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Growth of well-aligned carbon nanotubes on a large area of Co–Ni co-deposited silicon oxide substrate by thermal chemical vapor deposition

Cheol Jin Lee [a,*], Jeunghee Park [b], Seung Youl Kang [c], Jin Ho Lee [c]

[a] *School of Electrical Engineering, Kunsan National University, Kunsan 573-701, South Korea*
[b] *Department of Chemistry, Korea University, Jochiwon 339-700, South Korea*
[c] *Microelectronics Laboratories, Next Generation Semiconductor Research Department, ETRI, Taejon 305-350, South Korea*

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Abstract

We have grown vertically well-aligned multiwalled carbon nanotubes (CNT) on a large area of cobalt–nickel (Co–Ni) co-deposited silicon oxide substrate by thermal chemical vapor deposition using C_2H_2 gas, at 950°C. The diameter of CNTs is in the range of 50–120 nm and the length is about 130 μm. The grown CNTs have a bamboo structure and closed tip with no catalytic particles inside. As the particle size of Co–Ni catalyst decreases, the vertical alignment is enhanced. The CNTs exhibits a low turn-on voltage of 0.8 V/μm with an emission current density of 0.1 μA cm^{-2}.

1. Introduction

Since the first observation of carbon nanotubes (CNT) [1], extensive research has focused on the synthesis using arc discharge [2–4], laser vaporization [5], pyrolysis [6], and plasma-enhanced or thermal chemical vapor deposition (CVD) [7–10]. Synthesis of well-aligned CNTs on a large area is inevitably necessary for one of its important applications such as electron emitter of flat panel display. Arc discharge and laser vaporization techniques can produce a large amount of CNTs, but it is very difficult to obtain uniform alignment on a large area [4,5]. Many research groups have employed the CVD method for the purpose of controlling the growth of CNTs. Recently, Ren et al. demonstrated the possibility to control the alignment and the diameter of CNTs by using a plasma-enhanced CVD method [7]. However, the diameter of CNTs is still widely distributed. Li et al. [9] and Fan et al. [10] used mesoporous silica and Fe-patterned porous silicon substrates, respectively, for the synthesis of vertically aligned CNTs on substrates. However, these methods require complicated sample preparation, which may not be suitable for the fabrication process of flat panel displays. Furthermore, a large-area synthesis of CNTs seems difficult due to porous substrates.

Our research group had previously reported the growth of aligned CNTs on a large area of cobalt–nickel (Co–Ni) co-deposited SiO_2 substrate by using thermal CVD method [11]. Acetylene (C_2H_2) gas

* Corresponding author. Fax: +82-654-466-2086; e-mail: cjlee@ks.kunsan.ac.kr

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was used. In this Letter, we extend the work to control the diameter and alignment of CNTs grown on Co–Ni co-deposited SiO_2 substrate. The result shows that, as the density of catalyst particle increases, the diameter of CNTs decreases and their vertical alignment improves significantly. The surface of catalytic Co–Ni film on SiO_2 substrate is modified by dipping in HF solution and/or NH_3 gas pretreatment, which is a crucial step for controlling the size and vertically alignment of CNTs. High-resolution transmission electron microscopy (TEM) is used to reveal the structure of CNTs. We demonstrate a method of synthesis of vertically well-aligned multiwalled CNTs on a large area of substrate, which can be practically applicable to field emission displays.

