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CVD 에 의한 대면적 실리콘기판위에서 수직방향으로 정렬된 탄소나노튜브의 성장

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Growth of vertically aligned carbon nanotubes on a large area silicon substrates by chemical vapor deposition

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Abstract

we have grown vertically aligned carbon nanotubes on a large area of Co-Ni codeposited Si substrates by thermal chemical vapor deposition using C_2H_2 gas. The carbon nanotubes grown by the thermal chemical vapor deposition are multi-wall structure, and the wall suface of nanotubes is covered with defective carbons or carbonaceous particles. The carbon nanotubes range from 50 to 120nm in diameter and about 130 μm in length at 950 °C. The turn-on voltage was about 0.8 V/μm with a current density of 0.1 $\mu A/cm^2$ and emission current reveals the Fowler-Nordheim mode.

1. Introduction

Since the first observation of carbon nanotubes [1], extensive researches have been done for the synthesis using arc discharge [2], laser vaporization [3], pyrolysis [4], and plasma-enhanced chemical vapor deposition (CVD)[5]. Although massive production of carbon nanotubes has been realized by arc discharge and laser vaporization [4], controlling diameters, lengths, and preferable alignment of carbon nanotubes has never been easily accessible with such approaches. Synthesis of well-aligned carbon nanotubes with high quality on a large area is necessary for their applications, such as flat panel displays, chargable batteries, etc. Here we report the growth of well aligned carbon nanotubes on a large area of Co-Ni codeposited Si substrates by thermal CVD using acetylene gas.

2. Experimental method

The p-Si substrates with a resistivity of 15 Ωcm were thermally oxidized with the layer thickness of 300 nm. Co-Ni (Co:Ni=1:1.5) metal alloys with 100 nm in thickness were thermally evaporated in a vacuum of 10^{-6} torr on oxidized Si(100) substrates. The samples were dipped for 100-200 sec in deluted HF solution and were then loaded on the quartz boat inside the CVD quartz reactor. Ar gas was flowed into the quartz reactor in order to prevent the oxidation of catalytic metal alloys while increasing the temperature. Samples were pretreated using NH_3 gas with a flow rate of 50-200 sccm for 10-30 min at 850-950 °C. Carbon nanotubes 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 room temperature in Ar ambient after the growth. Samples were examined by scanning electron microscope (SEM) (Hitachi, S-800, 30 kV) to measure tube lengths, diameters, site distributions, alignment, density, and uniformity. High resolution transmission microscopy (TEM) (Philips, CM20T, 200kV) was used to determine the wall structure of individual tubes. Field emission measurement was conducted in a vacuum chamber ($1x10^{-6}$ Torr). A positive voltage was applied to the anode and the emission current was measured with a electrometer (Keithley 619).

3. Results and discussion

Figure 1(a) shows SEM micrograph of well aligned carbon nanotubes which were grown at 950 °C on a large area (20 mm × 30 mm) of Co-Ni codeposited Si substrates. The carbon nanotubes are oriented vertically to the substrate and are uniformly grown with the length of about 130 μm. Figure 1(b) reveals high density of nanotubes with the diameter range from 50 to 120nm, where nanotubes are straight. Basically, the diameter of carbon nanotubes is dependent on the size of catalytic metal particles. Top view of the vertically aligned carbon nanotubes is shown in Fig. 1(c). When the density of nanotuebs reaches high value, nanotubes grown in directions other than vertical direction are prohibited from growing due to the steric hindrance from the adjacent nanotubes and then change the growth direction to further grow vertically.

