Process Variables Controlling Consistency of Carbon Nanotube Forest Growth

by

Hanna Megumi Vincent

Submitted to the Department of Materials Science and Engineering
in partial fulfillment of the requirements for the degree of

Bachelor of Science in Materials Science and Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2014

Signature redacted

Author .....
Department of Materials Science and Engineering
May 2, 2014

Signature redacted

Co-Certified by .....
Brian L. Wardle
Associate Professor of Aeronautics and Astonautics
Co-Thesis Supervisor

Signature redacted

Co-Certified by .....
Carl V. Thompson
Stavros Salapatas Professor of Materials Science and Engineering
Co-Thesis Supervisor

Signature redacted

Accepted by .....
Jeffrey C. Grossman
Chairman of the DMSE Undergraduate Committee

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Abstract

Aligned arrays of carbon nanotubes (A-CNTs), called CNT forests, are the precursor for controlled-morphology macroscopic nanocomposites and nanoengineered composites due to theirscale-dependent, tunable physicall properties. Applications include polymer and ceramic matrix nanocomposites (PNCs and CMNCs), nanostiching as laminate interply reinforcement, as well as in supercapacitors, MEMS devices and electrodes for ion actuators and sensors. A key component of manufacturing materials comprised of A-CNTs is controlling the morphology and geometry of the CNT forest. Current laboratory findings show significant variability in CNT forest growth characteristics, and an experimental study was conducted to better understand and control for the observd process variations.

An exploratory investigation of growth parameters allowed for a local optimization of growth temperature and hydrocarbon flow rates, as well as an acceptable range of sample placement in the CVD furnace to achieve ~1mm tall CNT forests. Results from this investigation led to the conclusion that the significant inconsistencies between consecutive growths must be due to factors out of direct control, mainly humidity. A new system is being developed to better control for and monitor water in the furnace. A second investigation focused on post growth cool down effects, and the possible shortening (deforestation) of CNTs at high temperatures without a renewing source of the carbon precursor. Deforestation conditions did not lead to CNT shortening.

Co-Thesis Supervisor: Brian L. Wardle
Title: Associate Professor of Aeronautics and Astonautics

Co-Thesis Supervisor: Carl V. Thompson
Title: Stavros Salapatas Professor of Materials Science and Engineering

Acknowledgments

I would like to thank Sunny Wicks, Diana J. Lewis and Allison L. Yost for their help with knowledge of CNT forest growth, procurement of lab supplies, and providing wafers, and Itai Stein for the HRSEM image of a CNT forest. Thank you to Professor Alexandre Ferreira Da Silva for his insight and collaboration, as well as his support for this project. Finally, thank you to Professor Brian L. Wardle and Professor Carl V. Thompson for their advice and support.

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Chapter 1

Introduction

Carbon nanotubes have been suggested for incorporation into advanced composites because of their mass-specific mechanical [1, 2, 3, 4] thermal, and electrical [5, 6, 7, 8, 9, 10] properties, making them optimal for incorporation in high strength and low weight advanced composites. A variety of aerospace composites utilizing CNTs have been researched [11, 12, 13, 14]. Advanced composites are by nature more expensive than other structural materials such as steel and concrete, but CNT composites are also too expensive for widespread use in the aerospace industry at the current time.

Advancements in CNT growth procedures would allow for significant reductions in sample scrapping, which in turn reduces the amount of time necessary to produce accurate and acceptable forest samples for further testing and processing. The work detailed herein fills in some working gaps of knowledge of mechanisms surrounding CNT forest growth. Difficulty in growing forests with consistent height has prompted studies of CNT forest growth mechanisms. Forests on the 1mm scale in height are desired for manufacturing PNCs and CMNCs, and are the goal height of the work herein. Included is a summary of work conducted on pre-and during-growth variables, and a study of post-growth forest annealing as a possible kinetically-driven mechanism of forest shortening.

