

Synthesis of uniformly distributed carbon nanotubes on a large area of Si substrates by thermal chemical vapor deposition

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We have synthesized carbon nanotubes by thermal chemical vapor deposition of C_2H_2 on transition metal-coated silicon substrates. Multiwalled carbon nanotubes are uniformly synthesized on a large area of the plain Si substrates, different from previously reported porous Si substrates. It is observed that surface modification of transition metals deposited on substrates by either etching with dipping in a HF solution and/or NH_3 pretreatment is a crucial step for the nanotube growth prior to the reaction of C_2H_2 gas. We will demonstrate that the diameters of carbon nanotubes can be controlled by applying the different transition metals. © 1999 American Institute of Physics. [S0003-6951(99)03438-5]

Since carbon nanotubes have been first synthesized by arc discharge,¹ extensive research has been done for the synthesis using arc discharge,^{2,3} laser vaporization,⁴ pyrolysis,⁵ and plasma-enhanced chemical vapor deposition (CVD),^{6,7} its unique physical and chemical properties,⁸⁻¹³ and applications to nanoscale devices.^{14,15} Although massive production of carbon nanotubes has been realized by arc discharge¹⁶ and laser vaporization,⁴ controlling diameters, lengths, and preferable alignment of carbon nanotubes has never been easily accessible with such approaches.

Uniform large-scale synthesis of well-aligned carbon nanotubes with high quality is a prerequisite for their applications to sophisticated nanoscale devices. Recent successful synthesis on glass by the plasma-enhanced CVD demonstrated the possibility of controlling alignment and diameters of carbon nanotubes.⁶ Different approaches using porous silica¹⁷ and Fe-patterned porous silicon substrate¹⁸ have been also tried for synthesis of vertically aligned nanotubes. However, sample-preparation conditions are too complicated to apply for the fabrication of nanoscale devices and furthermore controlling diameters is very difficult due to different pore sizes in porous media. Moreover, fabrication of carbon nanotubes on plain Si substrates is of technological importance for the applications to future Si-based optoelectronic devices. Here we report uniformly distributed carbon nanotubes on a large area of plain silicon substrates grown by thermal CVD. The metal-catalyzed silicon substrates are prepared by a simple process of HF dipping and/or NH_3 pretreatment. Diameters of nanotubes are controlled by the choice of Co or Ni catalysts.

The *p*-Si substrates with a resistivity of 15 Ω cm were thermally oxidized with the layer thickness of 300 nm. Co or Ni alloys with 100 nm in thickness were thermally evaporated at room temperature in a vacuum of 10^{-6} Torr. These samples were further annealed at 400 °C in Ar ambient for 20 min. This annealing procedure was necessary for strong adhesion of the metal layers with oxidized Si substrate. Annealed samples were dipped for 100–400 s in a HF solution (HF:de-ionized water=1:16) and were then loaded on the quartz boat inside the CVD quartz reactor of 60 mm in diameter. The size of the samples was 20 mm×30 mm. The quartz boat was designed to load several samples. Ar gas was flowed into the quartz reactor in order to prevent the oxidation of transition metal until reaching the reaction temperature. Acetylene gas was then flowed into the quartz reactor at 850–900 °C. The reactor was cooled slowly down to room temperature in Ar ambient after the growth.

Figure 1(a) shows the scanning electron microscope (SEM) image of carbon nanotubes on the Co-catalyzed Si substrate dipped in the HF solution for 300 s. Acetylene gas flowed at 15 sccm for 20 min. Synthesized carbon nanotubes are uniformly distributed with a relatively high density. No carbonaceous particles are observed over the entire surface area of the substrate. The nanotube diameters are about 200 nm with high selectivity. All nanotubes are laid down on the substrate with long noodle shapes. We note that all nanotubes are terminated by the metal particles at the end, in good agreement with the previous observations.^{4,6,17,19} This strongly suggests that the metal particles play a crucial role as a catalyst at the tip of the nanotube for the growth.^{19,20} No nanotubes are synthesized on Co-coated Si substrates with the HF dipping time of 200 s, as shown in Fig. 1(b). Instead carbonaceous particles are formed. Nanotubes were grown uniformly over the whole area with HF dipping time of up to

