In Situ Measurement of Carbon Nanotube Growth Kinetics in a Rapid Thermal Chemical Vapor Deposition Reactor With Multizone Infrared Heating

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Understanding and controlling the growth of vertically aligned carbon nanotube (VACNT) forests by chemical vapor deposition (CVD) is essential for unlocking their potential as candidate materials for next generation energy and mass transport devices. These advances in CNT manufacturing require developing in situ characterization techniques capable of interrogating how CNTs grow, interact, and self-assemble. Here we present a technique for real-time monitoring of VACNT forest height kinetics applied to a unique custom designed rapid thermal processing (RTP) reactor for CVD of VACNTs. While the integration of multiple infrared heating lamps enables creating designed spatiotemporal temperature profiles inside the reactor, they pose challenges for in situ measurements. Hence, our approach relies on contrast-adjusted videography and image processing, combined with calibration using 3D optical microscopy with large depth-of-field. Our work enables reliably measuring VACNT growth rates and catalytic lifetimes, which are not possible to measure using ex situ methods. [DOI: 10.1115/1.4046033]

Keywords: carbon nanotubes, chemical vapor deposition, rapid thermal processing, reaction kinetics, catalyst lifetime

1 Introduction

Vertically aligned carbon nanotubes (VACNTs), also known as CNT forests, possess great potential for advancing interfacial materials with anisotropic energy and mass transport as well as for creating new structural composites.[1] To realize this potential, greater understanding of the atomic scale processes underlying their formation and self-organization is required. [2] Hence, numerous in situ nanoscale metrology and characterization techniques were developed for investigation of their growth, and self-assembly.

Of these measurements, observing the change in VACNT height in real-time, known as the height kinetics, is of paramount importance for understanding the catalyst behavior, as well as for revealing the factors affecting growth rate and limiting the terminal height of VACNT forests. In this paper, we present a method we developed for monitoring the height kinetics of forests grown in our unique custom-designed rapid thermal processing chemical vapor deposition reactor (RTP-CVD). We discuss our method based on using computer vision to resolve the height kinetics and calculate the catalyst lifetime and growth rate. We also present a calibration technique based on combining our in situ videography with ex situ 3D optical microscopy with large depth-of-field.

2 Methods for In Situ Kinetics Measurements

Many methods have been developed to measure in situ height kinetics of VACNT forests, a summary of which is presented in Table 1. These methods are herein divided into three approaches: direct imaging methods, laser-based methods, and growth interruption methods.

Direct imaging methods depend on real-time observation of the CNT forests as they grow with microscopy and/or video cameras during growth [3]. The main drawback for this approach is that the reactor design has to provide a direct field of view into the VACNT growth, which is challenging in all hot-wall reactors and some cold-wall reactor designs, especially reactors that involve infrared heating. Moreover, this approach is limited by the camera's spatial and temporal resolutions.

Laser-based methods utilize optical phenomena such as interference [5], diffraction [6], reflectivity [7] and triangulation [8] to estimate the forest height with time. As with videography, these techniques require special design accommodations in the reactor to allow the laser beam to interact with the forest either directly or through another interfacing medium. Methods where the laser beam directly interacts with the forest are limited to relatively short forest heights and depend on the optical properties of the CNT forest, which can change with time and reaction conditions and would require calibration. Nondirect laser interaction methods require cap placement on the top of the forest, which is lifted up during growth. If a laser is reflected off the cap and is detected on a laser sensitive element, the change in forest height can be estimated using triangulation [8].

In contrast to the two above-mentioned categories of in situ methods (direct imaging and laser-based methods), the third category represent indirect methods referred to here as growth interruption methods, which are based on ex situ measurements. It is based on the idea of creating marked segmentation during growth by momentarily changing growth conditions to stop and start growth at equal time intervals in a way that marks the forest along its height [10]. These markers are later imaged using scanning electron microscopy (SEM) to calculate an estimate for the height kinetics. Although this technique can be performed in any reactor, it involves stopping and restarting growth, hence changing the conditions of the growth and state of the catalyst, which hinders the accurate study of deactivation mechanisms responsible for growth termination.

