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Growth and field electron emission of vertically aligned multiwalled carbon nanotubes

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Abstract

Vertically well-aligned carbon nanotubes (CNTs) are grown on a Ni deposited silicon oxide substrate at 950°C by thermal chemical vapor deposition using C_2H_2. The uniformly grown CNTs with a diameter of about 60 nm have unique beak-like tips without any encapsulated Ni particles inside and exhibit high field emission current density, e.g. 2.9 mA/cm^2 at 3.7 V/μm, following a Fowler–Nordheim behavior. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The carbon nanotubes (CNTs), first observed in 1991 [1], show very unique physical and chemical properties [2–5]. Thus numerous potential applications such as flat panel displays [6,7], hydrogen storage [8], chemical sensors [9] etc. were proposed. The growth of high-quality CNTs is a prerequisite for these applications. Arc discharge [10–12], laser vaporization [13], pyrolysis [14], and plasma-enhanced [15,16] or thermal chemical vapor deposition (CVD) [17,18] methods have been developed to synthesize the CNTs. Since the synthesis of vertically aligned CNTs is of great importance for applications to field emission displays (FEDs), various CVD methods have been used in order to apply directly to FEDs. Vertically aligned CNTs on nickel (Ni) deposited glass were grown by a hot filament plasma-enhanced CVD method [15]. Recently, the microwave plasma-enhanced CVD method was employed to grow the vertically aligned CNTs on Ni patterned glass substrate [16]. The growth of vertically aligned CNTs on iron (Fe) nanoparticles embedded in mesoporous silica [17] and on Fe-patterned porous silicon substrate [18] by thermal CVD was also reported.

In this Letter, we report a growth of vertically well-aligned multiwalled CNTs on a large area of Ni deposited silicon oxide (SiO_2) substrate using thermal CVD method, showing a unique tip shape and excellent field electron emission property. The catalytic Ni particles on the substrate were prepared by the simple process of HF dipping and/or NH_3 pretreatment [19,20] and acetylene (C_2H_2) was used as a reactant.

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2. Experimental

The 20 mm × 30 mm size p-type silicon (100) substrates with a resistivity of 15 Ω cm were thermally oxidized. The thickness of the SiO_2 layer was approximately 300 nm. The Ni metal was thermally deposited onto the SiO_2 substrates under a vacuum of 10^{-6} Torr. The thickness of Ni film was about 100 nm. The Ni deposited SiO_2 substrates were dipped in diluted HF solution for 100–200 s and then were loaded inside a CVD quartz reactor. Argon (Ar) was supplied into the quartz reactor to prevent