2. Experimental

The 20×30 mm size p-type Si (100) substrates with a resistivity of 15 Ω cm were thermally oxidized. The Co–Ni (Co/Ni = 1:1.5) metal alloys were thermally evaporated on SiO_2 substrates under a vacuum of 10^{-6} Torr. The thickness of SiO_2 layer was estimated as approximately 300 nm. 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 alloys while raising the temperature. Samples were pretreated by NH_3 gas, with a flow rate of 50–200 sccm, for 10–30 min at a temperature range of 850–950°C. 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. The reactor was cooled down slowly to the room temperature (25°C) under Ar ambient after the growth. The CNTs grown on substrate were examined by a scanning electron microscope (SEM) (Hitachi S-800, 30 kV), to measure the length, diameter, alignment, density, and uniformity. High-resolution TEM (Philips, CM20T, 200 kV) was used to determine the wall structure of an individual CNT. A Raman spectrometer (Renishaw micro-Raman 2000) was also used to justify the structure and crystallinity of graphite sheets. 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–d are the SEM micrographs of the CNTs grown on a Co–Ni co-deposited SiO_2 substrate. The C_2H_2 gas flows with a rate of 40 sccm for 10 min, at 950°C. Fig. 1a shows vertically well-aligned CNTs grown on the substrate. The edges are peeled off using a razor, in order to be visualized. The CNTs are uniformly grown with a length of about 130 μm. Fig. 1b reveals high density and the diameters distributed in the range of 50–120 nm. Top view of vertically aligned CNTs is shown in Fig. 1c. Fig. 1d is a magnified view of Fig. 1c, showing the round-shaped tips.

TEM analysis was performed to determine the wall structure. Using an ultrasonic treatment in acetone, the CNTs were separated from the substrate, and then dispersed on a carbon TEM microgrid. TEM image in Fig. 2a shows the multiwalled CNTs in various diameters. An important feature is that the CNT consists of hollow compartments, looking like bamboo. The compartments are separated at various lengths. The arrow marks (1) and (2) indicate a tip and a root, respectively. The round tip is closed and its inside is hollow without any filled catalytic particles. The root is opened. It is noticed that the curvature of separation walls is directed to the root. Fig. 2b is a magnified high-resolution TEM image for the CNT having 40 walls. The outer and inner diameters are about 60 and 40 nm, respectively. The sharp fringe of inside walls indicates good crystallinity of graphite sheets. However, the fringe of wall surface shows defects in graphite sheet. It definitely shows that the central hollow is segment by the graphite layers.

We have also tried various growth conditions. The diameter, number of walls, length, and crystallinity are dependent on the growth temperature. The length always increases with increasing the growth time and temperature. However, the CNTs grown under the same experimental condition always gives reproducible SEM and TEM images.

Our research group reported the work that the CNTs are grown on the Co–Ni co-deposited SiO_2 substrate with the diameter of about 200 nm [11].

