Cobalt Ultrathin Film Catalyzed Ethanol Chemical Vapor Deposition of Single-Walled Carbon Nanotubes

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We report a simple and efficient chemical vapor deposition (CVD) process that can grow oriented and long single-walled carbon nanotubes (SWNTs) using a cobalt ultrathin film (∼1 nm) as the catalyst and ethanol as carbon feedstock. In the process, millimeter- to centimeter-long, oriented and high-quality SWNTs can grow horizontally on various flat substrate surfaces, traverse slits as large as hundreds of micrometers wide, or grow over vertical barriers as high as 20 μm. Such observations demonstrate that the carbon nanotubes are suspended in the gas flow during the growth. The trace amount of self-contained water (0.2−5 wt %) in ethanol may act as a mild oxidizer to clean the nanotubes and to elongate the lifetime of the catalysts, but no yield improvement was observed at the CVD temperature of 850 °C. We found that tilting the substrates supporting the Co ultrathin film catalysts can grow more, longer carbon nanotubes. A mechanism is discussed for the growth of long SWNTs.

Introduction

Growth of high-purity single-walled carbon nanotubes (SWNTs) with control over the tube orientation, length, and diameter is a continued challenge for fundamental research and future nanotube-based device applications.[1−4] Previous work on oriented growth required complicated sample preparation, specific growth procedures, or specific substrates.[5−12] For instance, strong electric fields were used to align the nanotube growth.[6−9] A "fast-heating" CVD process that involves a quick transfer of catalysts into a hot furnace was reported to grow long and aligned SWNTs.[13] A CVD growth with catalysts on elevated electrodes also resulted in long and oriented SWNTs.[14] It was also reported that high-density SWNT arrays can be oriented in growth on the *a*-place and *r*-plane of single-crystal sapphire substrates.[10,11]

Compared with methane and carbon monoxide, ethanol is potentially a better carbon feedstock because of its wide availability, safety, and ease in operation, and it does not tend to form amorphous carbon deposits that can inhibit nanotube growth.[15,16] Ethanol was previously used to grow long and oriented SWNTs in the absence of a fast heating technique,[16] and recently a 4-cm-long SWNT was also reported by using ethanol CVD though no orientation control was reported.[17] Amorphous carbon-free carbon nanotubes are very crucial for the applications ranging from nanoelectronics, biology, and surface functionalization. To grow high-purity SWNTs, a water-assisted CVD method, using metal thin film catalysts, was reported to synthesize impurity-free and vertically aligned SWNT forests, indicating that the addition of small amount of water can efficiently remove amorphous carbon at the CVD growth temperature and thus enhance the lifetime of the catalysts.[18] Metal thin films were used as efficient catalysts to grow SWNTs, especially those of long and vertically aligned, but so far the growth of long and horizontally oriented carbon nanotubes has not been reported.[18−21]

We report a simple and efficient CVD process that can grow high-purity, long SWNTs with good control over the tube orientation and length. We use ethanol with a trace amount of self-contained water (0.2−5 wt %) as the carbon source. The combination of ethanol and water may produce cleaner carbon nanotubes. Metal Co ultrathin films (0.5−2 nm) were used as the catalyst because they can be deposited by e-beam evaporation or sputtering, which is compatible with fabrication processes in the semiconductor industry. The ultrathin films can be used as the catalyst directly without further oxidative or reductive treatment. The process does not use external electrical fields or the "fast heating" technique. By using such a simple CVD process, oriented and long SWNTs can grow horizontally on substrates such as SiO_2/Si, Si, Si_3N_4, and Al_2O_3 and across narrow slits up to hundreds of micrometers wide and even grow over vertical barriers of micrometers high, which demonstrates the generality of this approach.

Experimental Section

The Si chips (∼4 × 4 mm) with slit structures (slit samples) were prepared from a Si wafer with Si_3N_4 epilayers on both sides. The slits (approximately 100 μm wide × 1 mm long) were fabricated by anisotropic KOH etching of Si using the Si_3N_4 layer as a mask. The Si chips with the slit structures on elevated stages (∼20 μm high) were also fabricated using standard photolithography and wet etching process. Co ultrathin films (approximately 0.5−2 nm, typically 1 nm in thickness) were deposited by using an e-beam evaporator (Semicore SC2000 E-beam evaporation system) with a deposition rate of 0.01 nm/s. A glass slide was used as a mask to make sure that