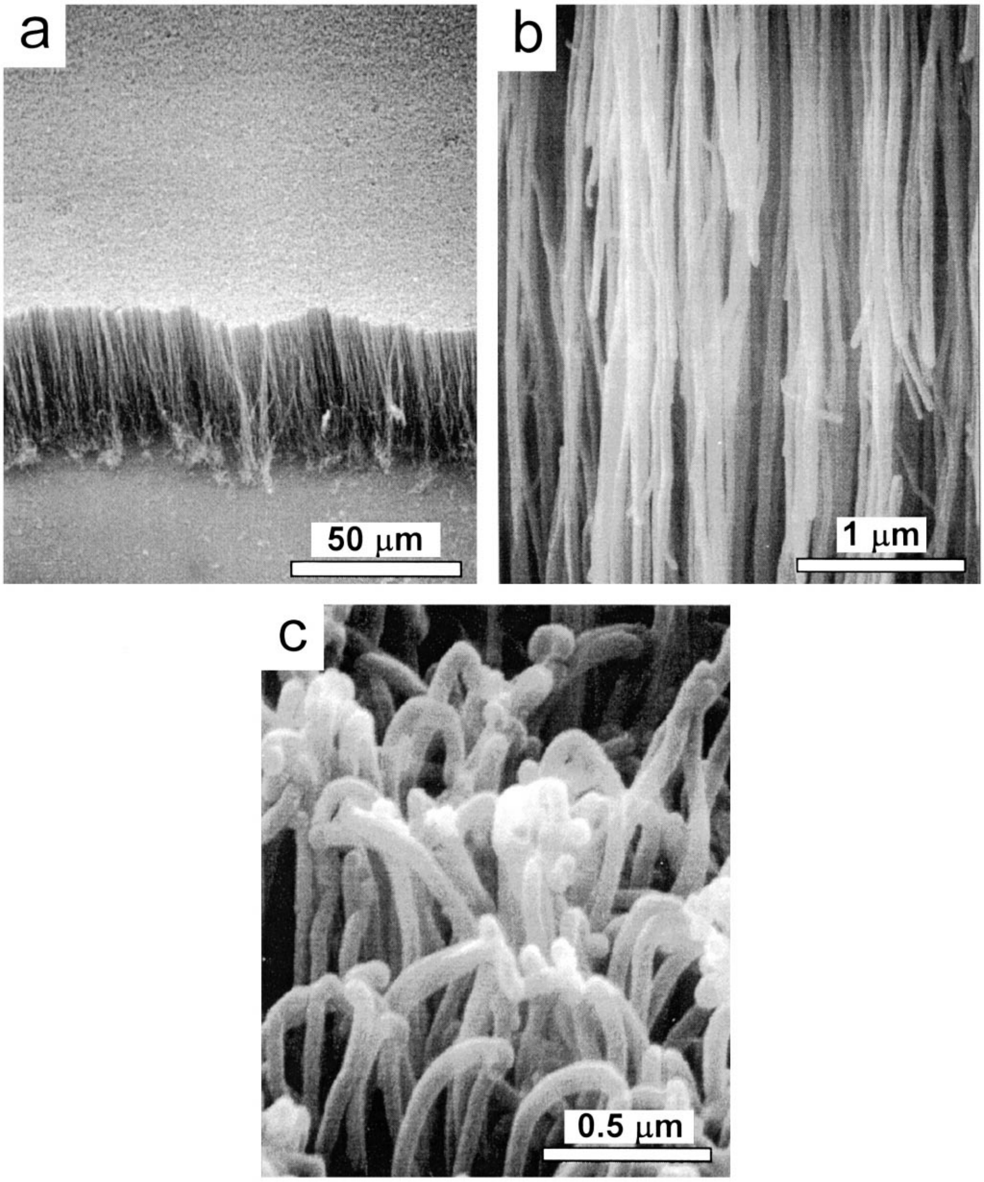

Fig. 1. SEM images of the vertically well-aligned CNTs grown on a large area (20 mm × 30 mm) of Ni deposited SiO_2 substrate. The C_2H_2 gas flows with a rate of 40 sccm for 10 min at 950°C. (a) Vertically well-aligned CNTs with a length of 50 μm. (b) A side view showing uniform diameter distribution. (c) Top view revealing the tip of CNTs with a diameter of about 60 nm.

the oxidation of Ni film. Samples were pretreated using NH_3 gas with a flow rate of 50–200 sccm, for 10–30 min at 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 to room temperature in Ar ambient after the growth. Samples were examined by a scanning electron microscope (SEM) (JEOL, JSM-6400, 20 kV) to measure length, diameter, and alignment of CNTs. Transmission electron microscopy (TEM) (Hitachi H-9000NA, 300 kV) was used to determine the wall structure of CNTs. Field electron emission measurement was conducted under the pressure of 1×10^{-6} Torr. The electron emission pattern of the CNTs was monitored by using a 20 mm × 30 mm phosphor coated indium tin oxide (ITO) glass electrode. The emission current versus the applied voltage was measured with an electrometer (Keithley 619). The distance between the anode and the tip of CNTs was about 200 μm.

3. Results and discussion

Fig. 1 is SEM micrographs showing the vertically well-aligned CNTs grown on Ni deposited SiO_2 substrate, at 950°C. Fig. 1a shows that densely packed CNTs are aligned vertically to the substrate plane and uniformly grown with a length of about 50 μm. Fig. 1b is a side view of vertically aligned CNTs,

