

***In situ* growth rate measurements and length control during chemical vapor deposition of vertically aligned multiwall carbon nanotubes**

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Time-resolved reflectivity is employed as an *in situ* diagnostic in thermal chemical vapor deposition of vertically aligned arrays of multiwall carbon nanotubes (VAA-MWNT). Fabry-Perot interference fringes and attenuation of a reflected HeNe laser beam are used to measure the length of VAA-MWNT throughout the first 3–8 μm of growth yielding *in situ* measurements of growth rates and kinetics and the capability to observe the onset and termination of growth. VAA-MWNT growth is characterized between 565 and 750 $^{\circ}\text{C}$ on Si substrates with evaporated Al/Fe/Mo multilayer catalysts and acetylene feedstock. Nanotube lengths were controlled by rapid evacuation of the chamber at predetermined reflectivities, and it was demonstrated that growth can be *restarted* at later times. The extinction coefficients of the VAA-MWNT were studied and correlated with nanotube wall structure. Growth rates for VAA-MWNT are found to vary depending on the catalyst preparation, temperature, and time. Both the highest growth rates (0.3 $\mu\text{m/s}$) and the tallest VAA-MWNT (0.75 mm long) were achieved at 730 $^{\circ}\text{C}$. © 2003 American Institute of Physics.
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Chemical vapor deposition (CVD) is conceptually the simplest method to grow carbon nanotubes. However, the mechanisms and kinetics of nanotube growth are the subject of much speculation due to the lack of *in situ* diagnostic techniques which can be employed in typical CVD reactors. Growth rates and ultimate lengths for nanotubes are limited by unknown factors at present, which hampers applications. Precise control over nanotube length is essential for many applications of nanotubes in electronic devices or sensors¹ while understanding how to grow long nanotubes at high rates is a major production challenge for their use in composites.²

Vertically aligned arrays of multiwall carbon nanotubes (VAA-MWNT) have been grown by CVD using lithographically patterned catalyst films, solutions, or materials to which floating catalysts will stick.^{1–9} Average growth rates reported for VAA-MWNT range from 0.4 to 50 $\mu\text{m/min}$ ^{3,4} with lengths typically terminating around 50–200 μm ^{1,2,5} (however, lengths of 1.5–2 mm have been achieved).^{3,5} Recently, Bonard *et al.* used *in situ* field emission from individual MWNT during thermal CVD to infer growth rates of 1–10 $\mu\text{m/s}$.¹⁰ The interpretation of these results requires several assumptions and the technique is limited to very low pressures.

Here *in situ* measurements of VAA-MWNT lengths and growth kinetics are described. Time-resolved reflectivity (TRR) is employed as an *in situ* diagnostic to control the lengths of VAA-MWNT, observe the termination of growth, and show that growth can be *restarted*.

The catalyst system used for all of the VAA-MWNT

growth in this report consisted of multilayered metal films (10 nm of Al, 1 nm of Fe, then 0.2 nm of Mo) prepared by electron beam evaporation onto Si (100) substrates. Sputtered films of this catalyst system were used by Delzeit *et al.* with ethylene to grow VAA-MWNT and single wall carbon nanotubes (SWNT) on various substrates.⁶ Recently, MWNT and SWNT growth on Si substrates with this catalyst system using acetylene was characterized.¹¹

For these experiments, a 3 in. inner diameter fused silica tube furnace reactor was constructed to permit rapid gas introduction and evacuation. The Si substrate was held vertically in the center of the furnace (1 m hot zone) with a fused silica mount to permit the entry and exit of a stabilized HeNe laser ($\lambda = 632.8$ nm, 4 mW, Laboratory for Science model 200) beam as shown in Fig. 1(a). The intensity of the beam reflected from the substrate and growing VAA-MWNT was recorded with a Si photodiode and computer-interfaced Keithley 196 digital multimeter.