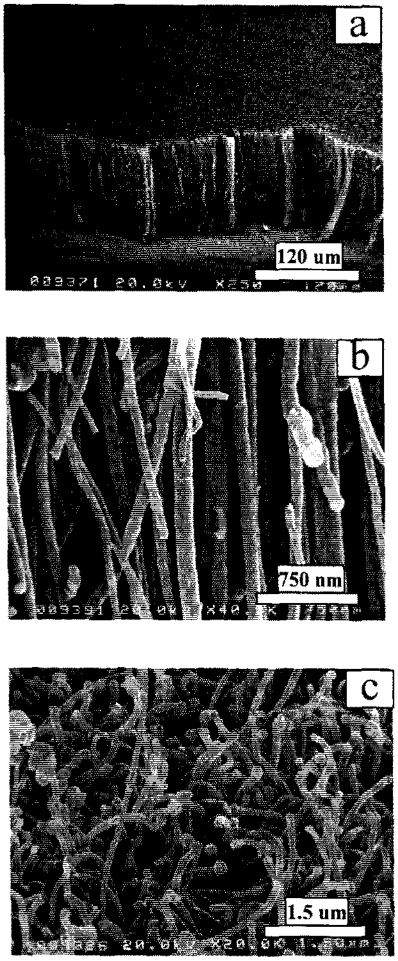

FIG. 1. SEM micrograph of well aligned carbon nanotubes grown with gas flow rate of 40 sccm at 950 °C for 10 min on a large area (20 mm × 30 mm) of Co-Ni codeposited Si substrates. Edges are vividly visualized by peel-off with a razor. (a) A uniformly distributed morphology of vertically aligned carbon nanotubes, (b) magnified side view of (a), (c) top view of the vertically aligned carbon nanotubes.

TEM analysis was performed on the carbon nanotubes grown at 950 °C to determine the wall structures. After ultrasonic treatment within aceton solution, Peeled nanotubes were dispersed on a copper carbon-microgrid. TEM image in Fig. 2(a) shows straight multi-wall nanotubes with an hollow inside and reveals different diameter of carbon nanotubes. Figure 2(b) shows the magnified TEM image of a carbon nanotube with 40 wall, where outer diameter of carbon nanotube is about 60 nm and inner diameter is about 40 nm. The magnified images show well-ordered lattice fringes of nanotube. In Fig. 2(b), the carbon nanotubes are multi-wall structure with good crystallinity but the surface wall of nanotubes has bad crystal structure due to the defective carbons. We have also tried various growth conditions. carbon nanotubes were grown well independent of growth temperatures within the temperature range of 850-950 °C, since C_2H_2 gases are highly decomposed in this range by the assistance of catalytic particles. The length of carbon nanotubes increased with increasing growth time and increasing growth temperature.

FIG. 2. TEM images show the carbon nanotubes were dispersed on a copper carbon-microgrid. Carbon nanotubes have discraped off a oxidized Si substrate directly onto a Cu TEM grid. The carbon nanotubes was grown with gas flow rate of 40 sccm at 950 °C for 10 min. (a) TEM image of carbon nanotubes. (b) High-resolution TEM image of the lattice structure of a single multi-walled carbon nanotube.

We note that the HF dipping and NH_3 pretreatment are very crucial steps to obtain high density of nucleation sites. Without NH_3 pretreatment, carbon nanotubes were grown uniformly but not vertically aligned. Therefore the NH_3 pretreatment is critical step in vertically aligning carbon nanotubes on Co-Ni codeposited Si substrates.

Figure 3 illustrates Field emission current density versus electric field from nanotubes grown on Co-Ni codeposited Si substrates. The anode was separated from nanotubes by a spacer in size of 200 μm. The chamber was maintained at 1 × 10^{-5} torr.

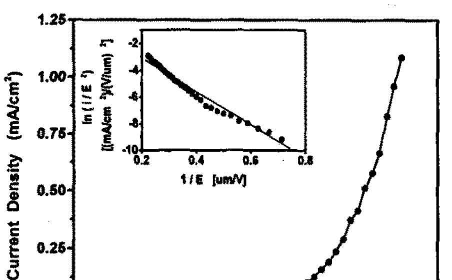

FIG. 3. Field emission current density versus electric field for well aligned carbon nanotubes grown on Co-Ni codeposited Si substrate. (Inset) Fowler-Nordheim plot. The linearity of this plot indicates that the emission is described by the Fowler-Nordheim equation.

The turn-on voltage was about 0.8 V/μm with a current density of 0.1 μA/cm^2, the maximum emission current density before electric breakdown was about 1.1 mA/cm^2 at 4.5 V/μm applied field. The presence of some protruded nanotubes gave rise to non-uniform emission current. The inset plot in Fig. 3 shows the Fowler-Nordheim plot for the aligned carbon nanotubes. In this figure, we observed nearly straight line to indicate Fowler-Nordheim behavior even though it was slightly deviated in the middle field region. Growth of vertically aligned carbon nanotubes on a large area of Si substrates using thermal CVD will allow a new era for field emission displays.

4. Summary

We have grown well aligned carbon nanotubes on a large area of Co-Ni codeposited Si substrates using the thermal chemical vapor deposition. The carbon nanotubes are multi-wall structure with good crystallinity but the surface of nanotube wall is covered with defective carbons or carbonaceous particles. Diameters of nanotubes are highly dependent on the size of catalytic metal particles. The turn-on voltage was about 0.8 V/μm with a current density of 0.1 μA/cm^2 and emission current reveals the Fowler-Nordheim behavior. The current approach with the thermal CVD is expected to be easily applicable to flat panel displays.

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