3 Videography in Our Rapid Thermal Processing-Chemical Vapor Deposition Reactor

In this section, we discuss the features of our custom-designed RTP-CVD reactor (CVD Equipment, Central Islip, NY) [12]. This reactor is specially designed to overcome many of the current limitations faced in CVD growth of VACNT forests such as growth inconsistency, slow heating rates, and coupling of conditions of multiple subsequent processes [13].

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Table 1 Methods for in situ measurements of height kinetics during CVD growth of CNT forests

Method	Type	Notes	Ref.
Videography	Direct imaging	+Requires special setup to allow direct imaging +No limitation on forest height	[3,4]
Optical interference	Laser-based	+Requires special setup to allow laser to reach top of forest +Limited to short forests +Laser-based method +Indirect method	[5]
Single-slit laser diffractography	Laser-based	+Laser-based method +Slit has to be etched through wafer +Requires special setup to allow laser to reach CNTs +Suitable only for floating catalyst methods +Indirect method	[6]
Time-resolved reflectivity	Laser-based	+Laser-based method +Requires special setup to allow laser to reach top of forest +Based on Attenuation of a reflected laser of VACNT +Calibration required	[7]
Laser triangulation	Laser-based	+Requires special setup to allow laser to reach top of forest +Cap required to be placed on top of forest	[8,9]
Inducing makers by intermittent growth	Growth interruption	+Growth marks created by stopping precursor gases +SEM required +"Pseudo" in situ method +Can be performed in any system	[10,11]

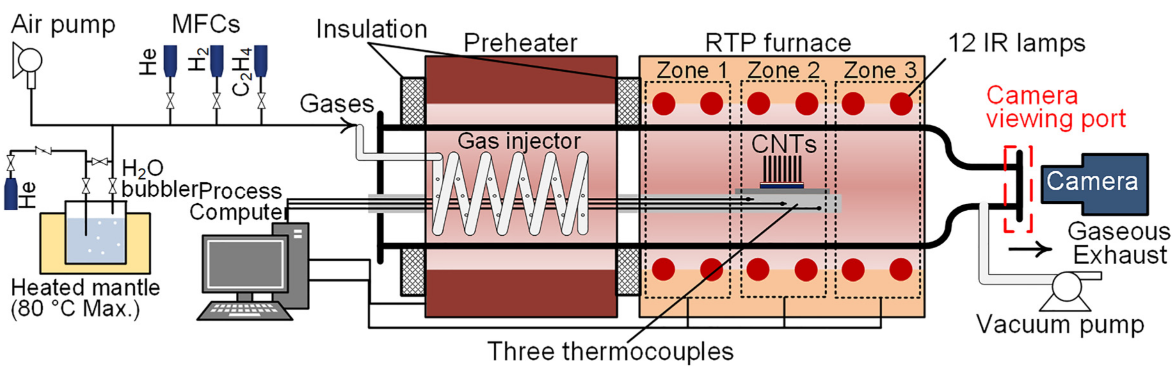

Fig. 1 Schematic of our RTP-CVD reactor and view port for monitoring the forest growth

3.1 Challenges in Carbon Nanotube Growth by Chemical Vapor Deposition. Forest growth is a collective process, in which billions of CNTs grow together from catalyst nanoparticles "seeding" growth. The main issue is that the process proceeds as a succession of a number of atomic-scale processes [2]. Typically, a single heated zone exists in most CVD reactors used to grow CNTs. A major challenge is that the conditions for the successive processes of catalyst pretreatment, precursor gas decomposition, and CNT nucleation/growth are either exactly the same or are dependent on each other in that heated zone. While some of these challenges have been previously addressed by adding a preheater for gas decomposition [14], or by rapidly moving the sample in and out of the reactor zone [15], separate control of temperature for each of the three processes mentioned above separately has not been achieved to date.