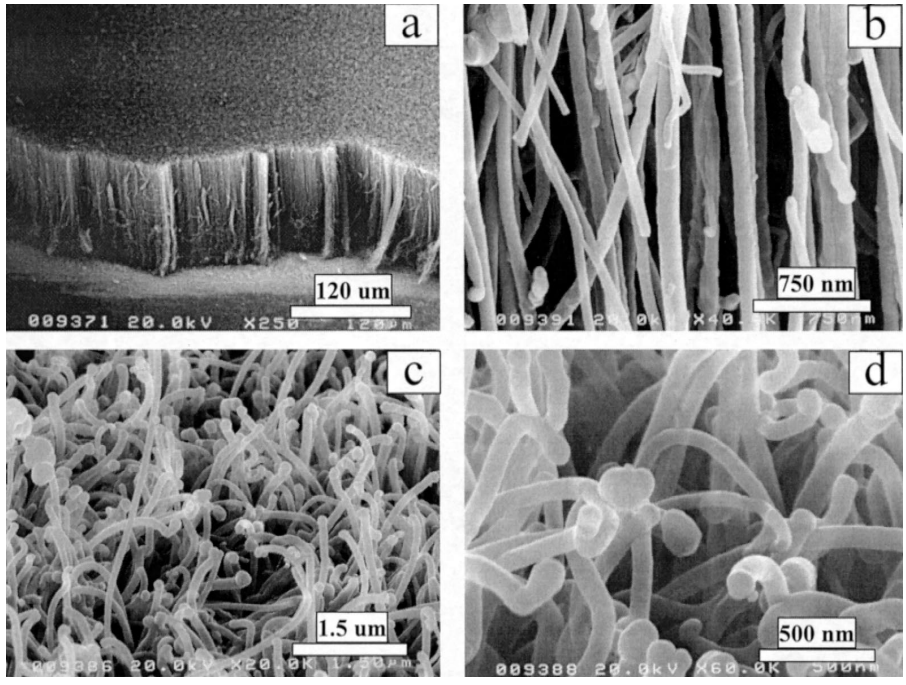

Fig. 1. SEM micrographs of well-aligned CNTs grown on a large area (20×30 mm) of Co–Ni co-deposited SiO_2 substrate, under the condition that C_2H_2 gas flows with a rate of 40 sccm for 10 min at 950°C. The edges are peeled off using a razor in order to be visualized. (a) A uniformly distributed morphology of vertically aligned CNTs with a length of about 130 μm. (b) A magnified side view of (a), showing high density and the diameters of 50–120 nm. (c) Top view of the vertically aligned CNTs. (d) A magnified view of (c), showing the round tips.

The Co–Ni co-deposited SiO_2 substrate was pretreated by using NH_3 gas, with a flow rate of 80 sccm for 10–20 min at a temperature range of 800–900°C. The CNTs are grown at the same temperature range. We showed that the HF dipping and NH_3 pretreatment steps are necessary to obtain the nucleation sites for the growth of CNTs. Without NH_3 pretreatment, the CNTs can be grown on the substrate, but not in vertical direction. We concluded that both HF dipping and NH_3 pretreatment are very crucial to control the surface morphology of catalytic metals and thus to achieve the vertical alignment of CNTs.

In present work, we have pretreated the Co–Ni co-deposited SiO_2 substrate by using a high NH_3 flow rate, at a high temperature range of 850–950°C, compared to those used in the previous work [11]. The growth temperature of CNTs is also higher than that of previous work. Then the diameter of CNTs decreases from 200 nm to 60–130 nm and the CNTs are more aligned in vertical direction. More NH_3 pretreatment reduce the grain size of metal particles and increase their density. Since the particle size of catalyst determines the diameter of CNTs [7–12], the smaller size of catalytic particles results in a smaller diameter of CNTs. The wide range of diameter could be due to two kinds of catalytic metal. The diameter of CNTs grown on the Co catalytic particles is larger than that on the Ni catalytic particles [12,13]. Comparison with our previous work [11] shows that as the density of catalytic metal particle increases, the vertically alignment of CNTs is significantly enhanced. When the density of CNTs reaches to a certain high level, the growth in non-vertical direction is prohibited due to the steric hindrance from adjacent CNTs. The vertically aligned CNTs can be bundled together by van der Waals force. We emphasize here that the diameter of CNTs can be altered by a simple surface treatment of metal catalyst.

The SEM image (Fig. 1c,d) showing the round-shaped tip may mislead to conjecture the catalytic metal particles filled in the tip. Therefore, in our previous work, we suggested a tip growth model for