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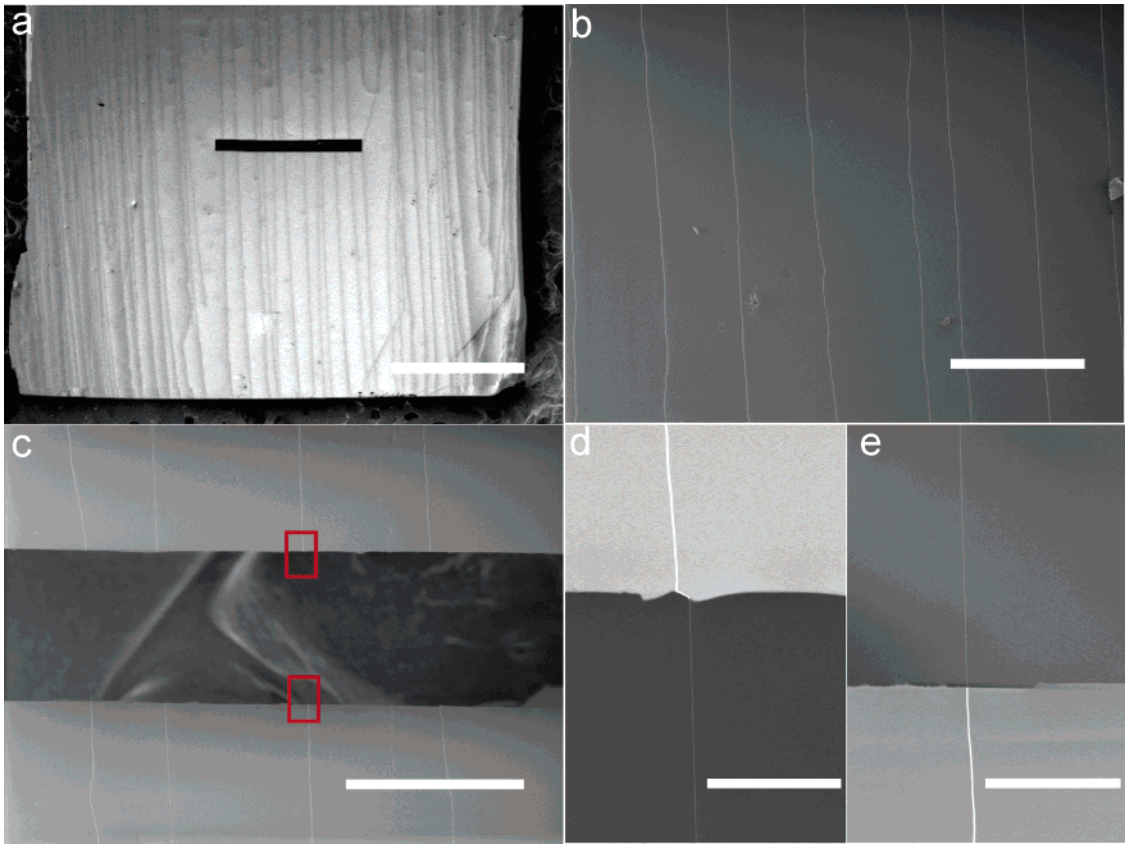

Figure 1. SEM images of (a) parallel array of SWNTs growing from one end (Co ultrathin film catalyst is on the top of the chip) to another end of a Si chip (~4 mm × 4 mm) with a narrow slit (90−100 μm wide) in the middle. The tube direction is parallel to the flow direction. Scale bar: 1 mm. (b, c) Higher magnification images of the SWNTs on the surface and across the slit, respectively. The feature between the slit is from the carbon tape underneath the chip. Scale bars: 50 and 100 μm, respectively. (d, e) Magnified contents in the two red rectangles in (c), showing SWNTs crossing both two edges of the slit. Scale bars: 5 μm. Ethanol with 5 wt % water was used as carbon feedstock for the growth.

Co only deposits on the edge of substrate (~0.5 mm away from the edge). The chips were placed in a CVD reactor with the slit perpendicular to the gas flow so that long nanotubes can be carried downstream over the slit. Ethanol with trace amount of water (0.2−5 wt %) was used as the carbon feedstock (Pharmco, ACS grade, 200 and 190 proof, respectively). The ethanol CVD was carried out in a 25 mm (o.d.)/22 mm (i.d.) quartz tube furnace at 850 °C for 20−80 min with the samples placed in the middle of the furnace.[16] The Co ultrathin film catalysts were gradually heated to 850 °C in an argon/H_2 (520 sccm/65 sccm) flow for 1 h before ethanol was introduced for nanotube growth. In a typical CVD growth, ethanol and water vapor was delivered by bubbling argon/H_2 mixed gas (10:1 by volume, 60−300 sccm) into an ethanol pool (0 °C). The ethanol was heated to boiling to remove any solvable O_2 and CO_2 before being used as the feedstock. Scanning electron microscopy images were taken on a Hitachi 4700 field emission SEM operated at 0.8 kV. Tapping-mode atomic force microscopy images were taken on a Nanoscope IIIa (Digital Instruments). Raman scattering was performed by a confocal microscope equipped with a Trix spectrometer. The tube diameters were estimated on the basis of d_t (nm) = 248 cm^{-1}/v_{RBM}.[22]