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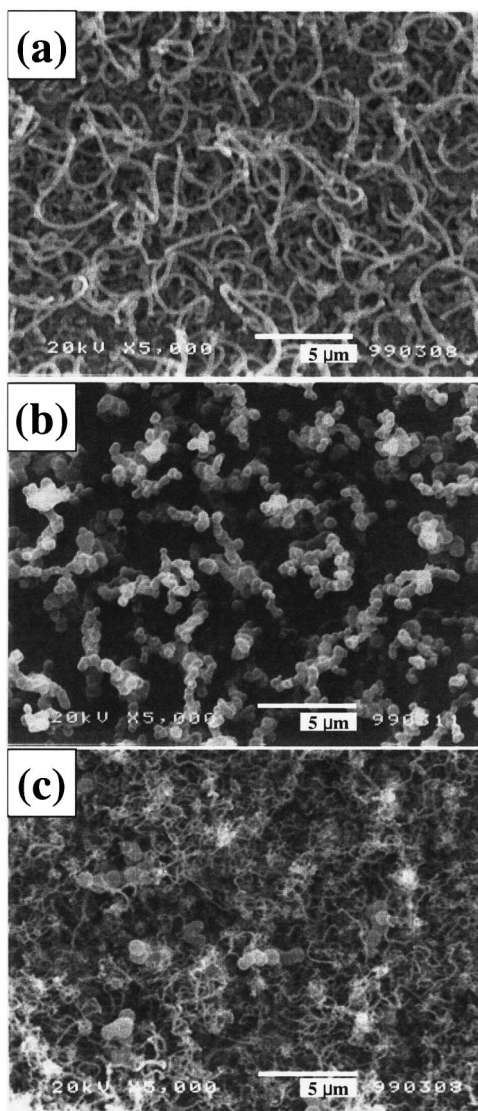


FIG. 1. SEM images of carbon nanotubes on Co-coated Si substrates with the HF dipping time for: (a) 300 s and (b) 200 s. No carbon nanotubes were grown for the shorter dipping time but instead carbonaceous particles were deposited. (c) SEM image of nanotubes on a Ni/Co-coated Si substrate.

300 s but catalytic layers were etched away after the HF dipping for 400 s. The choice of HF dipping time is correlated to the thickness of catalytic layers. Although the HF dipping time of 200 s was used, nanotubes were grown after the NH_3 treatment with a flow rate of 300 sccm for 10 min at 850°C . The diameter was the same but the density of nanotubes was reduced significantly.

In order to investigate the dependence of nanotube growth upon catalyst, Ni layers of 100 nm were further deposited on Co-coated Si substrates. The HF dipping for 200 s, followed by the NH_3 treatment of a flow rate of 300 sccm for 10 min at 850°C was done for surface treatment. Nanotubes were grown with the acetylene gas (flow rate: 40 sccm) for 10 min, as shown in Fig. 1(c). The diameter of nanotubes is about 100 nm, smaller than 200 nm on Co-coated surface. The density of nanotubes is low and the carbonaceous particles are also observed with nanotubes. We have also evaluated the effect of flow rates of NH_3 and HF dipping time on nanotube growth. The flow rates of NH_3 gas and HF dipping time controlled the densities of nanotubes but did not affect

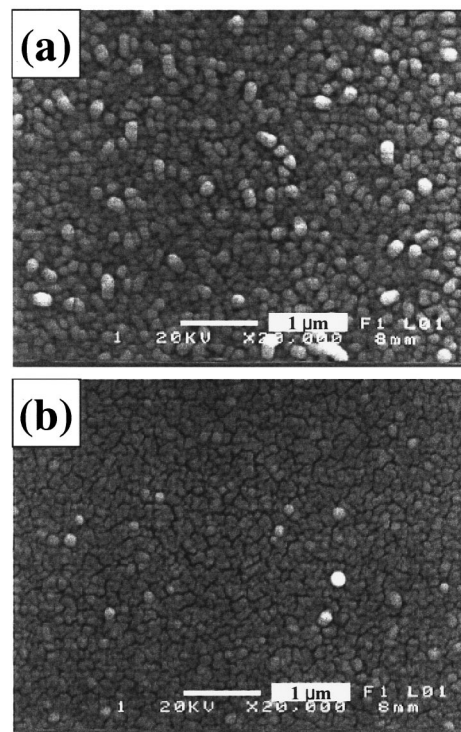


FIG. 2. The surface morphologies of Co metal layers on Si substrate, treated for different HF dipping times for: (a) 100 s and (b) 300 s.

diameters of nanotubes. A keen control is required to obtain dense and uniform nanotubes. This strongly suggests that the choice of metal particles is a way to control diameters. The domain sizes of the metal particles, which are directly correlated with the nanotube diameters,⁶ could be controlled by changing conditions of the metal evaporation.

Figure 2 shows the SEM images of the surface morphologies of Co-coated Si substrates with different HF dipping times. The HF dipping for 200 s [Fig. 2(a)] simply etches away the Co layer and increases the surface roughness. The HF dipping for 300 s further etches away the metal surface to make microcracks on the surface, as shown in Fig. 2(b). Further dipping for 400 s completely removes the Co layers on the oxidized Si substrate. This implies that the nanotube synthesis is critically dependent on the surface morphology of metal layers. We note that carbon nanotubes can be synthesized regardless of NH_3 treatment, contrary to the previous report that the NH_3 treatment can play a crucial catalytic role for the nanotube growth.⁶

