis of vertically aligned CNTs on the Co catalyst is efficient as much as that on the Co–Ni alloy catalyst [13], an independence of the Ni composition. Bamboo structure was found from the multiwalled CNTs produced by arc discharge [20]. It is quite remarkable that the bamboo-shaped CNTs are grown by thermal CVD method.

In one of our previous works, the tip growth model was suggested to explain the SEM images of CNTs [12]. Here, we can identify the structure of CNTs by TEM image analysis. The hollow tip with-

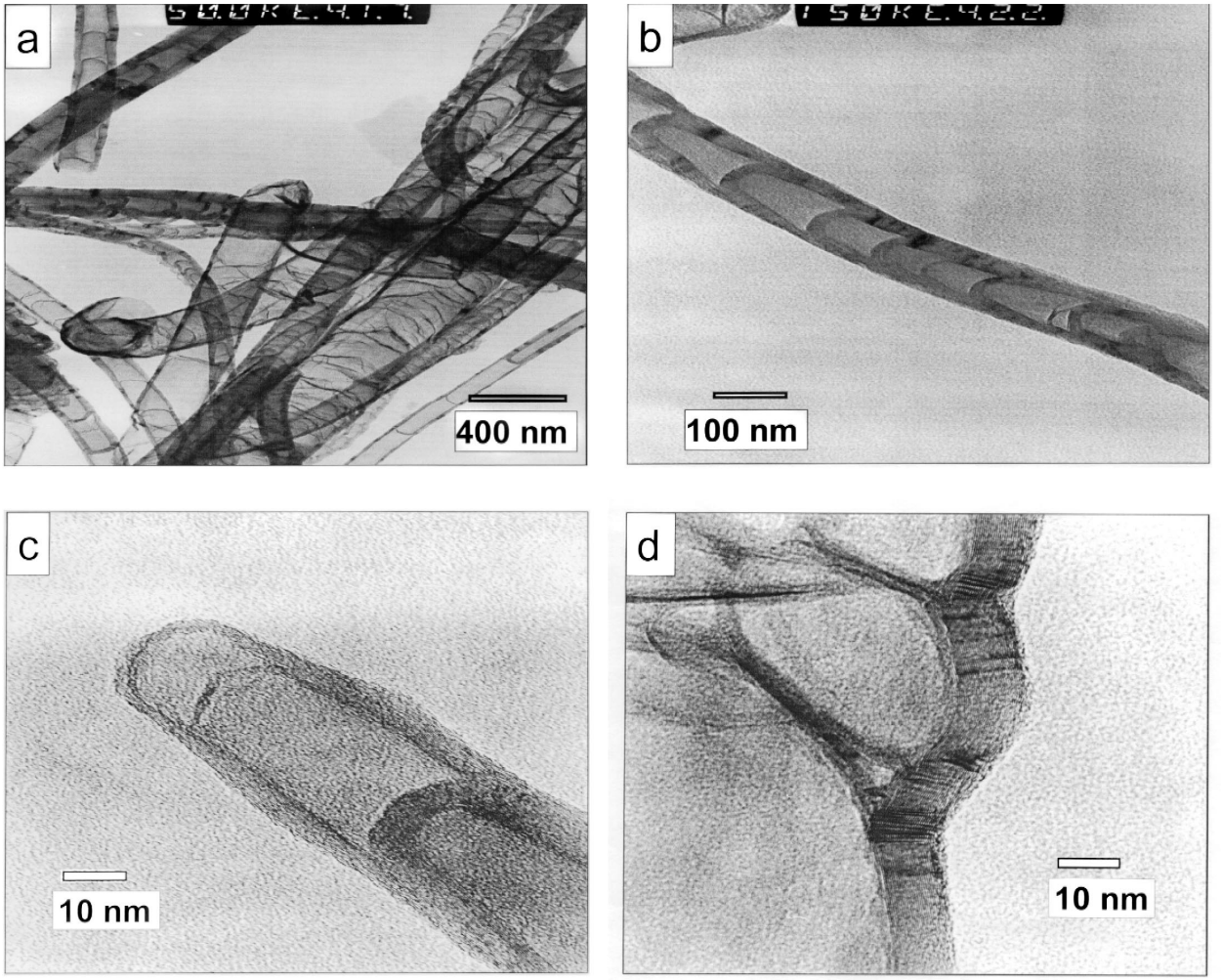

Fig. 2. (a) TEM image of CNTs dispersed on a grid after stripping from the SiO_2 substrate, showing the bamboo structure that the hollow tube consists of compartments. (b) High-resolution TEM image for a bamboo-shaped multiwalled CNT. The outer and inner diameters are about 80 and 50 nm, respectively. The central hollow is segment at about 100 nm by the conical shaped graphite layers whose curvatures are directed to the root of CNT. (c) High-resolution TEM image for tip part of a narrow bamboo-shaped CNT. (d) High-resolution TEM image for the joint part of graphite sheets in a bamboo-shaped CNT.

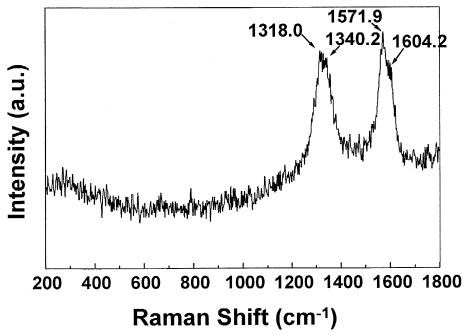

Fig. 3. Micro-Raman spectrum for the vertically aligned CNTs grown on the Co deposited SiO_2 substrate.

out any catalytic particles, as seen from Fig. 2a and c, is inconsistent with the tip growth model. When the plasma-enhanced CVD method was used for the CNT synthesis, the catalytic particles usually remain at the tip of CNTs [7–9], which was justified by the tip growth model. Therefore, in order to explain the hollow tip of CNTs as well as the bamboo structure, the base growth model would be rather suitable.

