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Phases of Carbon Nanotube Growth and Population Evolution from in Situ Raman Spectroscopy during Chemical Vapor Deposition

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The dynamical evolution of nanotube chemical vapor deposition growth was investigated by in situ spectroscopy of three main Raman bands: G, D, and RBM. The evolution in diameter distribution is inferred from RBM and G bands, and the evolution in crystallinity is determined from D and G bands. A consistent sequence of the growth evolution is observed, with four discernible phases: incubation, acceleration, linear growth, and termination. The temperature dependence of each of these stages of growth is experimentally determined, and characteristic energy scales apparently associated with each phase are extracted. The growth becomes slower as the temperature increases, with activated, parasitic reactions suggested as a cause. We explore to what extent one diameter grows in comparison to another and thus gain some insight into how the nanotube population changes with time.

Introduction

Chemical vapor deposition (CVD) is the most widely used method for synthesizing carbon nanotubes. Driven by developments in fundamental science and applications, increased importance is being placed on high precision control of the product of synthesis. To better understand growth, nucleation, and termination processes, a considerable effort has been made to investigate the dynamics of nanotube CVD growth in situ. Because Raman spectroscopy is a highly developed characterization tool for nanocarbons that can be adapted for in situ use during nanotube CVD,^{1–7} it is a good approach for obtaining dynamical growth data.

Before describing the results of this study, we briefly review some aspects of carbon nanotube growth dynamics from past work. Early electron microscopy studies, prior to even the fullerene nanotube concept, showed that carbon filaments did not grow at a constant rate. They were instead observed to have an initial accelerating phase, a linear phase, and a decelerating phase.^{8,9} A more recent TEM study of single-walled nanotube (SWNT) growth identified three phases, namely, an initial incubation stage during which no growth was observed, an accelerating elongation of the single SWNT, and subsequent decelerating growth.¹⁰ Another avenue to explore the SWNT growth dynamics of high yield growth has been mass gain in microbalance experiments. Early in situ microbalance experiments on carbon nanotubes revealed an incubation period with no mass gain, followed by accelerating mass gain, and then a linear mass increase.¹¹

Recently, a great deal of progress has been made in studies concerning the dynamics of vertically aligned nanotube forests due to their macroscopic size, strong optical absorption, and the relative ease by which forest height measurements can be obtained. In fact, the high yield samples studied here give rise

to vertically aligned forests. Early reflectance studies of such samples showed that forests undergo an initial growth rate increase, followed by linear growth, and a subsequently decelerating growth rate.¹² Linear growth and deceleration phases were clearly observed for water-assisted ethylene CVD and parametrized by an exponentially decaying growth rate.¹³ In different forest studies, this has been confirmed to provide a good parametrization of the deceleration phase by absorption measurements,¹⁴ as well as by in situ Raman measurements,⁵ and video height measurements.^{15–18} In some cases, for these vertically aligned forests, the termination phase depends on an exponential decay in growth rate, whereas in other cases, it may have a second sudden termination phase.^{17,19–21} Some related studies have revealed, in addition to the linear and termination phases, the presence of an initial accelerating transient.^{16,17,20} During a recent high-vacuum CVD experiment, the initial incubation phase was also resolved.²² In that reference, it was suggested that the existence of the incubation phase may provide evidence for a new model describing the basic chemistry of nanotube synthesis.

The use of Raman spectroscopy for such studies can be particularly informative. Raman spectroscopy^{1,7} and global Raman imaging² are compatible with CVD and can be used to study both ensembles and individual nanotubes. Not only can the D and G bands be tracked during growth,^{7,23} providing information about yield and crystallinity, but also the RBM bands can be tracked during CVD,^{5,6} which provides information about diameter distributions. In previous in situ Raman studies of CVD growth, Chiashi et al. reported a linear increase in G band intensity during growth.¹ In subsequent work, we observed an exponential initial stage, as well as a gradual saturation stage for both D and G bands during low-temperature growth.⁷ A similar shape for the Raman evolution can be discerned in data from laser heating CVD experiments.³ Very recently, phenomenological models have been developed that can be used to fit these evolution curves.²⁴

In this work, we study the evolution of G, D, and RBM Raman bands within a range of growth temperatures (650–900

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°C) for two different “catalyst” seed particle formulations that generate different nanotube yields. A small subset of this data (two temperatures and one catalyst only) was presented in ref 6. We routinely discern four phases of CVD growth: incubation, acceleration, linear growth, and termination. We measure the temperature scaling of all four phases and show how crystallinity (D/G) and diameter distributions (RBMs) evolve in time and how they depend on temperature, before extracting the energy scales that are involved from activation-type plots.