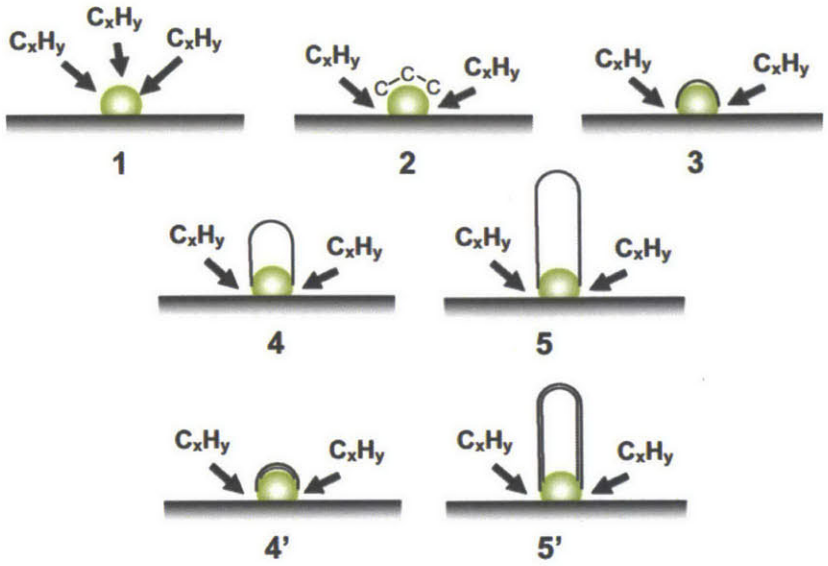

Figure 1-1: Depiction of base CNT growth around a metallic catalyst particle with a hydrocarbon precursor. Steps 4 and 5 show the growth progression of a single walled CNT, 4 ' and 5 ' a multiwalled CNT.

1.1 Overview of Carbon Nanotubes and CNT Forests

CNTs are tubes of graphene sheets, and are characterized by carbon atom geometry (armchair, zigzag, chiral) and number of walls (single walled, multi-walled). Individual CNTs have been shown to have Young's modulus values reaching 1 TPa [15], although it is dependent on the density of defects.

Aligned CNT arrays can be grown on a substrate with a catalyst layer, and are called "CNT forests" because the CNTs grow vertically from the bottom catalyst "seed" in a tree-like manner. Figure 1-2 is a SEM image of the side of a CNT forest, showing the aligned nature of the individual CNTs. The focus of this study is on growing 1mm tall CNT forests, although growth mechanisms are relatable to forests grown in general. At the onset of CNT growth, individual tubules will grow in random directions, until a significant number form and begin growing upwards to minimize energy. In the Chemical Vapor Deposition (CVD) method of growing CNT forests used here, a 1nm catalyst layer on a substrate is annealed to form nm-scale catalyst particles. A carbon precursor gas (C_xH_y) flows over the catalyst particles and begins

forming CNTs until growth terminates. A visual representation of this process is shown in Figure 1-1 [16]. This morphology allows for the wicking of polymers into the forest to make PNCs and CMNC precursors, and such processes can be accelerated with applied vacuum pressure.