The design of our reactor resolves these issues by allowing the decoupling of the decomposition of hydrocarbon precursor via preheating. Also the catalyst formation by thermal dewetting, and catalytic growth of CNTs are decoupled by rapidly changing temperatures in an infrared heater. Hence, our approach allows more control over the process and providing more insight into the limiting mechanisms. A schematic of the reactor is shown in Fig. 1. The reactor consists of two adjacent furnaces: a resistive preheater for thermal decomposition of hydrocarbon precursors (supplied through a coiled injector) and an infrared (IR) heater for catalyst treatment and CNT growth. The IR heater has 3-zone control along the axis as well as independent control of top and bottom lamps, to create thermal gradients and achieve fast heating (>50 °C/s).

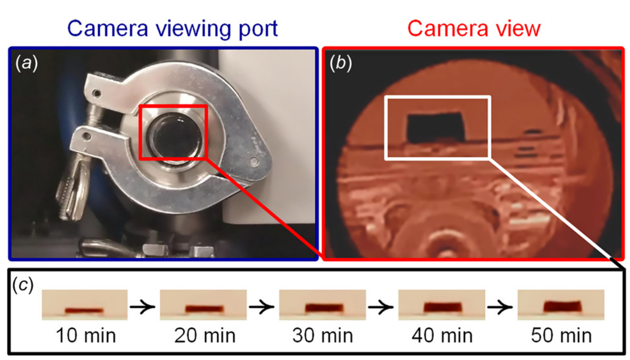

Fig. 2 (a) Photograph of the camera viewing port, (b) Camera view, and (c) Evolution of VACNT forest with time

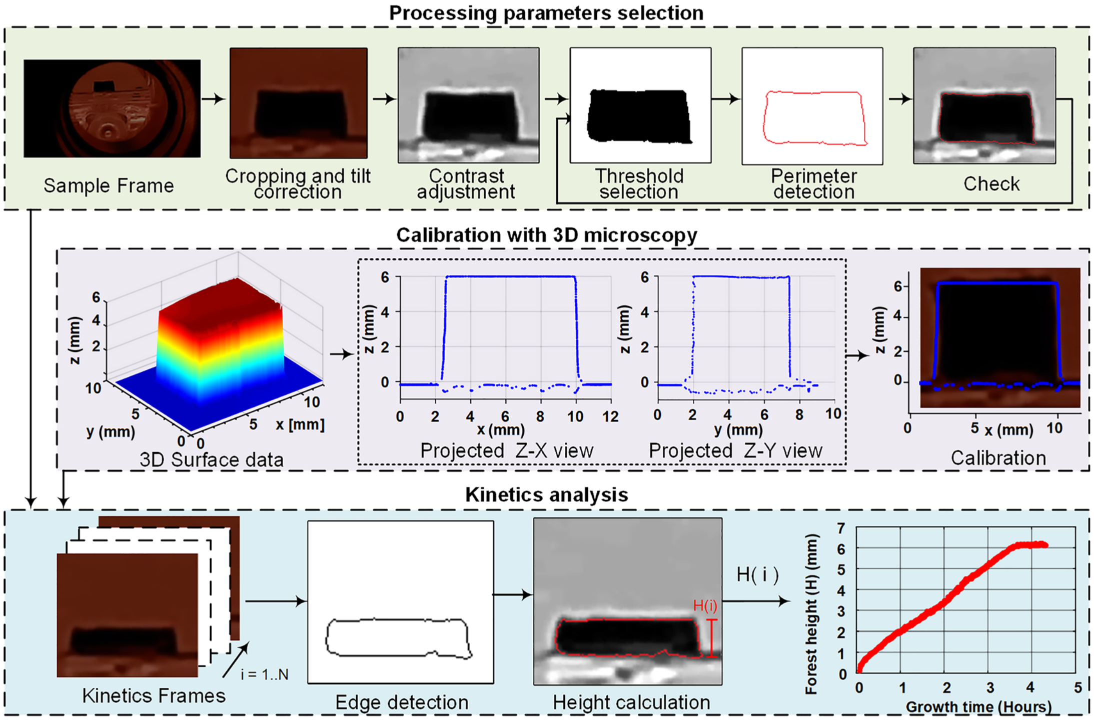

Fig. 3 Schematic illustrating the algorithm for deriving in situ height kinetics using computer vision from VACNT forest growth videography