Comparing the RBM band time evolution to the time evolution of the G band and to other RBMs allows us to explore the evolution of populations of nanotubes. That is to say, in an ensemble of nanotubes of different diameters and chiralities, we can explore to what extent one diameter or chirality grows in comparison to another and thus understand how the “population” changes with time.

We speculate on the origins of these phenomena. Different scaling observed for the two catalyst seed particle formulations suggests that the surface of the substrate plays an active role in the delivery of carbon to the growing nanotubes.

Experimental Methods

Raman spectroscopy in the spectral shift range of 100–1700 cm^{-1} was performed before, during, and after CVD growth. During growth, Raman spectra were taken at regular intervals, in order to construct a movie of the spectral evolution. The integrated intensity of each main spectral peak (G, D, and any visible RBMs) was computed, and the evolution of this integrated intensity as a function of time was obtained. This analysis was performed for a range of temperatures. The shape of the curve is described and characterized by four time scale parameters. The effect of growth temperature on these time scales was determined.

Experimental details were as follows. Substrates were silicon pieces (2.5 mm $\times$ 4 mm, 0.5 mm thick), with a 1 μm thermal silicon dioxide layer. A catalyst seed film was deposited by e-beam evaporation following two different recipes. For “Co samples”, only 1 nm of cobalt was deposited. For “Co-alumina samples”, 250 nm of alumina was deposited, followed by 1 nm of cobalt. In general, Co samples produced lower yields of surface nanotubes, but with higher SWNT crystallinity (i.e., lower D/G ratios) and higher RBM intensities, indicative of abundant SWNTs. Co-alumina samples produced much higher yields of nanotubes arranged in vertically aligned forests, but with lower crystallinity (higher D/G ratios) and significantly lower RBM intensities. Particularly at low temperatures, Co-alumina samples were likely predominantly MWNTs.

The reactor was a miniature hot walled tube furnace with optical access from one end (Linkam CCR1000).⁶ The temperature was measured by a thermocouple. A Raman spectroscopic imaging system was used to monitor the sample in plan view.^{2,6,7} Excitation was performed with a 532 nm laser beam at approximately 300 mW, defocused to an $\sim 100 \mu\text{m}$ diameter spot (with power density of $\sim 30 \mu\text{W}/\mu\text{m}^2$). Excitation and collection occurred through a 20 $\times$ long working distance microscope objective. The Raman signal was spectrally filtered and then dispersed by a 1800 line/mm grating on a 0.25 m spectrograph and detected by a TE cooled CCD. Along a separate optical path, the signal was also spectrally filtered but not dispersed to a TE cooled CCD camera, to obtain real-time images by global Raman imaging (GRI).^{2,7} The images were useful for verifying the uniformity and density of CNT growth. However, because nanotubes were too abundant, individual SWNTs could not be spatially resolved. Furthermore, the films

Figure 1. (a) Raman spectra for the Co sample grown at 850 °C. Growth proceeds from bottom to top at intervals of 22.5 s, from $t = 0$ s (when the ethanol valve opens) to $t = 1057.5$ s. Each frame has a 4.5 s exposure time. The green trace shows the time at which nanotube-related bands are just visible. The blue trace shows the time at which these bands are clearly visible. (b) Pregrowth (black) and postgrowth (red) Raman spectra at 850 °C and at (c) room temperature with 15 s exposure times. (d) Time evolution of the integrated G band (black) and RBM-1 (orange) intensities and the same data (e) scaled to the same final intensities.

were sufficiently uniform that GRI images showed virtually no spatial information beyond the laser excitation profile.