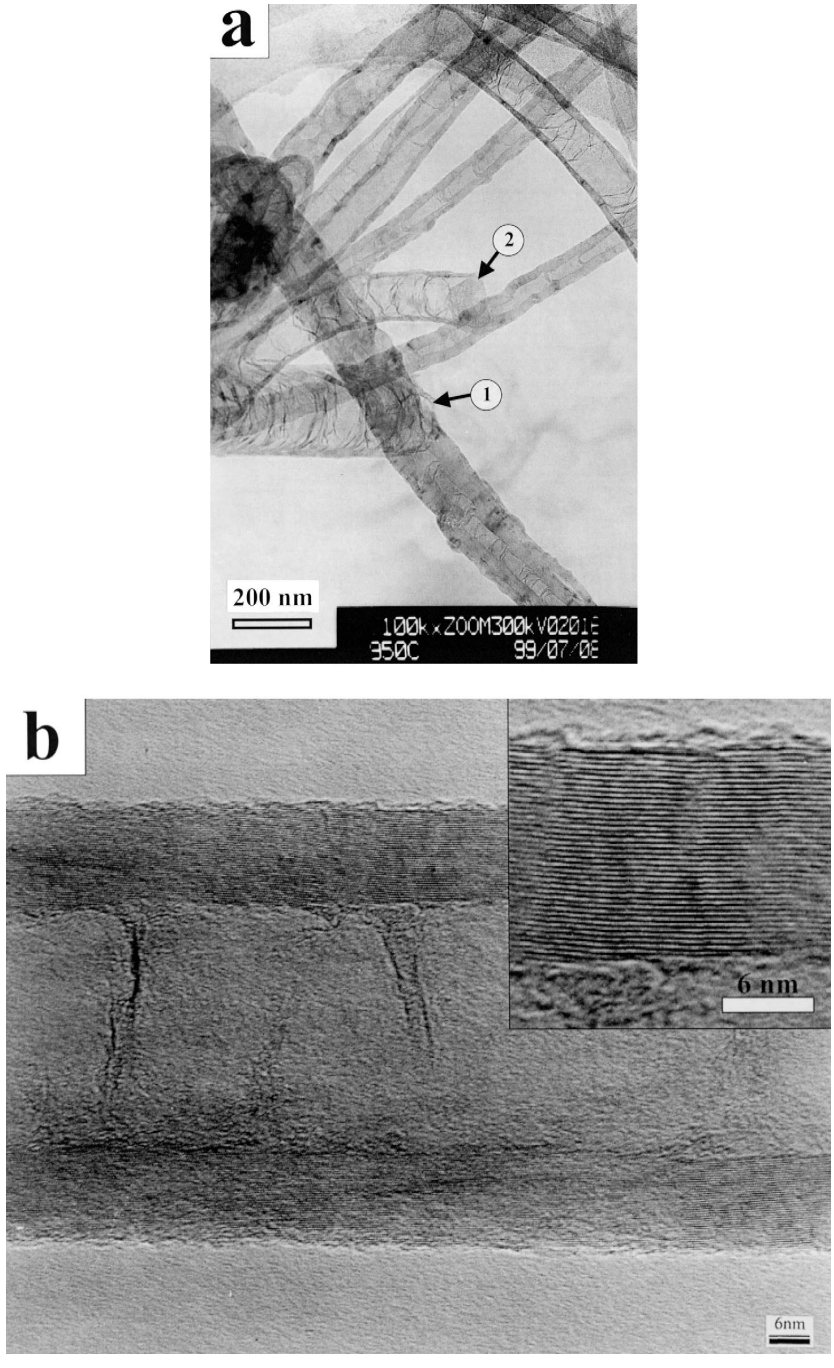

Fig. 2. TEM images of the CNTs dispersed on a carbon microgrid. (a) A TEM image of CNTs dispersed on a TEM grid after stripping from the SiO_2 substrate, showing a hollow closed tip (marked as (1)), an opened root (marked as (2)), and bamboo structure. (b) A high-resolution TEM image for a multiwalled CNT having 40 walls. The outer and inner diameters are about 60 and 40 nm, respectively.

the growth of CNTs [11]. Presently we can identify the structure of CNTs by TEM image analysis. The closed tip without any filled catalytic particles are observed from the TEM image (Fig. 2a), which is inconsistent with a tip growth model. The bamboo structure was found from the multiwalled CNTs produced by arc discharge [14]. It is remarkable that the bamboo-shaped CNTs are grown by using the thermal CVD method. We'll discuss more detailed growth mechanism in a following paper.

Fig. 3 is a micro-Raman spectrum of the CNTs grown on the Co–Ni co-deposited 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 1573.2 cm^{-1} with a small bump at 1595.3 cm^{-1} [15]. There is no second order peak at ~ 1720 cm^{-1}. The breathing mode peak at 190.5 cm^{-1} is significantly diminished, confirming the multiwall structure of CNTs. The peak at 1326.8 cm^{-1} indicates the existence of defect or carbonaceous particles on the surface of CNTs [16]. The small peaks at 463.1 and 665.8 cm^{-1} could be related to the finite length of CNTs [17]. We noticed that the relative intensity of 1573.2 cm^{-1} peak (G-line) to 1326.8 cm^{-1} peak is larger than that of our previous work [11], indicating that the crystallinity of graphite sheets is enhanced. Therefore, Raman spectrum analysis confirms the fact that the CNTs have crystalline multiwalls and there are some defects or carbonaceous particles on the wall surface.