Results and Discussion

The Co ultrathin film catalyst was deposited on the edge of a Si chip with a slit structure. Scanning electron microscopy (SEM) images (Supporting Information) show that, after treatment at 850 °C in a CVD reactor before the reaction with ethanol, the as-deposited Co ultrathin film (~1 nm) balled up to form individual nanoparticles (~2−10 nm in diameter), consistent with previous reports.[20,21] Using ethanol CVD, relatively dense carbon nanotubes can be grown from the Co ultrathin film, usually in an entangled and random form. Some of them grow beyond the film and become well separated from each other with good orientation (Supporting Information). Figure 1 shows the SEM images of 4-mm-long and parallel carbon nanotube array growing from one end (Co ultrathin film catalysts) to the other end of the Si chip (~4 mm × 4 mm) with a narrow slit (~1 mm long × 0.1 mm wide) in the middle. The growth direction of long nanotubes is always parallel to the gas flow direction (Figure 1a). Long and oriented U-shaped nanotubes are occasionally observed (Supporting Information). High magnification images show that the parallel carbon nanotubes grow on the surface (Figure 1b) and cross the slit (Figure 1c). Generally, the density of long carbon nanotubes varies between 1 and 5 tubes/100 μm. Figure 1d,e shows the higher magnification images of a carbon nanotube on both sides of the slit (the magnified contents in two red rectangles in Figure 1c), clearly showing that the nanotube grows up to, across, and away from the slit. The carbon nanotubes growing across the slit form suspended nanotubes. It can be observed that the suspended tubes are always securely attached and straightened to both sides of the slit through van der Waals (vdw) interactions. The carbon nanotubes grown by the ethanol CVD can be identified as single-walled, as discussed later. In addition, it was found that SWNTs can grow horizontally on a variety of flat substrates including SiO_2/Si, Si, Si_3N_4, and Al_2O_3.

Usually, carbon nanotubes travel straight across the slits. In some cases, they may also crawl along the edges of the slits for micrometers long before crossing the slits (Figure 2) possibly

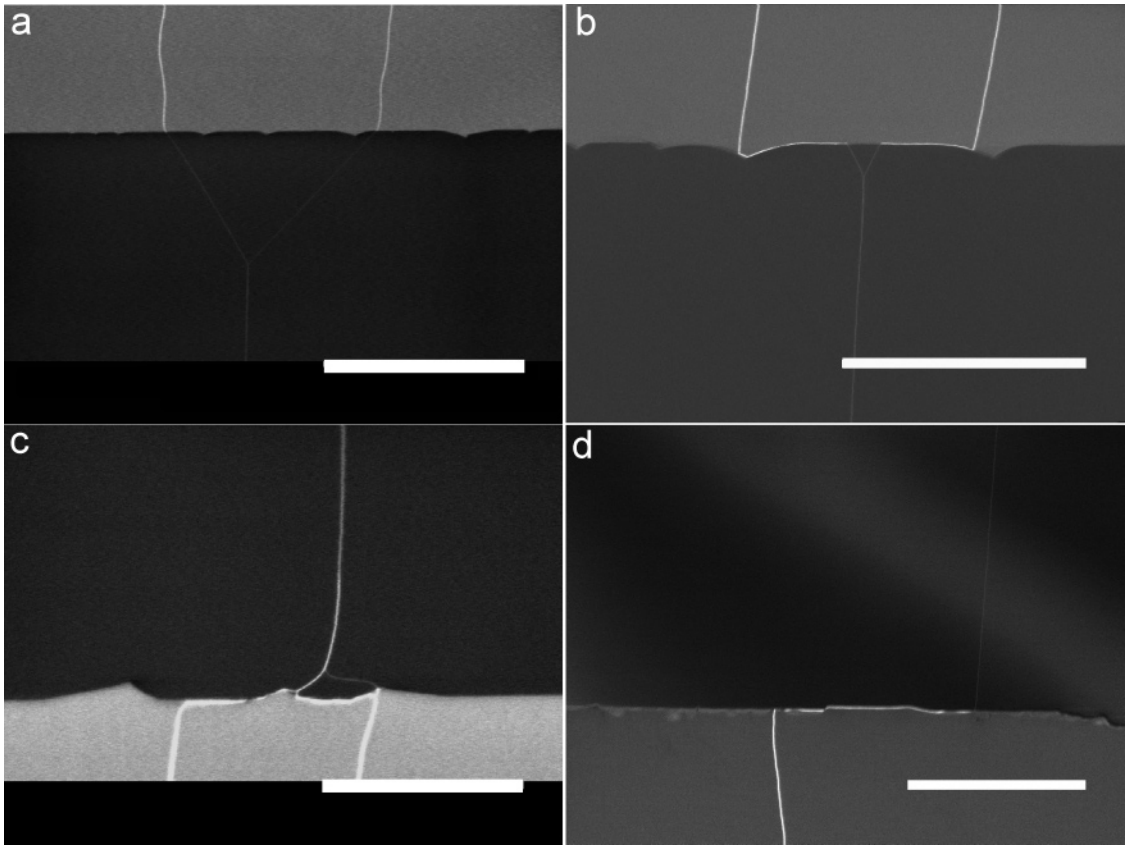

Figure 2. (a, c) SEM images of two neighboring SWNTs growing separately on the surface and jointly forming a small bundle in the slit. Scale bars: 10 and 3 μm, respectively. The nanotubes may crawl along the edge before going in (b) and off (d) the slits (b and d belong to two different slits). Scale bars: 5 μm.