The CVD process was as follows.⁶ Briefly, each sample was purged in ~ 90 sccm argon/hydrogen carrier gas (Ar, 98%; H_2 , 2%), first at room temperature and then again at 200 °C, before being heated to the desired growth temperature. The flow rate was dropped to 2 sccm, and the gas was diverted through a bubbler containing liquid ethanol that served as the carbon source. After several minutes, growth was terminated by bypassing the bubbler with the carrier gas. This period lasted 20 min for Co samples and 5 min for Co-alumina samples. The sample reactor was purged at an ~ 90 sccm argon/hydrogen flow and cooled to room temperature.

Results and Discussion

Figure 1a illustrates the Raman band evolution during CVD growth for a typical Co sample grown at 850 °C. The time sequence progresses from bottom to top with each curve representing a 4.5 s integration time snapshot presented at 22.5 s intervals. Time $t = 0$ s is defined as the point at which the valve to the ethanol bubbler is opened. It takes a finite amount of time for the carbon source to travel the lines and reach the

sample, causing a delay before growth starts. We believe there is also a finite incubation time for the precipitation of carbon into the nanotube even once ethanol reaches the sample. There is a structured background ($150\text{--}250\text{ cm}^{-1}$) originating from the substrate. RBM and G bands are just barely distinguishable after $\sim 120\text{ s}$ (green) after the input of ethanol and are clearly resolved after $\sim 180\text{ s}$ (blue), eventually saturating. The G band shows a clear G^+ peak (at 1572 cm^{-1}) and a barely resolved G^- peak. Two high-intensity RBMs can be seen, one strong peak at (197 cm^{-1}) and a weaker shoulder that is just barely distinguishable on the lower-energy side. We label the strong RBM peak “RBM-1”, and it corresponds to a nanotube with a diameter of about 1.2 nm .

Both RBM-1 and its weak shoulder appear to track one another. Additional RBMs emerge at ~ 210 to 290 cm^{-1} , but they are too weak to track (gray arrows). The D band is also too low to be distinguished, mainly due to the D band intensity of these samples being weak even at room temperature. Low D/G ratios such as these are typical of high-quality SWNT growth.

The pre- and postgrowth Raman spectra at the growth temperature are shown in Figure 1b and at room temperature in Figure 1c. At high temperatures, the gradually increasing slope of the spectra originates from blackbody radiation. Peaks are also broadened at high temperatures. At room temperature, the G^+ (at 1597 cm^{-1}) and G^- (at 1575 cm^{-1}) peaks are clearly resolved and are upshifted compared to their growth temperature energies. A faint D band is visible (around 1333 cm^{-1}), for an integrated D/G ratio of ~ 0.02 . Although only one RBM (at 197 cm^{-1}) was clearly resolved at high temperatures, multiple high-intensity RBMs are clearly visible at low temperatures (e.g., at $184, 207, 229$, and 240 cm^{-1}). A brief discussion of observed temperature-dependent spectral band frequency shifting and intensity changes is given in the Supporting Information.

Figure 1d shows the evolution of the corrected integrated intensity for the G (black) and RBM-1 (red) bands as a function of growth time. Because the background is both temperature- and time-dependent, it is necessary to correctly subtract the background. Details of the algorithm used here are provided in the Supporting Information. Other bands (D and RBM) are too weak to track. Figure 1e shows the same data scaled so that the initial intensity is zero and the final intensity is unity.

An important point is that the RBM and G band resonance conditions are not the same. There is a resonance for both incoming and outgoing photons, the difference between which is set by the phonon energy.²⁵ Because the RBM is of low energy (about 25 meV), its resonant window is small, experimentally measured at a few tens of millielectron volts.^{26,27} The G band is much higher in energy (about 196 meV), and thus, its resonant window is much broader.²⁸ The G band, therefore, likely represents the evolution of many species of nanotubes, all of which are within the resonant window, whereas the RBM represents only one specific diameter.⁶ Low-temperature Raman spectra do reveal that there are many RBMs present in these samples (most not discernible at high temperatures), meaning that there is a very broad range of diameters and very likely also chiral angles. The essentially identical evolution of the G and RBM-1 bands is, therefore, surprising because the two are expected to sample very different subsets of the total population of nanotubes. The easiest way to understand this is if all SWNT species evolve at the same rate, meaning that there is likely no net evolution in the diameter distribution.⁶