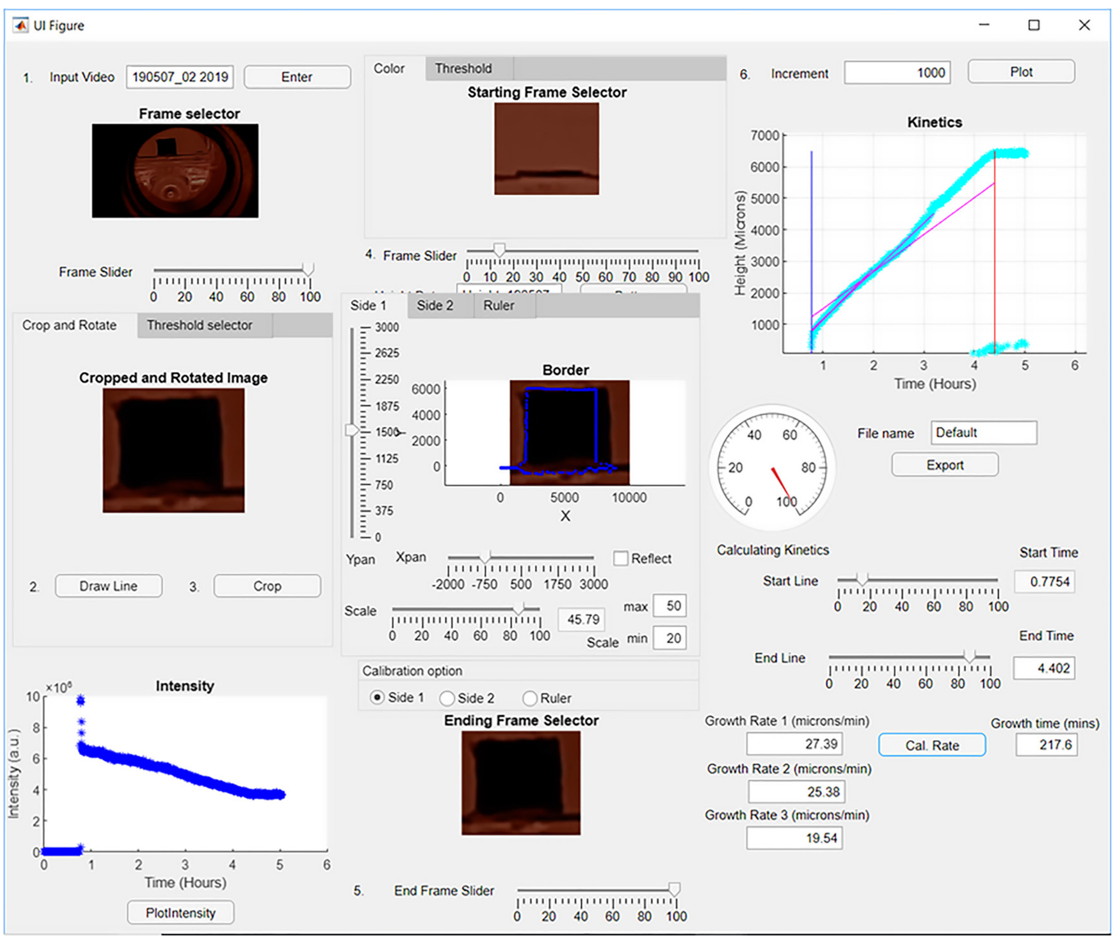

Fig. 4 Graphical user interface (GUI) of our image processing program for height kinetics measurements

The system is controlled via a programmable logic controller (PLC), allowing the programming of automatic dynamic recipes. The growth data (, e.g., time evolution of temperature, pressure, gas flow rates, etc.) are logged for analytics. A system of mass flow controllers allows the delivery and control of a variety of process gases like He, H_2, C_2H_2, C_2H_4, and CH_4. In addition, the delivery of growth enhancer H_2O is well controlled via a bubbler with accurate temperature and pressure control. Additionally, a vacuum pump is used for purging and an air pump used for bake-cleaning of the reactor's internal fused silica surfaces.