Figure 3 shows the Raman spectra of carbon nanotubes grown by various methods. Micro-Raman spectroscopy (Renishaw micro-Raman 2000) was used with an excitation wavelength of 632.8 nm of a He-Ne laser. The single-wall carbon nanotubes were synthesized by arc discharge [20 V, 50 A, 210 Torr, in 5% of Ni-Fe mixture (Ni:Fe=1:1)].²¹ The diameter was about 10 nm from a high-resolution SEM measurement. The *G* line at 1583 cm^{-1} is clearly shown in Fig. 3(a), which is a characteristic of graphitic sheets.²² In addition to the *G* line, the side peak at 1543.7 cm^{-1} indicates the existence of single-wall nanotubes with different diameters.²³ Prominent low energy peaks at 190.5 and 215.4 cm^{-1} are the breathing modes of nanotubes vibrating along the radial direction.²³ The peak at 1724 cm^{-1} results from

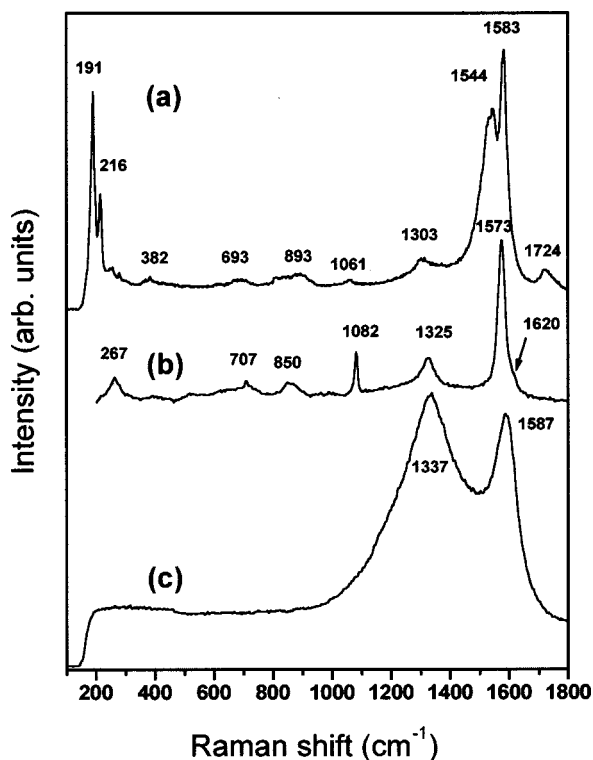


FIG. 3. Raman spectra of carbon nanotubes synthesized with various methods. (a) Single-wall nanotubes were catalytically synthesized with a Ni-Fe mixture at 360 Torr by arc discharge of a graphite rod. (b) Multiwall nanotubes were synthesized by arc discharge without transition metals at 500 Torr. (c) Carbon nanotubes were grown on Co-coated Si substrate by thermal CVD.

the second order Raman scattering of the breathing mode (190.5 cm^{-1}) and one of the *G* lines. This second order peak is also ascribed to the single-wall carbon nanotubes. The peak at 1303 cm^{-1} originates from either defective carbons or carbonaceous particles.²⁴ The peaks ranging from 400 to 1000 cm^{-1} are usually observed in single-wall nanotubes and could be related to the finite length of the carbon nanotubes.²⁵ We also show the Raman spectrum of multiwall nanotubes synthesized by arc discharge without metal particles (20 V , 50 A , 400 Torr),²¹ as presented in Fig. 3(b). The average diameter was about 100 nm . The clear *G* line at 1573 cm^{-1} with a small bump at higher energy side (1620 cm^{-1}) is assigned to the multiwall nanotubes. Note that no second order peak near 1720 cm^{-1} was observed in this case, indicating again the characteristics of multiwall nanotubes. Breathing modes are significantly diminished in the case of multiwall nanotubes. The above analyses strongly suggest that carbon nanotubes can be identified by Raman spectra. The Raman spectrum of nanotubes grown by the thermal CVD on Co-coated Si substrates clearly shows the *G*-line peak at 1587 cm^{-1} but no peak around 1730 cm^{-1} , as shown in Fig. 3(c). The broad peak near 1337 cm^{-1} indicates the existence of defective graphitic layers on the wall surfaces due to the relatively low growth temperature, although the surface morphology of the carbon nanotubes by the thermal CVD was clean and uniform over the entire area of the sample. No prominent peak on the lower energy side is observed. The Raman spectrum of CVD-grown nanotubes on Ni/Co-coated Si substrates was similar to that on Co-coated Si substrates, i.e., carbon nanotubes were multiwalled but not

straight, indicating again incomplete graphitization of the wall due to the low growth temperature. This analysis suggests that carbon nanotubes grown by the thermal CVD are multiwalled, although they include more carbonaceous particles on the wall surfaces.

In summary, we have grown uniformly distributed carbon nanotubes on a large area of plain Si substrates using thermal chemical vapor deposition. The surface was observed to be clean with no carbonaceous particles. Raman spectrum reveals clearly that the thermal CVD produces the multiwall carbon nanotubes. Diameters of nanotubes are highly selective with different choices of transition metals. It is very essential to control the surface morphologies of transition metal layers by HF dipping and/or NH_3 pretreatment for the growth of carbon nanotubes with high quality. The current approach with the thermal CVD is expected to be easily applicable to a larger size of the substrates.

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