All extracted G band, D band, and RBM band evolution curves for all growth runs at all tested temperatures are provided

Figure 2. (a) Raman spectra for the Co sample grown at $813\text{ }^{\circ}\text{C}$. Growth proceeds from bottom to top at intervals of 20 s , from $t = 0\text{ s}$ (when the ethanol valve opens) to $t = 700\text{ s}$. Each frame has a 5 s exposure time. The green trace marks the onset of the nanotube-related signal, which becomes more clearly visible in the blue trace. Two RBMs are clearly visible in the violet trace. (b) Pregrowth (black) and postgrowth (red) Raman spectra taken at $813\text{ }^{\circ}\text{C}$ and at (c) room temperature. Pre- and postgrowth spectra have 15 s exposure times. (d) Time evolution of the integrated G band (black), RBM-1 (orange), and RBM-2 (blue) intensities and (e) the same data scaled to the same final intensities. For the RBM-2 band, the intensity at $t = 175\text{ s}$ is set to 0.45 to match the corresponding G band value at this time (see text).

in the Supporting Information. Overall, the RBM tracked the G band to a reasonable approximation across all Co samples. Only the low-energy RBM-1 ($\sim 197\text{ cm}^{-1}$) was clearly resolved at high temperatures, whereas at low temperatures, only a higher-energy peak ($\sim 277\text{ cm}^{-1}$), henceforth referred to as “RBM-2”, was clearly resolved. (RBM-2 corresponds to a tube with a diameter of approximately 0.9 nm .) The shift to large diameters with higher temperatures is consistent with findings from previous reports indicating that larger diameter nanotubes grow preferentially at higher temperatures.^{29,30} Generally, RBM-2 peaks were found to track well with the G band, similar to the RBM-1 band tracking at higher temperatures.⁶

In an intermediate band of temperatures, RBM-1 and RBM-2 were intense enough to track concurrently for a time, although unfortunately neither RBM signal was strong. However, concurrent tracking of multiple RBM bands is important because this provides direct information about the evolution of diameter distributions during growth. From our data, the best example so far is the Co sample grown at $813\text{ }^{\circ}\text{C}$, whose evolution is depicted in Figure 2a. A 5 s integration time at 20 s intervals is

shown. The RBM-1 and RBM-2 peaks are distinct and well-separated, representing SWNTs with diameters that differ by over 30%. The RBM-1 and G signal onsets occur as early as 40 s (green) and are evident at 60 s (ca. frame 4, blue). Unfortunately, the RBM-2 signal lies between two substrate-related peaks at 240 and 306 cm^{-1} , and this makes it difficult to track until it becomes intense. The broader RBM-2 has emerged sometime before 140 s (violet), together with an even weaker RBM peak at $\sim 255 \text{ cm}^{-1}$. The remaining RBMs are too weak and unresolved to track.

The pre- and postgrowth Raman spectra are shown at the growth temperature in Figure 2b and at room temperature in Figure 2c. Although only two clear RBMs were resolved at high temperatures, many room-temperature RBMs are present (e.g., at 184, 207, 228, 240, 247, 283, and 301 cm^{-1}). At room temperature, the G+ (at 1598 cm^{-1}) and several G- (at 1551, 1528, and 1505 cm^{-1}) peaks are clearly resolved. The D band is visible (around 1327 cm^{-1}), with an integrated D/G ratio of ~ 0.04 that indicates lower crystallinity as compared with the higher-temperature 850 $^{\circ}\text{C}$ sample.

The RBM intensity distribution shift with temperature is evident here as well. For example, the 240 cm^{-1} peak is more intense on the 813 $^{\circ}\text{C}$ grown sample, whereas the 184 cm^{-1} peak is significantly less intense. This indicates a shift to larger diameter nanotubes at higher growth temperatures. Additionally, the G- peak in Figure 1b (at 1575 cm^{-1}) is at a higher frequency than the most intense G- peak in Figure 2b (at 1551 cm^{-1}), also indicating the presence of larger diameter nanotubes in the higher-temperature sample.³¹

Figure 2d shows the evolution of the integrated intensities of the G, RBM-1, and RBM-2 bands as a function of growth time. Both RBM peaks track the G band to a reasonable approximation. RBM-1 follows the G band very closely. The early stage of evolution of the RBM-2 band is unclear, and it appears at first glance that it may emerge later than RBM-1. This is mainly because it is difficult to isolate the initially weak signal of RBM-2 due to its position between substrate-related peaks. As a result, RBM-2 values are difficult to obtain prior to ~ 150 s.