Fig. 4 shows the field emission current density versus the electric field, for the CNTs grown on the Co–Ni co-deposited SiO_2 substrates. 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 with a current density of 0.1 μA cm^{-2}, which is much lower than that of previous work [11], 1.2 V/μm with 5 nA cm^{-2}. The maximum emission current density before the electrical breakdown is 1.1 mA cm^{-2} at 4.5 V/μm. The inset of Fig. 4 shows Fowler–Nordheim plot of the same emission data. The field emission at a field level above 2.4 V/μm shows enhancement, with the slope increased by a factor of 2. We cannot explain the existence of two slopes at this moment. However, the presence of protruded tips may play a role in determining the emission characteristics of CNTs. The vertically aligned CNTs on a large area of substrate exhibit the emission current density required for the field emission displays.

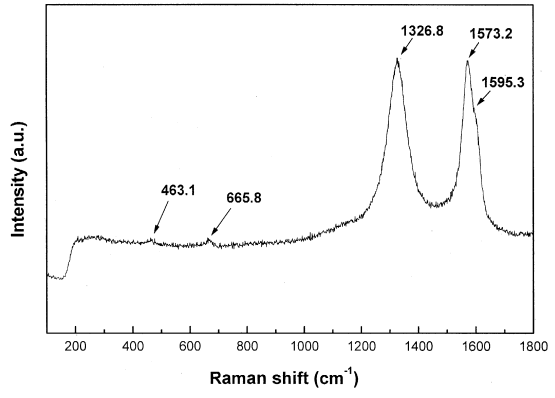

Fig. 3. Micro-Raman spectrum of vertically aligned CNTs grown on a Co–Ni co-deposited SiO_2 substrate.

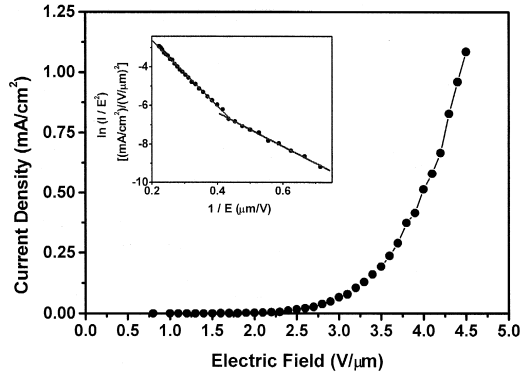

Fig. 4. Field emission current density versus electric field, for the vertically aligned CNTs on a Co–Ni co-deposited SiO_2 substrate. The inset shows Fowler–Nordheim plot.

In summary, we have grown well-aligned multiwalled CNTs on a large area of Co–Ni co-deposited SiO_2 substrates using thermal CVD method. We show that the diameter and the vertical alignment of CNTs can be controlled by the density and size of catalytic metal particles. As the particle density of Co–Ni catalyst increases, the diameter of CNTs decreases and the vertical alignment is enhanced. We suggest that the steric hindrance between CNTs would force to align in vertical direction. The CNTs are uniformly grown with a length of about 130 μm. The diameters are distributed between 50 and 120 nm. The multiwalled CNTs have bamboo structure,

closed tip without any catalytic particles inside, and crystalline graphite walls. These CNTs show a good electron emission property. The turn-on voltage is as low as 0.8 V/μm with a current density of 0.1 μA cm^{-2} and the maximum current density is 1.1 mA cm^{-2} at 4.5 V/μm. We demonstrate that the vertically aligned CNTs can be practically applicable to the electron emitter of flat panel displays.

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