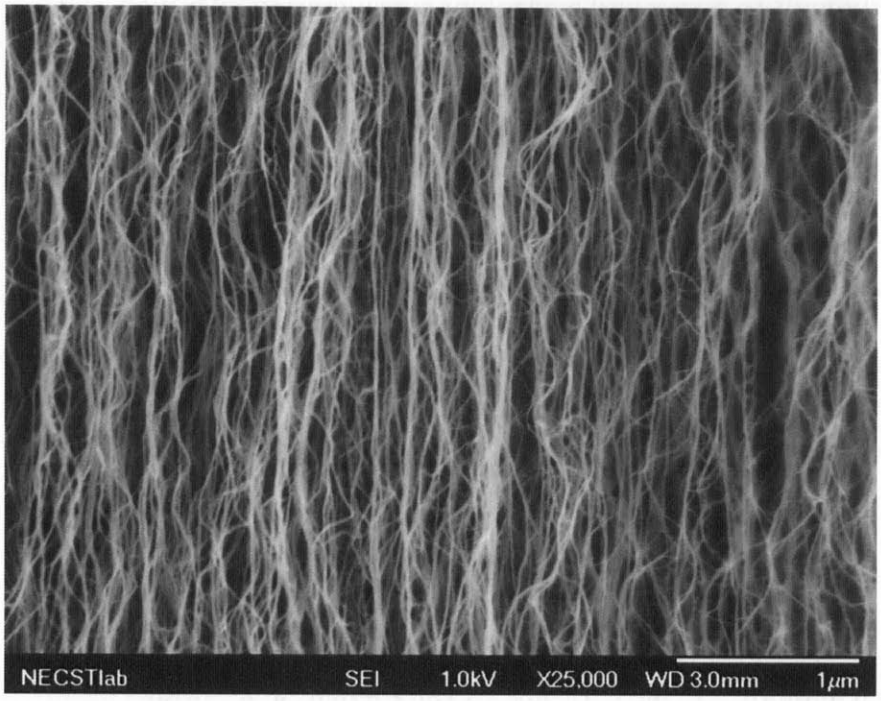

Figure 1-2: HRSEM image of CNT forest, courtesy of Itai Stein, MIT.

1.2 Current Issues and Motivations

Work on composite materials in the laboratory setting is currently limited to the rate at which acceptable CNT forests can be grown. A growth batch yields a maximum of 3-4 samples in the 1 inch" diameter furnace utilized here. Only ~25% of each hour long growth process is active growth. For forests grown to shorter heights, the active growing time percent drops to <1%. It has also been observed that there can be inconsistencies among forest batches grown on one day, or across multiple days. Several theories based on humidity [17, 18] and catalyst size [19, 20, 21, 22, 23] explain the difficulties of growing consistently tall forests in such systems, but they are difficult to test with the equipment available and the confluence of other non-controllable or

unknown variables.

1.2.1 Lack of Humidity Control

The most difficult to assess and control for consideration identified to date is humidity, which fluctuates with weather patterns and seasonal changes. While direct proof of the influence of ambient humidity in the gas lines and quartz tubes cannot be shown due to the lack of sensors and controlling equipment, it is evident in the irreproducibility of forest growths performed consecutively. First-of-day growths have been known to produce taller forests than subsequent growths. The most significant difference between a first-of-day growth and subsequent growths is the level of water in the system, as it is dried or flushed out during a growth cycle. In the interest of time, it is common to grow several batches in a row, which exacerbates the issue. Some anecdotal evidence has been passed down that forests grown the day after a rain storm are exceptionally tall. It is of course possible that other factors are contributing to these first-of-day growth phenomena, but humidity is the major known variable.

Ambient humidity gains entrance to the system by absorbing through the plastic gas line tubing, and inside the quartz growth tube. Due to EHS concerns, the furnace setup has changed over the last year by replacing the permeable plastic gas line tubing with flexible stainless steel tubing, and the entire system is now contained in fume hoods to minimize danger of working with flammable gases. The effect of the increased airflow is unknown. Direct comparison of growths from previous conditions is not an option, as the growth script used has also changed, and the previous technique for measuring forest height was less accurate and used less often. Old forests are no longer available to measure, because they have already been used to make research specimens.

1.2.2 Catalyst Annealing

Consideration of catalyst activation time and temperature has led to questions concerning the accuracy and reproducibility of the e-beam technique used to deposit

the catalyst layers on the silicon wafers. The combination of catalyst thickness with annealing time and temperature determine the size and number of catalyst particles during furnace ramp up. At the present time, it is not realistic to measure the deposited layers via AFM because the resolution of such imaging is on the order of the features being measured. According to the e-beam machine used, the 10nm Al_2O_3 layer is accurate within 1nm, and the 1nm Fe catalyst layer actually is between 1.0nm and 1.4nm. The only visible difference between wafers is color, based on the 500nm protective oxide layer. 20nm of variation around the 500nm of oxide correspond with colors ranging from purple to green [24]. Without a technique to measure the catalyst layer it is impossible to determine how 0.1nm changes in catalyst thickness affect forest growth. Forests grown in the post growth cool-down study were all grown on wafers made in the same batch, and are thus as close to identical as possible.

