Growth and structure of carbon nanotubes produced by thermal chemical vapor deposition

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Abstract

Vertically aligned carbon nanotubes are synthesized with high density on a large area of cobalt-deposited silicon oxide substrate by thermal chemical vapor deposition of acetylene at 950°C. The diameters of the carbon nanotubes are distributed in the range 80–120 nm and the length is about 20 μm. The carbon nanotubes have a bamboo-like structure in which the curvature of the compartment is oriented to the tip. The tips are closed and free of encapsulated catalytic particles. The emission current density is 1.1 mA/cm\textsuperscript{2} at an applied field of about 4.5 V/μm, following the Fowler–Nordheim behavior.

Keywords: A. Carbon nanotubes

1. Introduction

Carbon nanotubes (CNTs) have been considered for many different technological applications, e.g. field emission displays (FEDs) [1,2], hydrogen storage [3], chemical sensors [4] etc. Using CNTs as field emitters in the flat panel display is one of the most promising applications because of their unusual high aspect ratio, mechanical and chemical stability, and good conductance. The synthesis of vertically aligned CNTs on a large area substrate is of importance for applications to FEDs. Various synthetic methods such as arc discharge [5–7], laser vaporization [8], pyrolysis [9], plasma-enhanced and thermal chemical vapor deposition (CVD) [10–12] etc. have been developed. The CVD method is superior to other methods in respect to purity, yield, and controlled alignment, thus current attention has focused on developing new techniques for the preparation of vertically aligned CNTs using CVD method.

In this work, we report a growth of the vertically well-aligned CNTs on a large area of cobalt (Co) deposited silicon oxide (SiO\textsubscript{2}) substrate by thermal CVD of acetylene (C\textsubscript{2}H\textsubscript{2}). Before growing CNTs, the nanometer-sized Co catalytic particles are formed by wet hydrogen fluoride (HF) and subsequent ammonia (NH\textsubscript{3}) gas etchings of the deposited Co film, which is a crucial step to control the size and the vertical alignment of CNTs [13]. We investigate the structure of CNTs using scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. Field emission from the as-grown CNTs is examined.

2. Experimental section

The 20 mm×30 mm size p-type Si (100) substrates with a resistivity of 15 Ω cm were thermally oxidized. The thickness of the silicon oxide (SiO\textsubscript{2}) layer was estimated as ~300 nm. A 200-nm-thick Co film was thermally deposited on the SiO\textsubscript{2} layer under a pressure of 10\textsuperscript{−6} Torr. The Co-deposited SiO\textsubscript{2} substrates were dipped in a diluted HF solution for 100–200 s, and then loaded on a quartz boat in the CVD reactor. The substrates were pretreated by NH\textsubscript{3} gas with a flow rate of 50–200 sccm for 10–30 min at 950°C. The CNTs were grown using C\textsubscript{2}H\textsubscript{2} gas with a flow rate of 20–80 sccm for 10–20 min at the same temperature. Ar gas flowed into the CVD reactor while raising and lowering the temperature.

The CNTs grown on Co-deposited SiO\textsubscript{2} substrate were examined by a scanning electron microscope (SEM) (Hitachi S-800, 30 kV), to measure the length, diameter,
and alignment. A transmission electron microscope (TEM) (Philips, CM20T, 200 kV) was used to determine the structure of CNTs. The CNTs were separated from the substrate using ultrasonic treatment in acetone solution and then dispersed on a carbon TEM microgrid. A Raman spectrometer (Renishaw micro-Raman 2000) was also used to evaluate the structure and crystallinity of CNTs.

Field emission measurement was conducted for as-grown CNTs under a pressure of $1 \times 10^{-6}$ Torr. The emission current versus the applied voltage was measured using a diode-type structure with an electrometer (Keithley 619). A 200-nm-thick Ti film as a cathode layer was thermally deposited on the SiO$_2$ substrate, followed by the deposition of catalytic Co film. The vertically aligned CNTs were grown on Co-deposited Ti/SiO$_2$ substrate. Indium tin oxide (ITO) was used as an anode for an applied voltage. The distance between the anode and the CNT tips was about 200 μm.

3. Results and discussion

Fig. 1 shows SEM micrographs for the vertically aligned CNTs grown on Co-deposited SiO$_2$ substrate. The flow rate of NH$_3$ and C$_2$H$_2$ gas is 200 sccm for 30 min and 40 sccm for 10 min, respectively, at 950°C. Fig. 1a shows the vertically aligned CNTs on the substrate with a uniform length of about 20 μm. Fig. 1b is a top view of the CNTs, revealing the diameters distributed in the range 80–120 nm, the clean surface without carbonaceous particles, and the closed tip tilted from the vertical direction.