because of the van der Waals interactions with sharp slit edges. When two neighboring nanotubes grow very close, they tend to attract each other and join together over the slit, forming small bundles, especially when crossing wide slits. Figure 2a,c shows two individual tubes growing separately on both sides of a slit and forming two "Y" geometries and a small bundle in the slit. A more complicated geometry (with crawling and bundling) is displayed in Figure 2b. Rayleigh scattering spectroscopy can be used to identify individual metallic and semiconducting nanotubes from small bundles,[23] and it showed that up to half of the carbon nanotubes bridging 100-μm-wide slits are individual single-walled carbon nanotubes instead of small bundles.

The SEM results also show that the tube orientation is always parallel to gas flow direction. By a change of the slit direction relative to the flow direction, SWNTs can grow across slits at different angles. In addition, SWNTs can cross multiple slits, and suspended carbon nanotubes were observed across slits up to 0.5 mm wide (in the form of small bundles). A crossed carbon nanotube array was also fabricated by changing the sample orientation relative to the gas flow during a two-step growth process (Supporting Information). Furthermore, we also found that the growth of oriented long carbon nanotubes can be promoted by altering the position of the chip relative to the gas flow direction. By a slight lifting up of one side of the chip sample where Co thin film catalysts were located (tilting by 2−10°), more parallel and centimeter-long carbon nanotubes can be grown from one end to the other end of a substrate. In our experiments, both tilted and leveled samples were put in the same chamber to make sure the CVD conditions were identical. The early data show that by raising the catalyst side, the number of longer nanotubes (~2 cm) increases by 50% to 4×. Figure 3 shows the growth of 1.5-cm-long nanotube array within a CVD time of 80 min, and the length could be longer if not limited by the dimension of the substrate. An oriented 4-cm-long carbon nanotube array was also observed on a 4-cm-long SiO_2/Si substrate after growth time of 2 h. The results suggest that the nanotubes can grow to extremely long dimensions and the length of tubes is only limited by the dimension of substrates used.[17]

It has been reported previously that carbon nanotubes can grow over barriers of less than 1 μm.[24] We observed this to be the case with our growth technique. Further, we observe that, in a simple ethanol CVD process, carbon nanotubes can easily grow over vertical barriers of tens of micrometers high. A 20-μm-high stage was first fabricated on a slit structure (Figure 4a and inset), and then a Co ultrathin film was deposited on the edge of the chip, about 2 mm away from the slit. After the ethanol CVD growth, Figure 4a shows that carbon nanotubes grow from one end to the other, and more interestingly, the nanotubes can also grow over such a high step (~20 μm tall). Figure 4c clearly shows carbon nanotubes clambering over the stage before crossing a 100-μm-wide slit. Part of the third nanotube from the left becomes less visible because it is suspended between up level and low level of the stage. A schematic view of the growth is shown in Figure 4d. The flexible way the carbon nanotubes grow is useful for device fabrication and also strongly supports the growth mechanism discussed later.

Carbon nanotubes grown by ethanol CVD are believed to be predominantly singled-walled by our characterization techniques. Ultimately, single nanotube analysis is the only true way to confirm that every nanotube is single-walled. Raman scattering spectra at 632 nm excitation show clear radial breathing mode (RBM) peaks, which confirmed the existence of SWNTs (Figure