In Figure 2e, the RBM-1 and G are normalized so that their values are 0 at time zero and unity at the end of the experiment, as before. Unfortunately, the weakness of the RBM-2 signal and the magnitude of the noise at early times make normalization at early times subject to the noise and biased by the poor visibility of RBM-2. To sidestep this problem, instead of normalizing at $t = 0$ s, we chose a point where the RBM-2 signal was already well above the noise, at $t = 175$ s. We shifted the curve so that it matched at the others at this point. We then scaled the final point to unity as before. In other words, to compare RBM-2 to the other bands, we set its final value at $t = 800$ s to 1 and its value at $t = 175$ s to 0.45 (corresponding to the scaled G band value) (Figure 2e).

Scaled this way, all three peaks appear to track each other well for all later times. This provides evidence, at least to an approximation, that both RBM bands track each other. We understand the deviation at early times to be an artifact of the weakness of the signals at that time and the difficulty of subtracting the background. If correct, this is notable because it indicates that there is little or no change in diameter distribution during the growth process, even for nanotubes that differ in diameter by over 30%.

In comparison to the Co catalyst samples discussed above, the Co-alumina catalyst provides a much higher nanotube yield, potentially allowing us to examine early stage dynamics more

closely, while also providing some insight into which aspects of growth might be particular to the specific catalyst film. Co-alumina also produces material of lower crystallinity, which results in a higher D band that allows a comparison of D and G band evolution. One drawback here is that the yield on most samples becomes so high that visible light could not penetrate beyond some characteristic depth. This results in the loss of meaningful Raman tracking past certain forest opacity and also an increase in scattered light background as the surface went out of focus. We, therefore, only consider the initial stage of growth of the Co-alumina samples here.

We emphasize that these samples contain a mix of SWNTs, MWNTs, and other carbons. In the lower-temperature regime, with the Co-alumina catalyst, there may be very few or perhaps even no SWNTs. At high growth temperatures, however, low intensity RBMs are sometimes detected and thus some SWNTs are present. Compared with the Co catalyst samples, a higher D/G ratio provides indirect evidence that it is primarily MWNTs that are grown.

The evolution of the Raman spectra for a Co-alumina sample grown at 700 $^{\circ}\text{C}$ is shown in Figure 3a. Strong D and G bands were both obtained; however, no RBMs were detected, so this region is not shown. Spectra are shown at intervals of 4.9 s from $t = 0$ s to $t = 126.7$ s, with each frame representing a 0.7 s exposure. Both the D and the G bands emerge as early as ~ 60 s (green). The G and D peak intensities in Figure 3a appear to saturate at a maximum value after ~ 125 s (uppermost spectrum). At roughly the same time, the background starts to rise, obscuring the bands, and the data become difficult to analyze.

We were not able to clearly resolve RBMs during growth for the Co-alumina samples and thus were not able to determine how they scale or how their diameters evolve. Raman spectra suggest very few SWNTs grow at low temperatures. Samples grown below 775 $^{\circ}\text{C}$ showed no RBMs even at room temperature, whereas for samples grown above 775 $^{\circ}\text{C}$, low intensity RBMs did become visible at room temperature. However, the D band also becomes weaker at these higher temperatures, and although it qualitatively appears to evolve much like Figure 3a, it was too weak to extract a meaningful D band evolution curve. The yield dropped to 0 at higher temperatures, a result that might be caused by changes to the alumina³² or the mobility of defects.¹⁵

Pre- and postgrowth Raman spectra at the high growth temperature (775 $^{\circ}\text{C}$) are shown in Figure 3b and at room temperature in Figure 3c. Figure 3b also includes a spectrum taken at $t = 150$ s during growth, before the forest becomes completely opaque and goes out of focus. At room temperature, RBMs can be seen in the ~ 175 to 300 cm^{-1} region. As with the Co samples, the D/G ratio is lower for samples grown at higher temperatures, and for a given growth temperature, the D/G ratio is significantly higher for Co-alumina samples than for Co samples.