The reactor has a special viewing port on the exhaust side, as shown schematically in Fig. 1 and in the photograph in Fig. 2(*a*). The port allows a field of view into the process chamber for real-time monitoring of VACNT forest growth, as shown in Figs. 2(*b*) and 2(*c*). Since this is an IR-heated reactor, the process chamber is illuminated during the heated portions of the growth recipe, thus illuminating the growing forest. In order to avoid saturation of the CCD camera, automated contrast-adjustment is used, which is critical during temperature changes. Hence, using a high magnification camera, forest growth is recorded during growth through the port as shown in Fig. 2(*c*). By recording the growth, the evolution of forest height with time can be logged and viewed in real-time. Image processing then provides quantitative measurements for growth rate and catalyst lifetime.

4 Image Processing for Kinetics Measurements

To obtain the height kinetics for forest growth in our reactor, we develop a GUI in MATLAB to process the growth videos recorded in real-time. The GUI is based on an algorithm for measuring forest height from each of the frames making up the recoded video. The heights are then logged with time, based on the time-stamp of each frame in the sequence. A flowchart of the algorithm is shown in Fig. 3. The objective of the following step is to segment the forest and separate it from its surrounding environment to calculate its height in pixels. This is achieved through converting the gray scale image into a binary image (black and white) by specifying a certain intensity threshold. This step creates segmented portions, the biggest of which represents the VACNT forest. Any other segments representing nonforest regions in the image are automatically removed based on their size and location. The detected edges of the forest body are then overlaid over the original image to check if it matches correctly the visually distinct forest observed by the user. At this stage, the threshold value may need adjustment for a good match between the algorithm for edge detection and the user's evaluation.

After a suitable set of parameters is selected, the calibration process is performed to get a conversion factor from pixels into micrometers. To accomplish this, we utilize an advanced 3D microscopy system with large depth-of-field (VR-3000 series, Keyence) to generate 3D data ex situ for the grown forest geometry, for which two side views are used to compare to the in situ videography data. These side views are projected onto the final frame of the growth sequence and scaled until they match as shown in Fig. 3. Alternatively, a known length (like wafer thickness) can be used for calibration, but we found that using the 3D microscopy data for calibration gives more accurate results. A pixel-to-micrometer calibration factor is then derived which is used henceforth to convert pixel measurements to actual length measurements.

Using the selected parameters and the calibration factor, a routine is run over the entire growth sequence to plot the in situ height kinetics curve, as shown in bottom-right corner of Fig. 3. Using the derived forest body in the image, the vertical height of the body is measured in pixels and logged with the frame time. This is run in a loop to derive the entire forest kinetics. The program is also used to quantify the growth rate and growth lifetime. This procedure is programmed in a MATLAB GUI as shown in Fig. 4 to facilitate the process for the user.