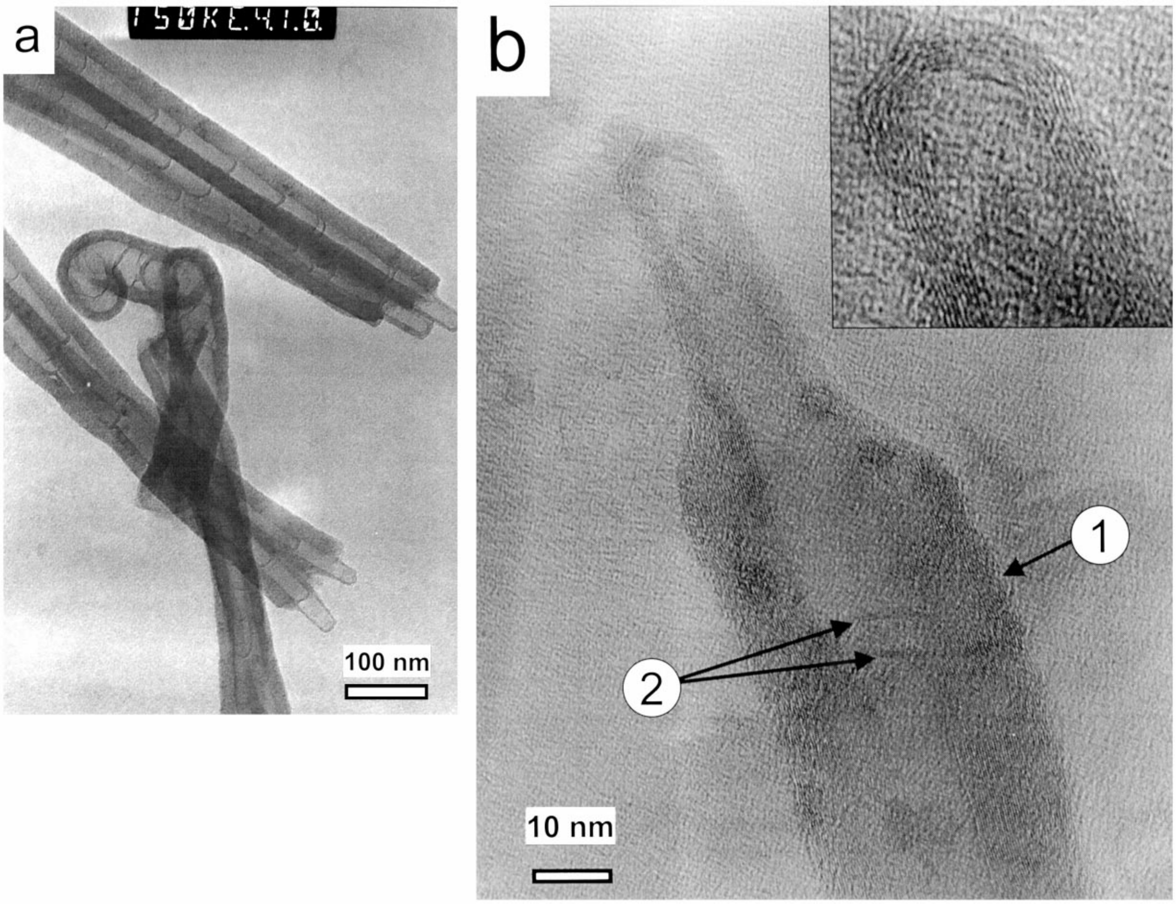

Fig. 2. (a) A TEM image of CNTs, showing the bamboo structure and sharp tips with no encapsulated Ni particles. The outer and inner diameters of CNTs are approximately 60 nm and 20 nm, respectively. (b) A high-resolution TEM image for a beak-like tip of CNT. The inset shows that the tip has approximately 9 graphite sheets with clean fringes.

showing uniform diameter distribution. Fig. 1c reveals that the diameter of CNTs is about 60 nm and most of tips are approximately perpendicular to the surface of substrate although a few of them are tilted or curved.

TEM analysis was performed to determine the wall structure of CNTs. The CNTs were separated from the SiO_2 substrate in acetone solution using ultrasonic treatment. Peeled CNTs were dispersed on a carbon TEM microgrid. Fig. 2a is a TEM image revealing the multiwall structure with a central hollow. The outer diameter of CNTs is about 60 nm and the inner diameter is about 20 nm. It is noticed that the CNTs have bamboo structure and sharp closed tip without any catalytic particles inside. The compartment layers appear at nearly regular distance and have a curvature directed to the tip. The outer diameter and the wall numbers decrease at the tip. The tips are 30–50 nm in length and 20 nm in outer diameter. Fig. 2b is a high-resolution TEM image for the sharp tip of a CNT, revealing beak-like shape. Noticed that the inner diameter remains approximately 7 nm for entire tube. On the other hand, the outer diameter is about 13 nm at the tip but it increases to about 33 nm. Defective graphite sheets can be observed at the wall surface (see arrow 1). The compartment graphite sheets with a curvature directed to the tip exist in the inside hollow (see arrows 2). The inset shows that the tip has approximately 9 graphite sheets with clean fringes.