In the growth reaction of CNTs, the diffusion of carbon in the catalyst metal has been believed to be the rate-determining step. The growth rate of CNTs can be described by an Arrhenius equation that the activation energy is the diffusion energy of carbon in the metal. Support for this diffusion model comes from experiments on the kinetics of growth of CNTs on the γ-Fe metal from acetylene at 1000°C, yielding the activation energy of 142 kJ mol^{-1} [21], which is close to the activation energy for diffusion, 148 kJ mol^{-1} [22].

The carbon radicals formed from the C_2H_2 decomposition are adsorbed on the catalytic particles, initiating the aggregation of carbons. Since the graphite formation reaction of carbons is exothermic, there must be a temperature rise at the reaction zone. The solubility of carbon in a metal is temperature dependent, thus more carbons are accumulated at hot reaction zone. The catalytic particle could be at the eutectic point of Co/carbon (2.65%), 1321°C [23]. The surface and bulk diffusions of carbons allows the CNT to grow continuously. In particular, the carbons accumulated underneath the cross-section of CNT, mainly via bulk diffusion, probably form the graphite sheet that appears as the separation layer of compartments. As a result, the CNT will be grown with the bamboo structure.

Assuming that the catalytic particle is a sphere, as the size of catalytic particle decreases the ratio of surface area to volume would increase rapidly. Therefore, it is expected that the surface diffusion of carbons becomes dominant to the bulk diffusion. Since the separation layers are grown mainly by the bulk diffusion of carbons, its rate decreases significantly as the particle size decreases. Consequently, the separation layers appear at longer distance, which is consistent with our result.