The substrate was heated under flowing Ar (2000 sccm) and H₂ (400 sccm) to the growth temperature and allowed to equilibrate for 10 min at atmospheric pressure. During the ramp-up of the furnace temperature, the reflected intensity reproducibly decreased 50% over 5 min time (not shown) as the rms roughness of the catalyst surface changed from 0.34 nm (as-deposited) to 1.6 nm (after heating to 675 $^{\circ}\text{C}$) as measured by atomic force microscopy. The reflectivity then remained constant until a pre-established 6 sccm flow of C₂H₂ was switched into the flowing Ar/H₂ gas mixture.

As shown in Fig. 1(b) for $T = 575$ $^{\circ}\text{C}$, 26 s later the reflected beam intensity began to decrease exponentially due to absorption and scattering from the growing nanotubes. In addition, the TRR intensity displayed reproducible oscillations

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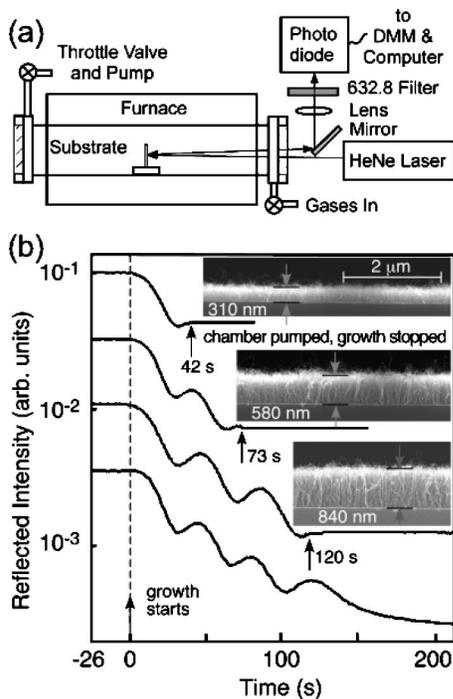


FIG. 1. (a) Schematic of the setup for time-resolved reflectivity measurements during CVD growth of nanotubes. (b) Photodiode voltages for four different growth runs at $T=575^\circ\text{C}$. Acetylene is introduced upstream at $t = -26$ s and after a transit time to the center of the tube furnace, growth reproducibly begins at $t=0$ s. Attenuation of the reflected beam is accompanied by a series of interference fringes (lower trace). In the top three traces (offset for clarity), growth is stopped by rapidly evacuating the chamber just past the first, second, and third minima at the indicated times, resulting in VAA-MWNT with heights indicated in the corresponding cross-sectional SEM images.

tions. Both the oscillations and the extinction of the beam can be used to gauge the length of the VAA-MWNT.

The oscillations result from interference between light reflected from the top of the VAA-MWNT and light which is reflected from the Si substrate and passes twice through the nanotube array. These Fabry-Pérot fringes serve as reference points to permit lengths and growth rates to be determined *during deposition*. Similar Fabry-Pérot fringes were observed and theoretically interpreted for thin specimens of porous Si.^{12,13}

Growth of the VAA-MWNT was halted after different numbers of fringes in several growth runs by evacuating the

chamber from 760 Torr to <10 mTorr in less than 3 s [as indicated by the zero slope of the photodiode voltage after the indicated pumpout points in Fig. 1(b)]. The Si wafers were scribed and broken at the optically monitored locations and the VAA-MWNT heights were determined by scanning electron microscopy (SEM) measurements. In several cases, VAA-MWNT grew at constant rate [as in Fig. 1(b), 7.1 nm/s] which permitted estimation of their heights exactly at the fringe minima. The fringes were found to occur for constant increments in VAA-MWNT height at a given growth temperature (300 ± 30 nm at 575°C and also at 600°C), with uncertainty in estimating the height principally governed by the surface roughness of the VAA-MWNT. This incremental height for successive Fabry-Pérot fringes corresponds to $\lambda/2n_{\text{eff}}$ for a single effective medium where n_{eff} , the effective index of refraction of the porous VAA-MWNT, is 1.05 at these temperatures. In subsequent runs, heights of VAA-MWNT grown at these temperatures could be directly inferred *throughout growth runs* from the temporal occurrence of these fringes.

