Synthesis of aligned carbon nanotubes using thermal chemical vapor deposition

Cheol Jin Lee a, Dae Woon Kim a, Tae Jae Lee a, Young Chul Choi b, Young Soo Park b, Young Hee Lee b,c,*, Won Bong Choi d, Nae Sung Lee d, Gyeong-Su Park e, Jong Min Kim d

a Department of Electrical Engineering, Kunsan National University, Kunsan 573-701, South Korea
b Department of Semiconductor Science and Technology, and Semiconductor Physics Research Center, Chonbuk National University, Chonju 561-756, South Korea
c Department of Physics, Chonbuk National University, Chonju 561-756, South Korea
d Display Laboratory, Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, South Korea
e Analytical Engineering Laboratory, Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, South Korea

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Abstract

Aligned carbon nanotubes have been synthesized on transition metal-coated silicon substrates with C2H2 using thermal chemical vapor deposition. It was found that nanotubes can be mostly vertically aligned on a large area of plain Si substrates when the density of metal domains reaches a certain value. Pretreatment of Co–Ni alloy by HF dipping and etching with NH3 gas prior to the synthesis is crucial for vertical alignment. Steric hindrance between nanotubes at an initial stage of growth forces nanotubes to align vertically. Nanotubes are grown by a catalyst-cap growth mechanism. Applications to field emission displays are demonstrated with emission patterns. © 1999 Elsevier Science B.V. All rights reserved.

Since the discovery of carbon nanotubes (CNT) [1], synthesis of carbon nanotubes for mass production has been achieved by several methods such as laser vaporization [2], arc discharge [3], and pyrolysis [4]. However, controllability of diameters, lengths, and chiralities has never been easily accessible with such approaches. In spite of considerable efforts for CNTs to apply for electron field emitters [5–8], practical approaches are still limited by the intricate sample-preparation processes and large area synthesis. In particular, synthesis of vertically aligned nanotubes is of great importance for applications to field emitters. Recently, vertically aligned CNTs have been synthesized on glass by plasma-enhanced chemical vapor deposition (PECVD) [9]. Aligned CNTs can be also grown on mesoporous silica [10] and Fe-patterned porous silicon [11] using the chemical vapor deposition (CVD) method. Despite such breakthroughs in the synthesis, the growth mechanism of the alignment are still far from being clearly understood. Furthermore, flat-panel emission displays on a large area has not been clearly demonstrated yet at a practical level. Here, we have synthesized vertically aligned CNTs on a large area of Co–Ni codeposited Si substrates by the thermal CVD using C2H2 gas. We demonstrate that CNTs can be
mostly vertically aligned on catalyzed Si substrate when the domain density reaches a certain value. Controlling the domain density of Co–Ni alloy by HF dipping and dry etching with NH$_3$ gas prior to the deposition is of crucial importance. Steric hindrance between nanotubes at an initial stage of the growth forces nanotubes to align vertically. Nanotubes are then further grown by the catalyst-cap growth mechanism. We further demonstrate the field emission patterns and $I$–$V$ characteristics obtained from vertically aligned carbon nanotubes.

We used p-type silicon substrates with a resistivity of 15 $\Omega$-cm, since it is of importance to use silicon substrates for future Si-based optoelectronic devices. Co–Ni (Co/Ni, 1:1.5) metal alloys with 100 nm in thickness were thermally evaporated at room temperature in a vacuum of $10^{-6}$ torr on oxidized Si(100) substrates. These samples were further annealed at 400°C in Ar ambient for 20 min, which enhanced the adhesion of metal layers to the oxidized Si substrates. The annealed samples were dipped for 100–200 s in HF solution (HF/DI water, 1:12) and were then loaded on the quartz boat inside the CVD quartz reactor of 60 mm in diameter. In order to prevent the oxidation of Co–Ni alloys, Ar gas was flowed into the quartz reactor during increasing the temperature to a desirable value. Samples werepretreated using NH$_3$ gas with a flow rate of 80 sccm for 5–20 min at 800–900°C. Then, CNTs were synthesized using C$_2$H$_2$ gas with a flow rate of 15–40 sccm for 10–20 min at the same temperature as the NH$_3$ pretreatment. The reactor was cooled down slowly to room temperature in Ar ambient after the synthesis.