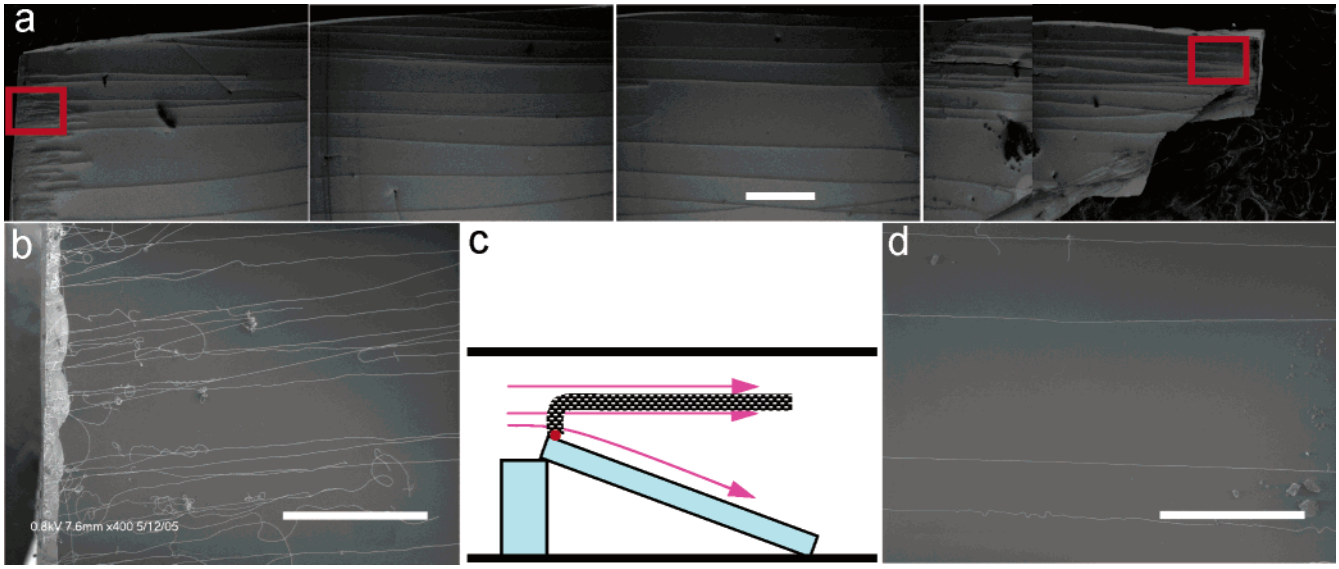

Figure 3. SEM images of (a) parallel array of centimeter-long carbon nanotubes growing on a SiO_2 (400 nm)/Si substrate (~1.5 cm in length). The growth starts from the left side of the chip (with Co thin film catalyst) to the right side of the chip. Scale bar: 1 mm. (b, d) Higher magnification images of the SWNTs on the left side (start point) and on the right side (two red rectangles), respectively. Scale bars: 100 μm. (c) Schematic view of the carbon nanotube growth. Ethanol with 5 wt % water was used as carbon feedstock for the growth.

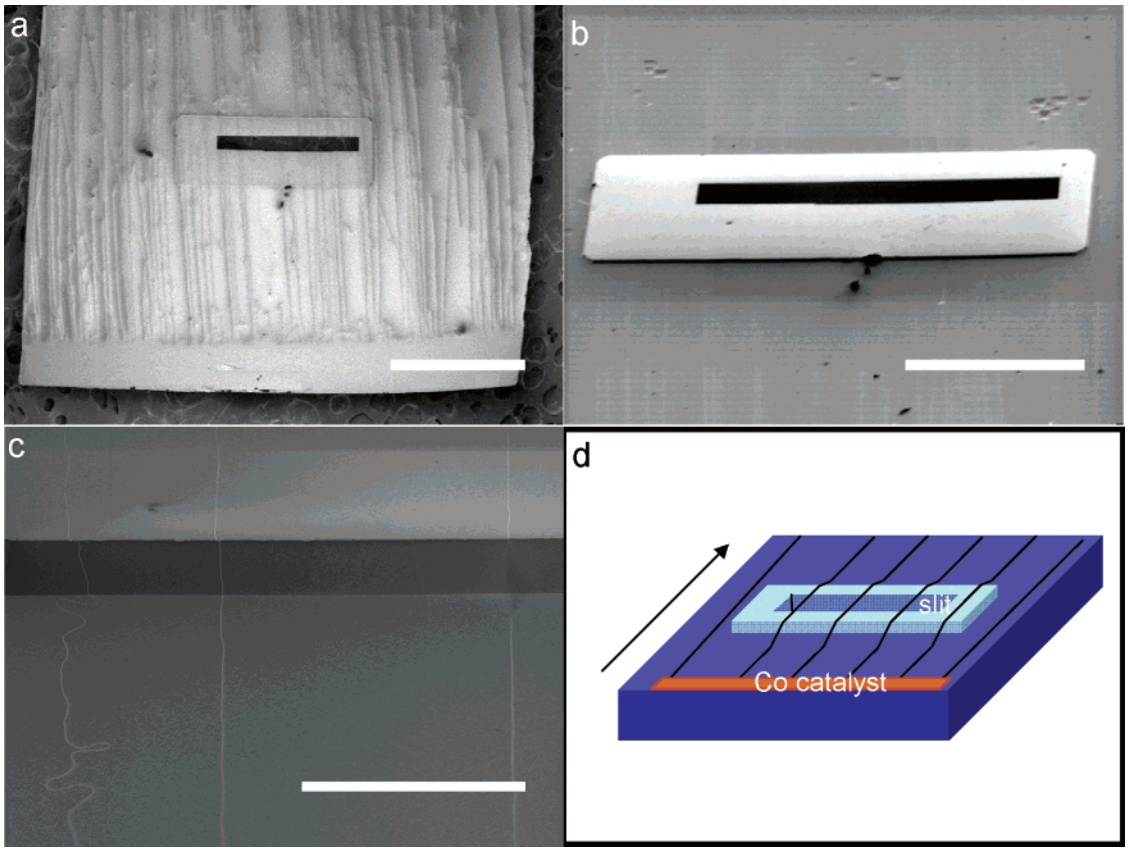

Figure 4. SEM images of SWNTs grow across a slit sample with elevated stage in the middle (~20 μm in height): (a) top view, scale bar 1 mm; (b) sample tilted by 45°, scale bar 500 μm. (c) High magnification image of the SWNTs in (b), showing the nanotubes clambering over the stage, with the sample is tilted by 45°. Scale bar: 50 μm. (d) Schematic view of the growth. The arrow shows the gas flow direction. Ethanol with 0.2 wt % water was used as carbon feedstock for the growth.