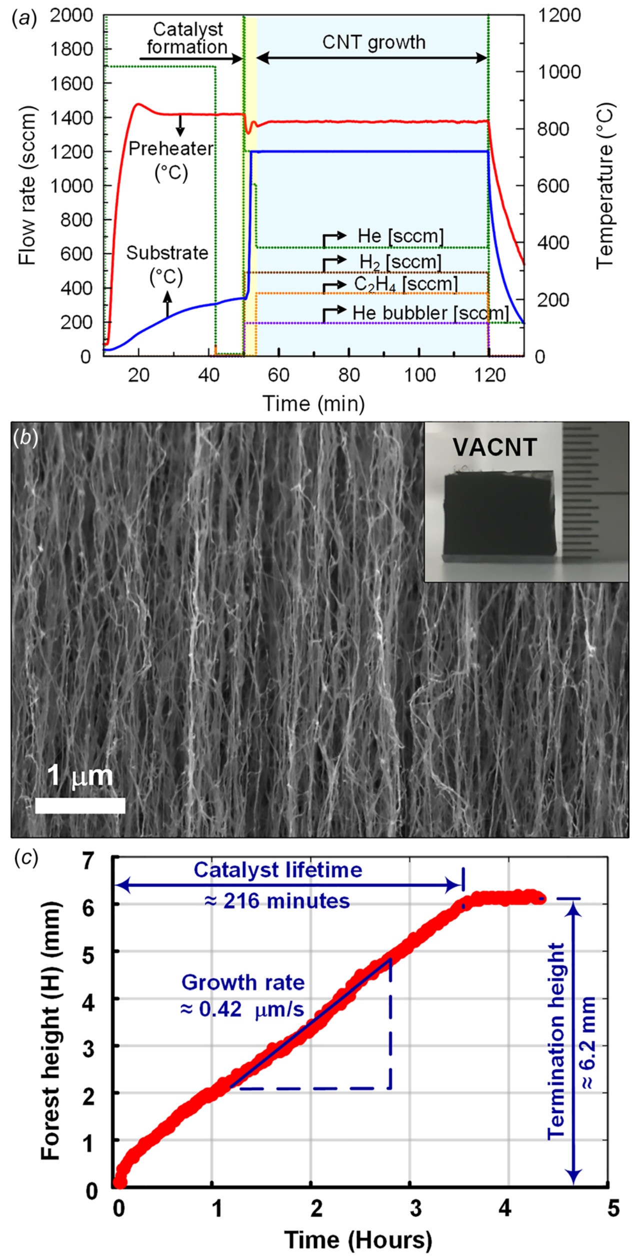

Fig. 5 (*a*) Growth recipe for a 6.2 mm tall VACNT forest grown in our RTP-CVD reactor. (*b*) SEM of a VACNT forest grown in our reactor (inset: photo). (*c*) Derived forest height kinetics, showing the calculated growth rate, catalyst lifetime, and the terminal height.

5 Insights into Vertically Aligned Carbon Nanotube Growth

Here we show the results for applying our image processing approach in order to calculate the height kinetics for a millimeter-tall (≈6.2 mm) VACNT forest, grown according to the recipe shown in Fig. 5(*a*). Scanning electron microscopy (SEM) imaging (Fig. 5(*b*)) demonstrates the high density and good alignment of CNTs in this forest. For this growth, the catalyst is prepared by deposition of 1 nm of Fe over 10 nm of Al_2O_3. The growth temperature was 710 °C in coupled recipe (annealing time = 60 s) with a preheater temperature of 850 °C in a 3 inch quartz tube. The water content was controlled by setting a helium line to go through the bubbler to achieve 100 ppm H_2O. We flow a combined 840 sccm of background He (by adding the flowrate of He through the bubbler to the He flow that does not go through the bubbler). We also flow 490 sccm (0.83 m^3/s) of H_2, and 370 sccm (0.62 m^3/s) of C_2H_4 (during the growth step). As seen in Fig. 5(*c*), our results show that the growth rate is mostly constant (linear kinetics) at $\approx 0.42\ \mu$m/s with a catalyst lifetime of ≈ 216 min.

6 Conclusions

We present a technique for measuring height kinetics of VACNT growth implemented for a custom-designed RTP-CVD reactor. Our approach relies on real-time videography as well an image-processing algorithm for identifying forest height. The procedure is programmed in a GUI, which is used to calculate the growth rates and catalyst lifetimes. This technique provides direct measurements and can be used to get live height readings of the forest automatically during growth for continuous process monitoring. We test the program on the growth of millimeter-tall VACNT forests and quantify their growth rate ($\approx$0.42 μm/s) and catalyst lifetime ($\approx$216 min).

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