Growths done when the furnace and preheater are not at ambient temperature result in variable catalyst annealing. Growths can begin with the furnace near 150 °C, such that samples spend less time reaching growth temperature, with less time to anneal before growth begins. Catalyst particle size and number density consistency is important to stabilize and keep constant [23, 16], while maintaining a balance of reasonable laboratory procedures. It would be unreasonable to wait for the furnace and preheater to reach ambient temperatures between growths, but it is currently not possible to isolate the effect of catalyst annealing on forest growth so it is kept constant.

1.2.3 Temperature Profile

Furnace temperature is controlled and monitored through software, but to a limited capacity due to the single, centrally located thermocouple in the tube furnace external to the growth environment. A set-point is specified based on the thermocouple reading and thus in-tube growth temperature is correlated with the set-point temperature, although it is not equal. The temperature inside the quartz tube varies with distance from the center, as shown in Figure 2-2, where the temperature inside the quartz tube with the furnace set to 750°C was measured with an external thermocou-

ple probe. Although the temperature set point was 750°C, the thermocouple probe measured over 800°C inside the tube. From this it can be deduced that the set-point temperature from the internal thermocouple correlates to hiehger temperatures in the furnace. This will be an important factor in Chapter 4 when discussing relative cool-down temperature profiles.

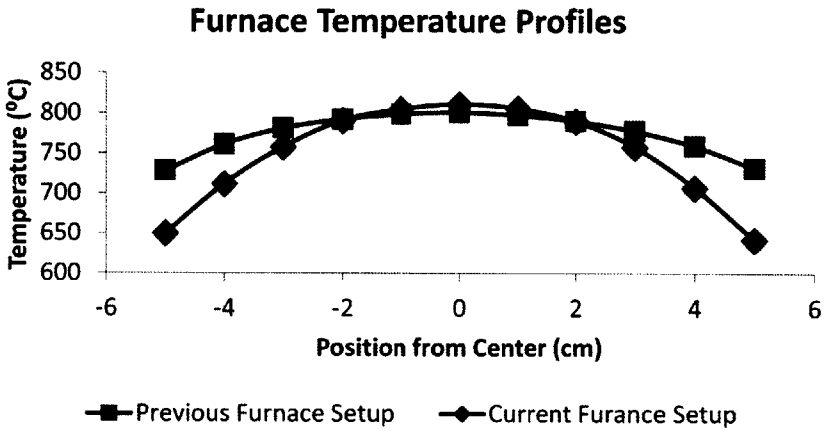

Figure 1-3: Temperature profile of the growth furnace measured via thermocouple, compared before and after the furnace was moved.

The larger decrease in temperature from the centerline in the current setup can be explained by the additional airflow in the fume hood, which actively cools the open ends of the furnace. During a growth cycle this profile would be slightly elevated due to the preheated gases flowing through the tube, thus pulling up the temperature, but not enough to significantly alter the growth zone. Insulating end-cap inserts were purchased for this furnace, but were not utilized during this study to follow previously determined best practices concerning wafer placement during growth. Implementation of these inserts could potentially increase the possible number of samples grown in a single batch. These experiments were conducted in the summer of 2013, with no gases flowing and the endcaps off.

1.2.4 "Easy Delamination"

A CNT forest is removed in one piece, or delaminated, from its substrate so that it can be used in a composite. CNT forests are cohesive films due to their entanglement

and Van der Waals forces, and prefer to stay in a rectangular mass. In order to facilitate the full removal of the forest from the wafer, Hydrogen gas is introduced after the hydrocarbon gas source is cut, reducing the cohesion between the CNTs and the catalyst ostensibly by weakening the amorphous carbon interface. The study detailed herein removed this step from the growth script, to maintain focus on the effect of heat and growth kinetics after CNT growth is terminated via gas shutoff.