Fig. 3 is a SEM micrograph showing the Ni particles deposited on a SiO_2 substrate, after the pretreatment of NH_3 at 950°C. The SEM image was taken from the substrate tilted by 45 degree. The number density of Ni particles is $3 \sim 4 \times 10^9/\mathrm{cm}^2$ and their shape resembles a standing egg. The diameters are distributed between 100 nm and 400 nm.

We have already reported that HF dipping and NH_3 pretreatment are very crucial steps to obtain high density of nucleation sites [19,20]. The HF and/or NH_3 etching results in Ni particles acting as the nucleation seeds for growth of CNTs. The diameter of CNTs is smaller than those of catalytic particles, which is consistent with other studies [15–17]. The vertical alignment of CNTs can be determined by the density of catalytic particles. When the density of CNTs reaches to a certain high level, the growth in non-vertical direction undergoes the steric hindrance from the adjacent CNTs and thus more vertical alignment can be achieved. The CNTs grown under the same experimental conditions always give reproducible SEM and TEM images.

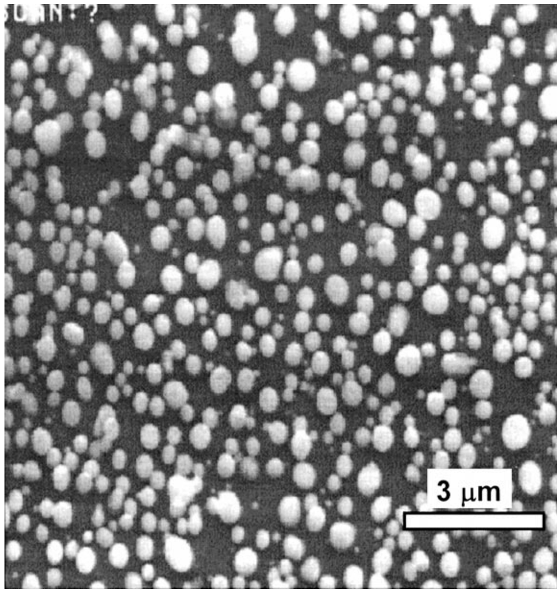

Fig. 3. A SEM image of standing-egg shaped Ni particles deposited on SiO_2 substrate.

The bamboo structure was first found in the multiwalled CNTs grown using arc discharge [21]. Recently, the bamboo shaped multiwalled CNTs grown by pyrolysis [22], microwave plasma-enhanced CVD [16] and thermal CVD [23] have been reported. Therefore, the formation of bamboo structure seems to be possible for multiwalled CNTs, regardless of growth methods.

For multiwalled CNTs grown using plasma-enhanced CVD, the catalytic particles usually remain at the tip [15,16,24]. Wang and his coworkers reported capped Fe catalytic particles of the vertically aligned bamboo shaped CNTs grown using pyrolysis [22]. Li et al. synthesized the bamboo shaped CNTs using Ni:Cu:Al alloy catalyst by thermal CVD, and found the metal particles either at the tip or encapsulated inside [23]. In contrast, Dai and his coworkers reported open tip of the vertically aligned CNTs grown on Fe patterned porous silicon substrate using thermal CVD [18]. However, in our thermal CVD growth of vertically aligned CNTs, we found no encapsulated catalytic particles at the closed tip, which is different from those previous works. The closed tips without encapsulated catalytic particles can be explained by employing a base growth model [25]. Therefore, the unique tip shape can be related with the standing egg shape of Ni particles. More detailed base growth model including the formation of bamboo structure will be discussed in a separated paper.