Figures 2(a) and 2(b) show TRR photodiode intensities and the corresponding lengths of the VAA-MWNT obtained from the position of the fringes at three different growth temperatures. At 550°C , no growth is observed. At 565°C , growth begins at $0.01 \mu\text{m/s}$ but rapidly decreases to nearly stop after 400 s, growing VAA-MWNT only $0.6 \mu\text{m}$ long. At 575°C , growth begins and continues for 175 s at $0.01 \mu\text{m/s}$, then slows after growing $1.7 \mu\text{m}$ long. Increasing the temperature to 600°C results in an almost linear growth rate of $0.025 \mu\text{m/s}$ to $3 \mu\text{m}$ lengths. Inadvertent variations in catalyst preparation or intentional changes in processing conditions resulted in different growth kinetics and lengths achieved before growth terminated.

Alternatively, in the absence of pronounced Fabry-Pérot fringes in the TRR signal (above 600°C) extinction of the laser beam can be used to estimate length. Similar arrested growth experiments as those shown in Fig. 1 were first used to estimate the extinction coefficient ($\alpha = [\ln(I_0/I)]/2d$) at each growth temperature through a calibration of reflected intensity, I , and the different measured film thicknesses, d . The α values were found to be consistent for VAA-MWNT of different lengths at a given temperature, so the TRR signals throughout a growth run could be directly converted to

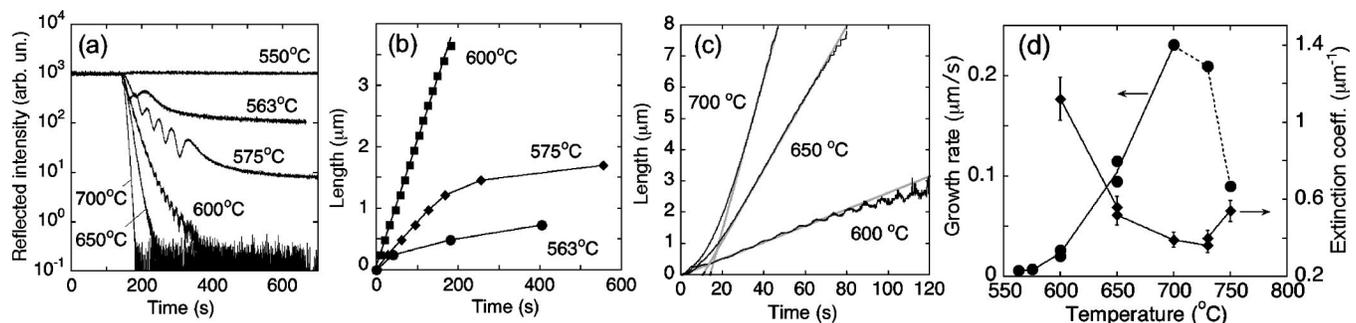


FIG. 2. (a) Intensity of the specularly reflected laser beam for nanotube growth at six temperatures. (b) Lengths of VAA-MWNT derived from Fabry-Pérot fringes in (a). The point corresponding to the longest time for each run includes the fraction of the final oscillation achieved (estimated from other growth runs). (c) Lengths of VAA-MWNT vs time calculated from the measured extinction coefficient at each temperature and the corresponding TRR signals in (a). Maximum slopes are indicated by shaded lines. (d) Extinction coefficients (open circles) and growth rates (filled circles) for VAA-MWNT grown at different temperatures. The decrease in growth rate above 700°C (dashed lines) correlates with the appearance of SWNT breathing modes in the Raman spectra of the films.

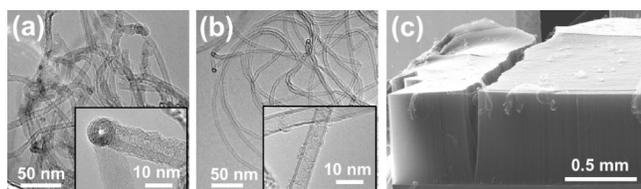


FIG. 3. TEM images of multiwalled carbon nanotubes grown from metal multilayer catalyst films at (a) 575 and (b) 725 °C. Double-wall nanotubes predominate at 725 °C. (c) SEM image of 0.75 mm tall VAA-MWNT grown at 730 °C.