The G and D bands of the Co-alumina samples track each other. Figure 3d shows the evolution of the G and D bands of the 700 $^{\circ}\text{C}$ grown sample, along with the first-order silicon band (at $\sim 513 \text{ cm}^{-1}$), for reference. The silicon peak drops off as the nanotube film becomes thick and opaque, and the spectral background increases significantly, obscuring the G and D bands. It is, therefore, not very meaningful to track the G and D band evolution once the silicon peak becomes very weak.

There is some evolution of the silicon peak on many samples at an early stage, perhaps indicating an evolution in the opacity of the catalyst film. Other groups have seen reflectivity changes

Figure 3. (a) Raman spectra for the Co-alumina sample grown at 700 °C. Growth proceeds from bottom to top at intervals of 4.9 s, from $t = 0$ s (when the ethanol valve opens) to $t = 126.7$ s. Each frame has a 0.7 s exposure time. The green trace marks the time when the carbon nanotube-related bands are just barely visible. (b) Pregrowth (black), postgrowth (red), and intermediate growth (blue) Raman spectra at 775 °C and at (c) room temperature, using 15 s exposure times, except for the intermediate spectrum. The intermediate growth spectrum is taken at 150 s, just prior to the change in spectral background due to excessive growth, using a 0.7 s exposure time. Its intensity is, therefore, scaled by a factor of 15/0.7. (d) Time evolution of the integrated G band (black), D band (violet), and substrate-related first-order Si band (green) intensities. (e) The same data scaled to the final saturated intensities. All data are sampled continuously with a 0.7 s exposure time and are background-corrected.

due to roughening of the catalyst at this stage.³³ It is possible that the small signal change is related to this effect. Regardless, as long as the silicon peak remains relatively strong, the grown layer is reasonably transparent and we consider the nanotube-related Raman signals to be representative of the actual nanotube growth.

As seen in Figure 3e, consistent G and D tracking is evident after signal normalization. The curves have been normalized by scaling the evolution curves so that they reach the same maximum value, normalized to unity.

At higher growth temperatures, the D band intensity is lower and it becomes difficult to compare G and D scaling. The initial growth of the D band may lag slightly behind the G band, but this may just be a consequence of the D band falling below the noise level for the very initial stage. Regardless, the matching evolution of the growth curves of the G and D bands likely signifies that both sp²-like and sp³-like carbon are deposited at the same rate. In other words, the crystallinity of the grown nanotubes does not evolve in time.

Figure 4. Proposed four-step growth sequence for all G, D, and RBM integrated intensities: (a) incubation in the presence of the source gas, (b) accelerating growth, (c) linear growth, (d) growth termination/saturation.

All growth evolution curves share a common characteristic shape that can be divided into separate growth steps, as schematically depicted in Figure 4. Here, we divide this into four separate steps: incubation, acceleration, linear growth, and termination. We characterize each of these steps by a time scale. The acceleration phase and termination phase are fitted by exponentials, and the time scale is the characteristic time of the exponential. The incubation and linear growth phases are characterized by their duration. Equations used to fit these kinetic curves and examples of fits are provided in the Supporting Information. Characterizing each phase in this way avoids any dependence on the temperature-dependent Raman signal and any variability in yield that could arise either across a sample or run-to-run.

After opening the carbon-containing source gas valve, we consistently observe a delay period prior to any detectable spectral band change. Part of this delay is due to the time it takes for the gas to travel through the gas lines and reach the sample. We used the same fixed gas flows for all growth runs, so we assume that this gas transient was the same for all samples and set it equal to the minimum observed delay time, which was 30 s for the lowest-temperature Co samples. Clearly, this part of the delay is dependent on the particular gas delivery system.

After subtracting this minimum travel time, there was generally still a measurable, additional temperature-dependent incubation time (t_{inc}) required to nucleate SWNTs and obtain a detectable Raman signal. We defined this incubation time as the time elapsed between the end of the 30 s gas travel time and the time at which the G band was just above the signal-to-noise level.