Fig. 1a–d shows scanning electron microscope (SEM) (JEOL JSM-6400, 20 kV) images of CNTs with various magnifications. CNTs are well aligned over the large area ($20 \times 30$ mm$^2$) of the substrate, as shown in Fig. 1a. The surface morphologies of CNTs are clean and uniform with the length of about 5 $\mu$m and the diameter of about 200 nm. The white bundles of CNTs shown in Fig. 1a are peeled off due to scratches. Note that top of the aligned nanotubes is terminated by a transition-metal cap, the white spots, as shown in Fig. 1b, which is similar to the previous reports [9,10]. Fig. 1c reveals high density of nanotubes, where nanotubes are curly at the bottom but rather straight near the top of nanotubes. The density of nanotubes is about $3 \times 10^8$ cm$^{-2}$, about 100 times larger than the typical density of microtips in conventional Spindt-type field emission arrays. Some nanotubes are kinky at the initial stage of growth, as shown in Fig. 1d. We evaluated the wall structures by the transmission electron microscopy (TEM) (Hitachi H-9000NA, 300 kV), as shown in Fig. 1e,f. Peeled nanotubes were dispersed on a copper carbon-microgrid. TEM images show long and straight multi-wall nanotube with an hollow inside (Fig. 1e). The lattice images are shown in Fig. 1f. However, long-range lattice images are not formed due to relatively low growth temperature. This was also confirmed in our Raman scattering measurement that a relatively large defective peak at 1295 cm$^{-1}$ was observed with the main graphitic G-peak at 1595 cm$^{-1}$. Fig. 2 shows the Raman spectrum of aligned carbon nanotubes using FT-Raman spectrometer (BRUKER RFS 100/S) with the excitation laser of Nd:YAG (wavelength: 1064 nm). Besides two main peaks, several peaks at low wavenumbers were also observed in our multiwall nanotubes, although these were usually observed in single-wall nanotubes [12–14].

Nanotubes were reproducibly grown with the above conditions. We have also tried various growth conditions [14]. CNTs were grown well independent of growth temperatures within the temperature range of 800–900°C, since C$_2$H$_2$ gases are highly decomposed in this range by the catalytic assistance of transition metals [10]. Tube lengths increased with increasing growth time. However, some carbonaceous particles appeared with longer growth time. The growth rate was 30 $\mu$m/h, similar to that from the CNT growth on porous Si [10]. We note that the HF dipping and NH$_3$ pretreatment are crucial steps to obtain high density of nucleation sites. Without NH$_3$ pretreatment, CNTs were grown uniformly but not vertically aligned. Therefore, the NH$_3$ pretreatment is a very critical step in vertically aligning carbon nanotubes on Si substrates.

Fig. 3 shows the SEM images of surface morphology for Co–Ni alloy. The HF dipping etches metal surface and increases the surface roughness with increasing the HF dipping time, as shown in Fig. 3a,b. The subsequent NH$_3$ pretreatment further etches the surface and forms small domains inside the metal cluster, as shown in Fig. 3c, acting as nucleation
Fig. 1. SEM images of carbon nanotubes grown with gas flow rate of 40 sccm at 850°C for 10 min. Edges are vividly visualized by peel-off with a razor. (a) A uniformly distributed morphology of vertically aligned carbon nanotubes in large area of 20 × 30 mm². (b) Magnified top view. (c) Magnified tilted view of carbon nanotubes at the peeled edge. (d) Magnified view of (c). (e) TEM image of a single carbon nanotube in higher resolution. (f) The lattice image of a nanotube.
seeds for vertical alignment of nanotubes. The size of small domains within the metal cluster in Fig. 3c is about 200 nm, the same as the diameter of CNTs. This strongly suggests that carbon diffusion within the small domain is limited by the domain wall. With the absence of NH₃ pretreatment, nanotubes were laid down with a low density. Both HF dipping and NH₃ pretreatment were necessary to control the surface morphology to align nanotubes vertically in case of using the Co–Ni alloy.

Nanotubes grown on Ni-coated substrates had a diameter of about 100 nm, whereas diameters of nanotubes grown on Co-coated substrates were about 200 nm. However, nanotubes were not vertically aligned in both cases [14]. In case of the Co–Ni alloy, Ni particles have faster etching rate than Co particles during dry NH₃ etching. We found that Ni particles were etched away during dry etching of NH₃, which resulted in the increase of the density of nucleation sites within Co particles. This was confirmed by the energy-dispersive X-ray (EDX) spectrum (Fig. 3d). The amount of Co left on the surface after NH₃ treatment was about six times larger than that of Ni. Note that the amount of Ni was 1.5 times larger than that of Co in as-deposited samples. When the density of nucleation sites reaches a certain value, nanotubes grown in directions other than vertical direction are prohibited from growing due to the steric hindrance from the adjacent nanotubes and then the growth direction is changed to further grow vertically. This can be confirmed from some kinky nanotubes at the early growth stage, as can be clearly seen in Fig. 1d.