VAA-MWNT heights as shown in Fig. 2(c). The slopes of these curves yields the growth rate which increased tenfold between 600 and 700 °C, as shown in Fig. 2(d).

Interestingly, the extinction coefficients decrease approximately a factor of three in the same region [Fig. 2(d)]. While porosity of the VAA-MWNT is difficult to quantify, it did not appear to vary sufficiently to explain the decrease. A more likely explanation is the pronounced decrease in the number of walls of the MWNT grown with increasing temperature. As shown in Figs. 3(a) and 3(b), high-resolution transmission electron microscopy (TEM) (200 keV, Hitachi HF-2000) images reveal that thicker, more defective MWNT with 6–10 walls are grown at 575 °C while cleaner, predominantly double-walled nanotubes grow at 725 °C.

Above 700 °C, the VAA-MWNT growth rate decreases as indicated in Fig. 2(d). This correlates with the sudden appearance of SWNT breathing modes in the Raman spectra of these samples (onset between 675 and 700 °C, and continuing up to >900 °C). Although VAA-MWNT were obtained for temperatures up to 900 °C and beyond, the TRR signals in the mixed SWNT/MWNT growth regime revealed more complex, bifurcated growth kinetics which, along with more detailed modeling of the TRR signal, will be the subject of another report. This work demonstrates that TRR and other optical diagnostics will be quite useful to study the interdependence of growth rate and wall structure for different processing conditions.

TRR affords the opportunity for a great variety of *in situ* experiments. For example, in Fig. 4 it is demonstrated that

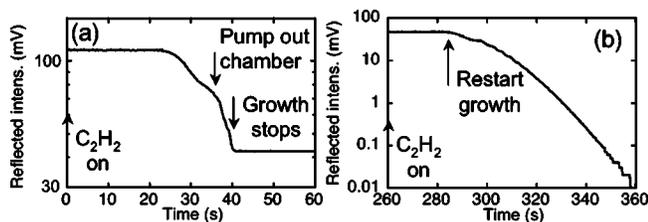


FIG. 4. (a) Reflected HeNe laser beam intensity of VAA-MWNT growing at 700 °C. Growth is stopped after rapid evacuation of the Ar/H₂/C₂H₂ mixture. Ar and H₂ flows are reintroduced at 260 s. (b) Drop in reflectivity after reintroduction of C₂H₂ indicates that growth is successfully *restarted*.

nanotube growth can be halted and then *restarted* after several minutes. This ability to observe the resumption of nanotube growth during CVD may prove valuable for assessing ways to reactivate poisoned or overcoated catalyst nanoparticles for the growth of very long nanotubes. TRR was also found to be effective for screening of catalyst activity, which here were likely caused by inadvertent ($\sim \text{\AA}$) variations in the evaporated catalyst film thicknesses. An excellent predictive test for catalyst films capable of growing very long VAA-MWNT at 700–730 °C was their ability to grow longer nanotubes at 575 °C before growth terminated. This was revealed by seven or more Fabry-Pérot fringes in the TRR signals at 575 °C [compare to those shown in Figs. 1 and 2(a)]. This permitted screening identically prepared catalyst films to enable the growth of VAA-MWNT to lengths of 0.75 mm at 730 °C in 30 min, at maximum growth rates of 0.3 $\mu\text{m/s}$ under these processing conditions [Fig. 3(c)].

In summary, time-resolved measurements of nanotube array lengths have been performed *in situ* during CVD. Fabry-Pérot fringes and extinction of a laser beam reflected from VAA-MWNT growing on Si were used to characterize carbon nanotube growth kinetics as a function of the growth parameters. Control over nanotube length was demonstrated via rapid evacuation of the growth gas at predetermined reflectivities, and *restarting* of growth was observed *in situ*.

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