5). The high ratio of G/D bands in tangential modes indicates that the SWNTs have high structural integrity. The size of the SWNTs was estimated from the resonant RBM peaks to be in the range of 0.88−1.76 nm (on the basis of d_t (nm) = 248 cm^{-1}/υ_{RBM}).[22] About 10 long nanotubes were traced with tapping-mode atomic force microscopy (AFM) and were found to be individual SWNTs with diameters ranging from 1 to 2 nm (Supporting Information). The result is in good agreement with other observations that long SWNTs exist as single isolated tubes instead of small bundles.[22] High-resolution transmission electron microscopy (HRTEM) images of the slit samples also indicate that the suspended nanotubes are single-walled, and double-walled or multiwalled carbon nanotubes were rarely found (Supporting Information). Most of the suspended nanotubes have

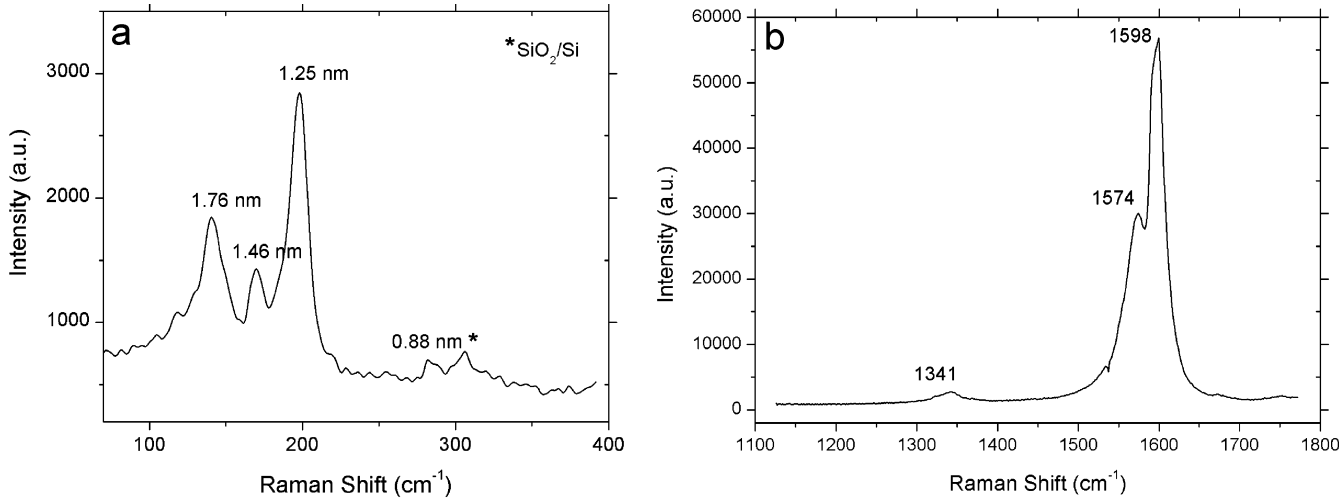

Figure 5. (a) Radial breathing modes of Raman spectra showing the presence of SWNTs on SiO_2/Si substrate surface. The laser excitation wavelength was 632.8 nm. (b) Tangential modes ($G(G_+, G_-)$ and D bands) of Raman spectra of the SWNTs grown on substrates. The laser excitation wavelength was 514.5 nm. The carbon nanotubes were grown using ethanol with 5 wt % water as the carbon feedstock.

a tube diameter of 1−2 nm, and a few tubes with diameters as small as 0.8 nm and as large as 2.5 nm were also observed. In addition, it is expected that the carbon nanotubes as-grown tend to be cleaner when using ethanol with trace amount of water as the carbon feedstock. However, some of the high-resolution TEM observations still showed a little amorphous phase on the nanotube surface. We found that the deposition of amorphous carbon phase could occur if the furnace was opened up too soon after turning off ethanol, so that the remaining carbon feedstock in the carrying gas may deposit amorphous carbon phase at lower temperatures. The TEM images (Supporting Information) show that the SWNTs become cleaner when the furnace was cooled naturally or stayed at the CVD temperature of 850 °C for a while (5−10 min) after disconnecting the carbon feedstock.