Fig. 2 is an SEM image of the surface morphology of the Co catalytic particles formed on the SiO$_2$ substrate after the NH$_3$ pretreatment. The catalytic particles with diameters in a similar range as those of CNTs can act as the nucleation seeds for the growth of CNTs. The density of those Co catalytic particles is about $1-2 \times 10^3$/cm$^2$. Some large catalytic particles with a diameter of several hundred nm probably cannot contribute to the CNT growth.

Fig. 3 is a TEM image showing that all CNTs consist of hollow compartments, looking like bamboo. Fig. 3a reveals closed tips without any encapsulated catalytic particles (see arrows (1)), open roots separated from Co particles (see arrows (2)), and the compartment layers with a curvature toward the tip (see arrow (3)). Fig. 3b shows that the compartment layers appear at a longer distance as the diameter of CNT decreases (see arrows (4)).

The growth of bamboo-shaped CNTs were reported in a number of works employing arc discharge [14–18], pyrolysis [19], vapor phase growth [20], and plasma-enhanced CVD [21,22] methods. We found that all of the vertically aligned CNTs grown on Co–Ni alloy [23], Ni [24], and Fe [25,26] catalysts deposited SiO$_2$ substrate using thermal CVD method have a bamboo-like structure.

Fig. 1. SEM images of vertically aligned CNTs grown on a large area (20 mm×30 mm) of Co-deposited SiO$_2$ substrate. (a) Uniformly grown CNTs with a length of about 20 μm. (b) A top view showing the diameters in the range 80–120 nm.

Fig. 2. SEM image for the surface morphology of the Co catalytic particles formed on SiO$_2$ substrate after the NH$_3$ pretreatment.
These bamboo-shaped CNTs have no encapsulated catalytic particle at the closed tip and the compartment layers’ curvature is oriented to the tip, irrespective of the catalysts. However, in the syntheses of vertically aligned bamboo-shaped CNTs using pyrolysis [19] and plasma-enhanced CVD [22] methods, the catalytic particles are encapsulated at the tip and the curvature of the compartment layer is directed to the substrate (or root).

Two growth models, i.e. tip growth model [27] and base (or extrusion) growth model [28], have been frequently adopted to explain the growth of CNTs on the substrate. The encapsulation of catalytic particle at the tip suggests that the growth of CNTs follows the tip growth mechanism. For instance, Wang et al. observed the capped Fe catalytic particles on the CNTs synthesized by pyrolysis method, and proposed a tip growth model [19]. On the other hand, a base growth mechanism would be adequate to describe our results that the closed tips are free of encapsulated catalytic particles and the curvature of compartment layers is directed to the tip. Thus we suggest that the growth of bamboo-shaped CNTs using our thermal CVD method follows the base growth mechanism.

Fig. 4 is a TEM image of the bamboo-shaped CNT with an outer diameter of about 120 nm. The conical-shaped compartment layers appear periodically. The thickness of the wall changes at the joint of the compartment layer, but the outer diameter remains approximately the same for the entire tube.

Fig. 5a is a high-resolution TEM (HRTEM) image showing a typical tip of the CNTs. It clearly shows that...
there are no encapsulated catalytic particles at the closed tip and the compartment layer has a curvature directed to the tip. The thickness of the wall changes along the tube (see arrow-marked positions). The number of graphitic sheets at the wall increases at the joint of the compartment layer. Fig. 5a, revealing that the graphitic sheets of the wall combine with those of the compartment layer without any defects as indicated by arrow 1. The graphitic sheets are aligned with an angle of about 5 degrees toward the tube axis (see the marks △, ▽, and ◊). The outer graphitic sheets become defective and disappear as indicated by arrows 2 and 3.

TEM images reveal the features of the bamboo-like structure as follows. The curvature of the compartment layer in the bamboo-like structure is directed to the tip. The graphitic sheets at the wall are aligned toward the tube axis with an angle of a few degrees. The compartment layers join with the wall without any defects, resulting in an increase of wall thickness. The outer graphitic sheets continuously vanish along the tube, thus the outer diameter remains almost the same.