It is noticed that the shape of compartment layers are dependent on the catalytic species. The conical shaped thick compartment layers are frequently found in the CNTs grown on the Co catalytic particles (Fig. 2b,c). In contrast, the conical shaped or thick compartments were never observed from the CNTs grown on the Ni catalytic particles [15]. The diffusion energy of carbon in Co and Ni metals is ~152 kJ mol^{-1} at 450–1400°C and 137.3 kJ mol^{-1} at 600–1400°C, respectively [22]. Therefore, the growth rate of CNTs on the Ni metal is expected to be faster than that on Co metal. We could confirmed that the total length of CNTs grown on the Co metal is shorter than that of Ni the metal, 50 μm [15], when the same flow rate of C_2H_2 has been used at the same growth temperature for same growth time. In the case of Ni metal, the eutectic point of Ni/carbon (2.0%) is 1326°C [23], showing less carbon composi-

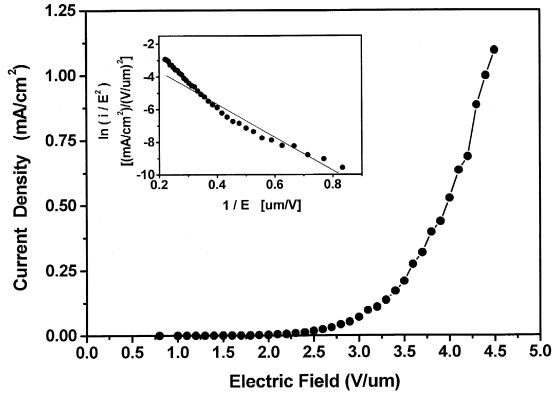

Fig. 4. Field emission current density vs. the electric field, for the vertically aligned CNTs on the Co deposited SiO_2 substrate. The inset shows the Fowler–Nordheim plot.

tion than that of Co metal at similar eutectic points. The diffusion coefficient of carbon in Co metal has been reported to be 0.0872 cm^{-2} s^{-1} at 450–800°C and 0.31 cm^{-2} s^{-1} at 800–1400°C [22]. The diffusion coefficient of carbon in Ni metal is 0.12 cm^{-2} s^{-1} at 600–1400°C [22], which is less than that of Co metal at 800–1400°C. From these data, we can expect that more carbons would dissolve and accumulate in the Co catalytic particles than Ni particles. While the growth rate of CNTs is slower in Co metal, the more accumulation of carbons occurs, which results in thicker compartment layers compared to that of Ni metal. More detailed growth mechanism will be described in a following paper.

Fig. 4 shows the plot of the field emission current density versus the electric field, for the CNTs grown on the Co deposited SiO_2 substrate. The anode was separated from the CNTs by a 200 μm spacer. The chamber was maintained at 1×10^{-6} Torr. The turn-on voltage is about 0.8 V μm^{-1} with the current density of 0.1 μA cm^{-2}, which is much lower than that of previous work [11], 1.2 V μm^{-1} with 5 nA cm^{-2}. The maximum emission current density before the electrical breakdown is about 1.1 mA cm^{-2} at 4.5 V μm^{-1}. The inset of Fig. 4 shows a nearly linear plot, indicating that the emission current of CNTs follows the Fowler–Nordheim behavior. The electrical properties are almost same as those of CNTs grown on Co–Ni alloy catalyst [13]. The vertically aligned CNTs grown on the Co deposited SiO_2 substrate using thermal CVD method possess the excellent emission property which is sufficient for the electron emitter of field emission displays.

In summary, we have grown the vertically well aligned multiwalled CNTs on a large area of Co deposited SiO_2 substrates using the thermal CVD method. The diameter of CNTs is 80–120 nm and the length is about 20 μm. The multiwalled CNTs have the hollow tip and the bamboo structure that the hollow compartments are separated with the graphite layers. The multiwalls are in good crystalline phase. The base growth mechanism is suitable for the CNTs grown by thermal CVD. We suggest that surface and bulk diffusions of carbons play an important role in determining the structure of CNTs. The maximum emission current density before the electrical breakdown is about 1.1 mA cm^{-2} at 4.5 V μm^{-1} and the emission current follows the Fowler–Nordheim behavior. The vertically aligned CNTs grown on the Co deposited substrate can be practically applicable to the electron emitter of field emission displays.

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