Following this step, we observed an accelerating growth phase. This part of the data was fit well by an exponential function, $\propto \exp(t/\tau_{acc})$, from which an associated characteristic acceleration time (i.e., τ_{acc}) was extracted.⁷ (Sample fits of all phases are shown in the Supporting Information, Figures D1 and D2.) This phase likely corresponds to an initial accelerating lengthening step. Stochastic-like nucleation may also be a cause, however, and further work is needed to determine the relative importance of these two effects.

After this, there is a steady linear growth phase, most likely corresponding to steady lengthening. Although this linear step is well-defined in some cases, in many cases, it may not represent a truly well-defined step, but rather just a brief crossover between the initial exponential acceleration and the

subsequent termination step. Regardless, we parametrize it by the duration in which the increase in Raman signal is nearly linear (t_{lin}).

Finally, we obtain a good exponential fit to the final growth termination phase, which is consistent with previous studies.^{3,13,34} We fit to an exponential, $\propto \exp(-t/\tau_{\text{term}})$ and parametrize this step by the characteristic time (i.e., τ_{term}). In some cases, growth did not stop completely but instead continued to experience a very slow, but steady, increase in Raman intensity. For the Co samples, we did not observe any additional sudden termination. This is perhaps not surprising because these were surface tubes, and sudden termination has only been reported for forests. For the Co-alumina samples, we cannot say whether or not sudden termination occurred because of the problem of the opacity of the forest and scattering from the top surface.^{17,19–21}

We investigated the temperature dependence of all four steps. Here, the characteristic times of each step were found to increase at higher temperatures. Chemical processes usually run faster at high temperatures, so this suggests that processes that prevent carbon from being properly incorporated into the crystalline lattice of the nanotubes are important. There may be one or more competing processes that remove carbon at a rate faster with increasing temperature than the rate of the proposed carbon-addition processes. Chemical reactions do not only take place at the nanotube growth front; competing reactions can also occur in heated volumes or surfaces. For example, carbon might be removed in the gas phase before reaching the substrate surface by accumulating on the reactor walls. It also may desorb from the surface or diffuse away from catalyst particles. It is likely that the very low rate that ethanol vapor is supplied in this experiment increases the sensitivity of this process to such effects.

The temperature dependence of the time scales extracted from the G band for all four steps of the Co samples and the first two steps for the Co-alumina samples is plotted on “activation plots” in Figure 5. The steps may or may not be limited by activated processes. Such processes can be revealed in activation plots. Although the relationships between these characteristic times, step durations, and growth rates are not always straightforward, it is still useful to plot the characteristic times in this way. A straight line on such a plot is a good indication that activated processes are important to the dynamics either in the formation of nanotubes or in competing processes.

The corresponding data for other bands are presented in the Supporting Information. For the sake of comparison between the two sample types, characteristic energies could be extracted in all cases (Table 1). All of these, interpreted as “activation energies”, would give negative values, meaning that the growth is slower at higher temperatures. Such negative characteristic energies can arise naturally if a parasitic process is consuming material faster than the process being monitored. For example, these may be the result of normal (positive) activation energies for carbon sink processes that compete with and inhibit nanotube formation and lengthening. It should be noted that, because the sampling rate for Co samples was once every 5 s, any corresponding Co t_{inc} values on the order of 5 s are not meaningful and represent only the sampling rate.

For the Co samples, the incubation and acceleration steps have similar associated energies, suggesting that the same process, possibly a carbon removal process, might limit these two steps. The large energy (~ 4.5 eV) suggests that a chemical process, such as a gas-phase reaction (e.g., pyrolysis), or a highly energetic surface process, such as desorption of chemisorbed carbon, may be responsible.

Figure 5. Characteristic energy plots for the (a) incubation time, (b) acceleration time, (c) linear time, and (d) termination time. Times derived from the integrated G band intensity of the Co (white circles) and Co-alumina (black squares) samples are plotted. Characteristic energies correspond to the slope of the linear plots (red lines).