It was reported that a small amount of water can boost the growth of SWNTs using ethylene CVD at 750 °C.[18] We have also studied the effect of water on ethanol CVD growth at 850 °C. Within a small range of water content in EtOH (5 wt %), the expected yield improvement on the nanotube growth was not observed. When significant amounts of water was introduced to the EtOH CVD process (>30 wt %), long and oriented carbon nanotubes can still grow while the density of the carbon nanotubes appears to decrease. Strikingly, more large diameter carbon nanotubes could be produced, as suggested by the Raman spectra in Figure 6. The detailed investigation of the effect of water on the tube diameter and tube quality is ongoing within our research program.

It is accepted that, in order to grow long and oriented carbon nanotubes (either vertically or horizontally), the nanotube should grow above the surface because strong van der Waals interactions between the tubes and surface may hinder the smooth growth of the nanotube. The fact that the SWNTs can grow across slits or trenches as wide as hundreds of micrometers and grow over vertical barriers as high as 20 μm strongly indicates that the growing nanotube should float in the gas flow during the CVD growth rather than sliding along the surface of the substrates. The growth direction always follows the gas flow direction, and the nanotube can grow as long as possible without interfering with the surface. We propose that, at the early nucleation stage, a nanotube (with probability greater than 50%) can grow upward or vertically without any interactions with the surface and can therefore be caught by the gas flow. If the flow inside the CVD reactor is laminar flow, the growing

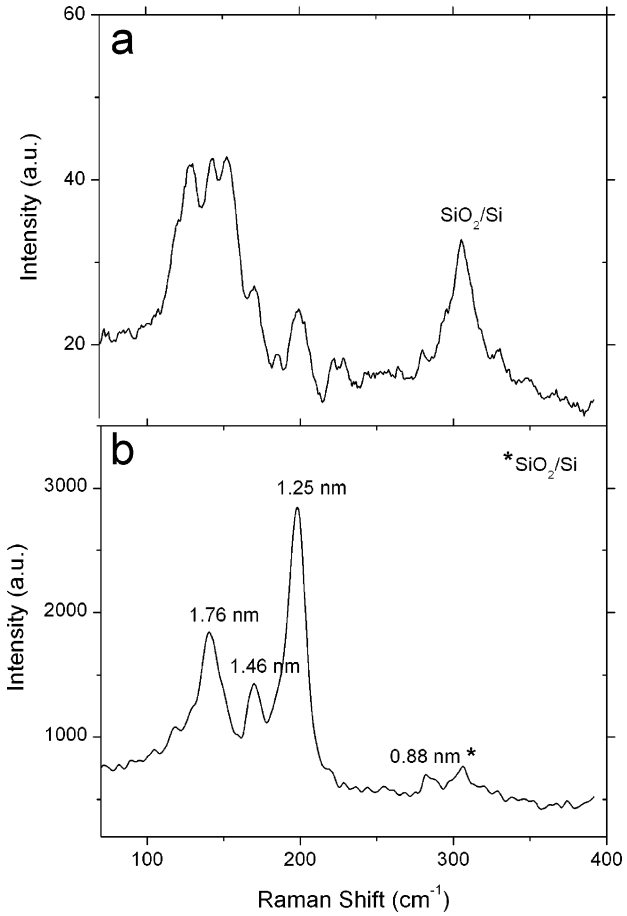

Figure 6. Radial breathing modes of Raman spectra of carbon nanotubes on SiO_2/Si substrate. The carbon nanotubes were grown using ethanol with (a) 30 wt % water and (b) 5 wt % water as the carbon feedstock, respectively. The laser excitation wavelength was 632.8 nm.

nanotube can grow freely in the direction parallel to the gas flow direction (Figure 7a), while turbulent flow or many nanotubes growing at the same time may cause the growing nanotubes to crash onto the surface and stop growth quickly.[25] The type of flow (turbulent or laminar), which is described by the Reynolds number, is dependent on multiple factors such as gas type, flow, temperature, and reactor size.[26] Calculations show that a laminar flow dominates inside the quartz tube during

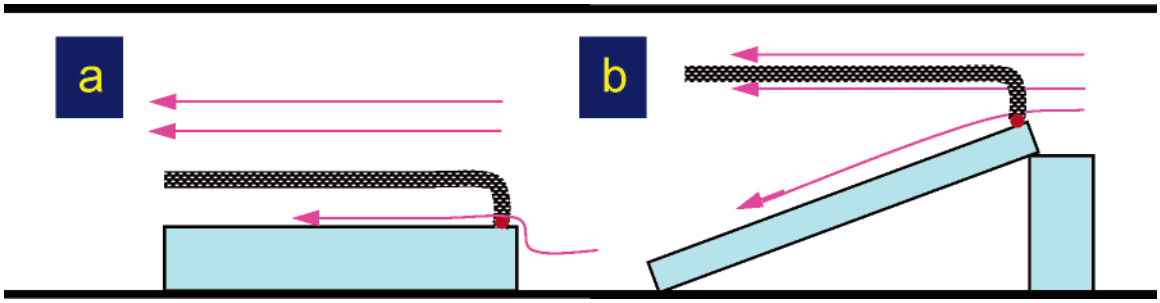

Figure 7. Schematic views of a possible mechanism of CVD growth of carbon nanotubes: (a) a carbon nanotube first grows upward and gets caught by the stable and ordered laminar flow and then grows in the flow steadily until gravity drags the tube down to the surface; (b) by a slight tilting of the sample to raise the catalysts, the carbon nanotube can stay in the gas flow for more time and hence grow longer.

the CVD growth (in the flow rate range of 60−300 sccm and the growth temperature of 850 °C). In addition, because of the enhanced lifetime of catalysts expected for the ethanol/water CVD, the nanotube could grow in the flow as long as possible until the catalyst nanoparticle loses its activity and the tube is pulled down to the substrate.