Saito and Yoshikawa reported a HRTEM image for the bamboo-shaped CNTs grown by arc discharge [14,15]. The image shows that the graphitic sheets of the wall are tilted with an angle of a few degrees to the tube axis and the graphitic sheets at the outside continuously vanish. One end of the tube is encapsulated with a conical-shaped Ni catalytic particle. They proposed a growth model that the dissolved carbons diffuse into the bottom of the conical encapsulated Ni particle, segregating as graphite at the bottom and the side of the Ni particle. There are more studies to conjecture the growth model of bamboo-shaped CNTs particularly grown by arc discharge [16,18]. Terrones et al. proposed a growth model for the stacked cup-like structured BCN (boron–carbon–nitrogen) nanotubes grown using the pyrolysis method [29]. All those models describe the vapor phase growth of
nanotubes on the catalytic particles not attached on the substrate. However, few growth models were proposed for the vertically aligned bamboo-shaped CNTs grown on the substrate. Therefore our group has recently developed a base growth model based on the TEM images of the CNTs grown on Fe-deposited SiO₂ substrate [25]. The model can explain no encapsulated catalytic metal particles at the closed tip as well as the features of the bamboo-like structure.

Here we summarize as follows. Carbons generated from the decomposition of C,H₂ adsorb on a hemispherical-shaped catalytic particle. They diffuse via surface and bulk of metal particle to form the 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 a stress accumulated under the graphitic cap. The size of the catalytic particle limits the diameter of the growing tube. Since the wall grows toward the vertical direction with an angle of a few degrees, the outer graphitic sheets disappear continuously due to a pushing-out force from the reaction site of the catalytic particle. The accumulation of carbons at the inside surface of the catalytic particle occurs probably mainly via bulk diffusion, which produces a compartment layer. The compartment graphitic sheets would grow by joining with the graphitic sheets of the wall, resulting in an increase of wall thickness at the joint. Then the compartment layer will eventually leave from the catalytic particle due to stress. Thus the curvature of the compartment is directed toward the tip, which is in the same direction of tip curvature. While the wall grows upwards continuously, the next compartment layer is produced on the catalytic particle and will be combined with the wall. If the carbons are supplied under steady-state conditions, the compartment layers can appear periodically.

Baker reported that the rate of carbon filament growth has an inverse of square root dependence with the size of catalyst particle [27]. It was also suggested that the growth rate of CNTs increases with the decreased size of catalytic particle because of the shorter diffusion length of carbons [30]. Therefore, as the diameter of CNTs (or particles) decreases, the increased growth rate results in a less frequent formation of the compartment layers.

Fig. 6 is Raman spectrum for the vertically aligned CNTs grown on 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 1580 cm⁻¹ [31,32]. The breathing mode peak at ~190 cm⁻¹ disappears, confirming the multiwall structure of CNTs. It is known that the D mode corresponding to 1335 cm⁻¹ is related with the defects of graphitic sheets or carbonaceous particles on the surface of tubes [33]. Since the SEM images reveal no carbonaceous particles at the surface of tubes, the D band must be due to the existence of defective graphitic sheets at the wall, which is consistent with the TEM analysis. The relative peak intensity of D band to G band is about 1.2, which is higher than that of CNTs grown on Fe-deposited SiO₂ substrate at 950°C [26]. This may indicate that the crystallinity of CNTs is dependent on the catalyst.

Fig. 7 shows the emission current density versus the electric field for the vertically aligned CNTs grown on Co-deposited Ti/SiO₂ substrate. The turn-on voltage is about 0.8 V/μm with the current density of 0.1 μA/cm². The maximum current density before the electrical breakdown is 1.1 mA/cm² at an applied field of about 4.5 V/μm, which is sufficient for the applications to FEDs. The inset of Fig. 7 indicates that the field emission follow a Fowler–Nordheim behavior. The field emission at a field level above 2.2 V/μm shows an increased slope by a factor of 2. The two linear slopes in the Fowler–Nordheim plot have been found in some studies [21,22], showing a
decreased slope at a higher voltage level. We cannot explain exactly the appearance of two slopes at this moment. However, the presence of protruded tips may play a role in determining the emission properties of CNTs.

In summary, we have grown the vertically aligned CNTs on a large area of Co-deposited SiO$_2$ substrates using a thermal CVD method. The diameter of CNTs is 80–120 nm and the length is about 20 μm. The CNTs have closed tips that are free from encapsulated catalytic particles. They exhibit a bamboo-like structure with the tube consisting of hollow compartments. The curvature of the compartment layer in the bamboo-like structure is directed to the tip. As the diameter of CNT decreases, the compartment layers appear at a longer distance. The graphitic sheets at the wall are aligned to the tube axis with an angle of a few degrees. The compartment layers join with the wall without any defects, resulting in increasing wall thickness. The outer graphitic sheets continuously vanish along the tube, thus the outer diameter remains almost the same. The base growth mechanism is suitable for CNTs grown by thermal CVD. The maximum current density is 1.1 mA/cm$^2$ at an applied field of about 4.5 V/μm. The vertically aligned CNTs grown on Co-deposited SiO$_2$ substrate can be practically applicable to the CNT-based FEDs.

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References