The field emission was measured by using a phosphor screen, to determine the emission site density. The electron emission from the CNTs grown on Ni deposited SiO_2 substrate was monitored with a 20 mm × 30 mm phosphor coated ITO electrode as an anode at an applied voltage of 3.7 V/μm, as shown in Fig. 4. The distance between the anode and the CNT tips was about 200 μm. The field enhancement at the tip generally governs the emission property of CNTs. The emission spots are not uniformly distributed over the area, which can be due to protruded tips. The electron emission starts at 0.8 V/μm. The emission site density is about $2 \times 10^3/cm^2$ at 2.5 V/μm and increases to roughly $7 \times 10^3/cm^2$ at 3.7 V/μm, showing almost quadratic increase. We could not measure the emission site density at the higher voltage than 4 V/μm because the phosphor screen becomes electrically breakdown.

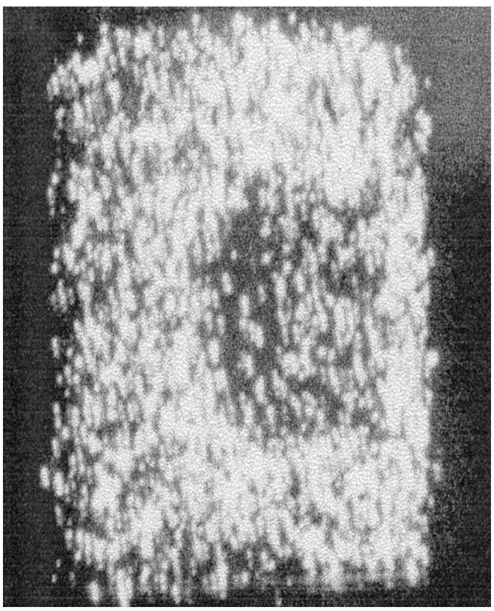

Fig. 4. Electron field emission from the well-aligned CNTs grown on Ni deposited SiO_2 substrate, monitored by a phosphor screen at the voltage of 3.7 V/μm. The size of the image is 20 mm × 30 mm.

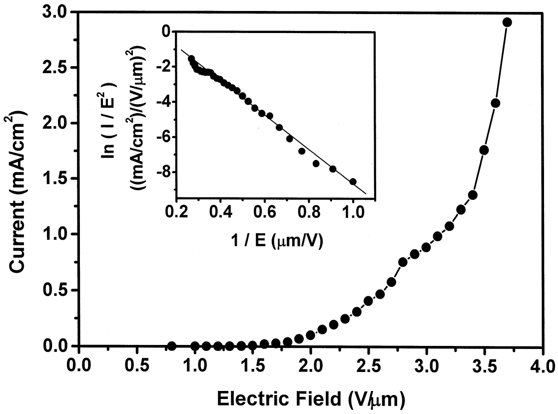

Fig. 5. Field emission current vs. electric field for well-aligned CNTs grown on Ni deposited SiO_2 substrate. The inset is a linear fit of a Fowler–Nordheim plot.

Fig. 5 illustrates the emission current density curve from the CNTs grown on Ni deposited SiO_2 substrates. The distance between the anode and the CNT tips was about 200 μm. The turn-on voltage is about 0.8 V/μm with an emission current density of 0.1 $\mu A/cm^2$. The emission current density is as high as 2.9 mA/cm^2 at 3.7 V/μm, which is sufficient for the electron emitter of a flat panel display. We reported a field electron emission property of the CNTs grown on Co catalytic particles deposited on SiO_2 [26]. The maximum emission current density was about 1.1 mA/cm^2 at 4.5 V/μm, corresponding to about 1/3 of the present value. We suggest that high emission current of the CNTs grown on Ni particles could be due to their sharp tips. The inset of Fig. 5 shows a good linear fit, indicating that the emission current of CNTs follows the Fowler–Nordheim behavior.

In summary, we have grown vertically aligned CNTs on a large area (20 mm × 30 mm) of Ni deposited SiO_2 substrates using thermal CVD. The diameters and lengths of CNTs are uniformly distributed as 60 nm and 50 μm, respectively. The multiwalled CNTs are revealed to have bamboo structure and sharp closed tip with no encapsulated catalytic particles. The CNTs show low turn-on voltage as 0.8 V/μm and high emission current density, e.g. 2.9 mA/cm^2 at 3.7 V/μm. The emission current follows the Fowler–Nordheim behavior. The excellent field emission property may be due to the sharp tips. We have demonstrated that the CNTs grown on Ni deposited SiO_2 substrates have high emission current density enough to be applicable to FEDs.

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