Fig. 4 illustrates our proposed growth model. C₂H₂ molecules are adsorbed on the metal domains. As carbon atoms are further supplied, a carbon–metal eutectic alloy can be formed, decreasing the melting temperature of the alloy. Formation of carbon–metal eutectic alloy promotes the diffusion of carbon in the metal alloy, initiating carbon aggregations followed by the nanotube formation, as shown in Fig. 4a. The carbon diffusion is limited by the domain size within the metal particles and thus the diameter of nanotubes should not be larger than the domain size. As the nanotube grows further, part of the metal domain is pushed upward, forming a metal cap, as shown in Fig. 4b. The metal cap saturates dangling bonds of the nanotube at the edge, stabilizing nanotube edges. Presuming sufficient supply of carbon atoms and high density of domains within the metal...
cluster, nanotubes are forced to align vertically, as shown in Fig. 4c. Some nanotubes at the edge of the cluster may not be aligned vertically at the initial stage but will be eventually aligned vertically by the steric hindrance from other nanotubes for further growth, as shown in Fig. 4c. As CNTs become longer, C$_2$H$_2$ gases may not easily reach the bottom of the substrate due to the compact CNTs highly populated on the surface. Instead, they will have a better chance to reach the top metal cap and then, adsorbed carbon atoms can diffuse into the edge of nanotubes. Formation of complete hexagons are catalytically promoted by the assistance of the metal cap [15], giving rise to the continuous cap growth. This model is able to provide uniform height of nanotubes in large area and control the height with growth time. Uniform growth in height may not be achieved on catalyst-patterned substrates with the model of base growth suggested in another report [11]. Our model can also explain the existence of the metal caps at the top of nanotubes after the growth, as observed from our SEM and TEM images and other reports [9,10].

The field emission patterns were observed from vertically aligned carbon nanotubes. Fig. 5 illustrates the emission patterns from 1.4 × 1.6 cm$^2$ in size with bias conditionings for (a) 30, (b) 60 and (c) 90 min. Fig. 5d shows typical $I$–$V$ curve from Fig. 5c.
Fig. 4. Schematic diagram of our growth model. (a) Formation of nucleation process, (b) cap growth, and (c) mechanism for vertical alignment at the initial stage.
along with the corresponding Fowler–Nordheim plot (inset). The anode, an ITO (indium tin oxide)-phosphor-coated glass, was separated from the bottom layer of nanotubes by a spacer in distance of 570 μm. The chamber was maintained at $1 \times 10^{-6}$ Torr during the $I-V$ measurements. Although samples were clean, as seen in Fig. 1a, they were annealed initially by repeatedly applying 100 and 1000 V in
order to burn unintentionally protruded nanotubes. This improves the emission patterns as shown in Fig. 5a–c. The turn-on voltage was about 1.2 V/μm with a current of 10 nA, which is much smaller than the other reports obtained from patterned nanotube–epoxy composite [8] and from single-wall nanotubes produced by arc-discharge [16]. Turn-on voltage also varies with the resistance of the transition metals.

For comparison, we have also fabricated patterned graphite powder–epoxy composite, which resulted in higher turn-on voltage, as shown in Fig. 5d. In spite of smaller effective emission area from CVD-grown samples, the emission current was much larger than that of graphite. The current increases sharply after turn-on voltage and saturates near 3 V/μm. The inset clearly shows that this field emission follows the Fowler–Nordheim equation. The presence of metal particles at the top of nanotubes prohibited efficient emission and some protruded nanotubes gave rise to non-uniform emission patterns. A keen control with bias annealings is required to have large emission currents by removing metal caps and uniform emission patterns over a large area. We emphasize that the present approaches are easily integrable within the current semiconductor process.

In summary, we have synthesized aligned carbon nanotubes on plain Si substrates using thermal CVD method. Vertically aligned nanotubes are uniformly synthesized on a large area of Si substrates. A new metal-cap growth mechanism is proposed based on the experimental observations. This approach should be easily applicable to a large area synthesis without loss of generality. We have also demonstrated the field emission patterns from the aligned nanotubes.

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References