Also, for the Co samples, the linear and termination phases have similar associated energies, but these energies are much lower than those of the first two phases. This suggests that termination is caused by an entirely different process than that which limits the nucleation and acceleration.

For the Co-alumina samples, we were only able to extract the incubation and acceleration times. The associated characteristic energies are the same to within experimental error. Their magnitude is about half that of the Co-alumina samples. Interestingly, the Co-alumina incubation and acceleration times are longer than those of the Co samples. One possibility is that

TABLE 1: Characteristic Energies Associated with Each Stage of Growth

sample/growth stage	Co (eV)	Co-alumina (eV)
incubation	4.7 ± 0.8 ^a	1.8 ± 0.6 ^b
acceleration	4 ± 1 ^c	2.0 ± 0.4
linear growth	1.4 ± 0.6	
termination	0.6 ± 0.5	

^a 800–875 °C. ^b 775–875 °C. ^c 825–875 °C.

the alumina acts as a reservoir for carbon that must be filled. Another possibility, given that the yield is so high, is that the same amount of carbon is distributed over many more actively growing nanotube nuclei, meaning that, for the same carbon supply rate, it might take much longer to reach saturation and precipitate nanotubes in the presence of alumina. Due to their similar time scales, it is possible that “incubation” may not be a distinct phase from “acceleration” but may instead correspond to the tail of the exponential acceleration. Again, these phases could arise from stochastic nucleation or from exponential lengthening. An initial accelerating transient in height for tall, vertically aligned forests has recently been reported by several groups.^{16,18,20,22}

Alternatively, the difference between the two catalysts might mean that surface diffusion or bulk diffusion in or on the substrate itself may be a rate-limiting step. This is an interesting possibility because, although diffusion of carbon in the gas phase on the surface and/or the bulk of the catalyst particle is well-studied, the effects of the surface supporting the catalyst particle are seldom explicitly analyzed. The surface may thus play a role beyond simply being a support for the catalyst.

There appears to be an inflection point in the temperature dependence of the incubation time for Co-alumina samples. In a previous video study of vertically aligned carbon nanotube growth rates using a similar catalyst, we observed a critical point in vertically aligned nanotube height, growth rate, and termination rate.¹⁵ This may be a manifestation of the same critical point. Others have proposed that catalyst–oxide intercalation to the alumina support may cause such effects.³⁵ Alumina type is reported to affect growth, and it is possible that alumina may also change over a temperature range.³²

Conclusions

To summarize, in situ Raman spectroscopy enables the identification of four distinct steps of CVD growth of carbon nanotubes: incubation, acceleration, linear growth, and termination. All investigated bands (G, D, and RBM) exhibit these phases. In fact, up to experimental uncertainty, there is no significant evolution in the weights associated with each band. The G band and RBM bands track each other very well, and two different RBM bands also appear to track each other well. This implies that any evolution in diameter distributions with time is relatively small.

The temperature scaling of all four steps was determined. In this study, the length of all four steps increases with increasing temperature. Activation plots suggest that temperature-activated processes prevent carbon from becoming properly incorporated into growing nanotubes. Such processes might be gas-phase pyrolysis, pyrolysis on the surface of the reactor or sample, or desorption of chemisorbed species. Comparisons between different sample types suggest that surface effects are important during the incubation and acceleration phases.

In the future, it will be interesting to explore how dependent the observed spectral evolution is to the particular growth

method that was used, in terms of the process steps or the CVD apparatus itself. Specifically, we would like to determine to what extent this evolution is “intrinsic” to the carbon nanotube material system versus how this evolution is “extrinsic” and, therefore, a function of the particular synthesis process steps and synthesis setup. In future work, it will be important to constrain any time scales or other extracted parameters with greater precision to allow a more rigorous connection with growth theories. Clearly, in situ Raman spectroscopy is maturing as an important tool for characterizing the evolution of nanotube samples during growth and processing.

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Supporting Information Available: Supporting Information is available, describing (a) changes to the postgrowth Raman spectra with varying temperature, (b) the spectral background correction method, (c) waterfall plots of Raman band growth evolution for the complete set of all grown samples, (d) the equations and methods used to fit the kinetic curves, and (e) characteristic energy plots with RBM-1 and D band data in addition to the G band data shown in the main text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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