From previous reports, tip-growth and base-growth mechanisms are suggested for the horizontal and vertical growth of aligned and long SWNTs, respectively.[18,24] In our case, neither growth mechanism can be ruled out, and possibly both are responsible for oriented growth. Although the tip-growth mechanism is popular for the horizontal growth of long tubes,[24] the possibility of base-growth mechanism in this case is also considered. Since a uniform heating process was applied in our synthesis, there is little convection heating, as suggested in the "fast-heating" CVD process, which helps lift up the catalyst nanoparticles. We have demonstrated oriented growth by using CoMo-doped nanoporous silica catalysts.[27] Similar oriented growth was also observed for Co nanoparticles on Al_2O_3-coated substrates. In both cases, the Co nanoparticles are believed to be attached to the silica or Al_2O_3 matrix suggesting base growth. Further, the observation of long U-shaped nanotubes supports conjecture for a base-growth mechanism in which both ends of the nanotubes are pinned down on stationary catalyst particles/or surface: it is possible to conceive that a short tube might start to grow and that its end would graft to something and then growth would continue along the gas flow direction, generating a U-shaped configuration. Some indirect evidence shows that the Co thin film catalysts on the sample edge can repeatedly grow long carbon nanotubes after being reactivated by burning off the carbon nanotubes grown at previous time. There is no sign of reducing tube density due to the migration of catalytic Co nanoparticles as suggested by the tip-growth mechanism. AFM images suggest that the long single-walled carbon nanotubes do not necessarily have individual nanoparticles as tips although more convincing evidence should come from direct TEM observations. The results suggest that a base-growth mechanism is also possible for the horizontal growth of long carbon nanotubes, in addition to the reported vertical growth.[18] Because of the small mass of SWNTs and the motion of their growth, we believe the nanotubes are floating in the laminar flow while carbon species are continuously supplied to the catalyst nanocrystals pinned down on the surface. Thus, the nanotubes keep growing in the smooth laminar flow until the catalyst particles lose their activities or the growing tubes are pulled down by the gravity and finally rest on the substrate surface. Also, it makes sense that by slightly raising the Co thin film catalysts on one end of a chip with small angles (~2−10°), more carbon nanotubes can stay in the flow for a longer period and therefore grow longer (Figure 7b).

Conclusions

We have developed a simple CVD approach using Co ultrathin films as the catalyst and ethanol as the carbon source. The process does not rely on external electrical fields or any special heating techniques for growth. High-quality, oriented and long SWNTs can be grown horizontally on flat substrates such as SiO_2/Si, Si, Si_3N_4, and Al_2O_3, traverse slits of hundreds of micrometers wide, and even grow over vertical barriers of tens of micrometers high, which demonstrates the generality of this approach. The approach takes advantage of thin film technology and CVD growth using ethanol. It seems that ethanol−water is a better carbon feedstock in terms of its safety, ease in handling, supreme performance, and steam-cleaning capability. Ethanol with trace amount of self-contained water ($\leq$ 5 wt %) is an azeotropic liquid, so the compositions do not change during evaporation. Also, it is much cheaper than anhydrous ethanol, which suggests a great potential for scale-up production. The effect of water on SWNT yields, diameter control, and other properties is still under investigation. Metal Co ultrathin films are deposited by e-beam evaporation or sputtering technique, and after annealing, they are converted to individual Co nanoparticles as catalysts. Furthermore, the technique can be combined with ultrahigh-resolution lithographic patterning to prepare individual ultrathin catalyst islands with precise control over their location and diameter, which, in turn, affords better control over nanotube location and diameter.[28] In addition to the Co catalyst, the simple CVD process also works when Fe or FeMo nanocrystals are used as catalysts. The controlled growth of high-quality SWNTs is useful for fundamental research on individual carbon nanotubes. For instance, the suspended tube geometry allows characterization by multiple techniques, including Rayleigh scattering,[23] Raman scattering,[29] spectrofluorometry,[30] high-resolution transmission electron microscopy, and electron diffraction,[31] as well as mechanical transfer on arbitrary substrate by using recently developed transfer technique.[32] The controlled growth will also benefit the development of nanotube-based devices for future applications, such as FETs, sensors, NEMS, etc.

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Supporting Information Available: SEM images of Co ultrathin film, SWNTs growing across multislits with angles, a crossed carbon nanotube array, and AFM and HRTEM images of SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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