1.2.5 Tube Bake-out

After each successive growth, the growth tube accumulates carbon deposits on the inner surfaces, generally nearer the center of the tube. After several growths, enough deposits accumulate that it is impossible to see and position samples inside. The cleaning process, called bake-out, is a simple 30 min procedure where the end caps of the tube are left open, and the furnace is left at 800°C to allow the debris to burn off. The carbon debris reacts with the O_2 in the air and converts to CO_2.

1.3 Deforestation

Most variables considered affect the system before or during growth, and post growth considerations are rarely mentioned. However current practice is to leave the system closed after growth has ended. This is because growths are long, and only require direct attention when putting samples in and taking samples out. It is therefore common to open the furnace lid whenever one remembers that their growth is finished. At the high temperatures sustained in the furnace after growth has finished it is reasonable to assume that kinetic reactions between the CNTs and the catalyst may cause shortening or eating away of CNTs. This phenomena has been seen in individual CNTs, where the catalyst switches between growth and "gasification" as the Carbon precursor gas is pumped in and out [25]. If not accounted for in laboratory practice, this deforestation action would negate the effort put into growing tall forests. The second part of this study will present the extent to which post growth cool-down profiles affect forest height.

1.4 Objectives

It is known that humidity affects CNT growth, and there is plenty of evidence to say that first-of-day growths tend to result in taller than subsequent growths. It is however important to understand why and how these things effect CNT growth, so that they can be controlled. At the present time, ~25% of samples targeted for 1mm are of acceptable height, and of those as few as 10% can be properly delaminated without significant damage. To that end, the goal of this work is to further understand the variables affecting CNT forest growth, and if current laboratory procedures are shortening forests after growth has terminated.

Chapter 2

Previous Work

Growing consistent forests has always been difficult, and moving the furnace into a fume hood and changing the plastic gas lines to stainless steel exacerbated the problem by adding unforeseen variables. Several lab members, including Visiting Professor Alexandre Ferreira Da Silva and this author performed a study in the summer of 2013, after it became clear that the change in location was significantly affecting observed forest growth. Our work attempted to compare previously grown forests with those grown in the new lab setting to understand the mechanisms contributing to the changes. While significant progress was made in increasing forest heights in the new lab setting, the issue of growth repeatability has remained. Forest height control is important to current graduate student work. Much of the forest height observations from old forests are ballpark estimates made with a ruler, and were often merely categorized as too short, around 1mm, or super tall. With the additional problem of an unreliable ambient humidity sensor, it is very difficult to compare pre-and post-move forest heights. Therefore the primary goal of any current studies is extending knowledge of CNT forest growth mechanism variables in an attempt to be able to grow forests of consistent desired height of $\sim$ 1mm.

Pre Summer 2013 Growth Script

```
' Cleaning the lines
turn log on
set helium to 920 sccm
set hydrogen to 400 sccm
set ethylene to 121 sccm
turn helium on
turn hydrogen on
turn ethylene on
wait for 0.5 min
turn ethylene off
wait for 0.5 min
turn hydrogen off

' Cleaning the tube
wait for 4.5 min
set helium to 73
turn hydrogen on


' Ramp to temperature
set zone 1 to 750 deg C
set zone 2 to 800 deg C
turn zone 1 on
turn zone 2 on
wait until zone 1 temperature > 748
deg C
wait for 5 min


' Growing CNTs
set ethylene to 200 sccm
turn ethylene on
wait for 12.5 minutes
turn ethylene off


'Delamination Process
wait 5 minutes

' Shut down

turn hydrogen off
turn zone 1 off
turn zone 2 off
set helium to 920 sccm
wait for 10 minutes
set helium to 73 sccm
wait until zone 1 temperature < 125
deg C
turn helium off
turn log off
```

Post Summer 2013 Growth Script

```
' Cleaning the lines
turn log on
set helium to 254 sccm
set hydrogen to 475 sccm
set ethylene to 295 sccm
turn helium on
turn hydrogen on
turn ethylene on
wait for 0.3 min
turn ethylene off
turn hydrogen off
wait for 0.1 min

' Cleaning the tube
set helium to 1473 sccm
wait for 3 min
set hydrogen to 200 sccm
turn hydrogen on

' Ramp to temperature
set helium to 37 sccm
set zone 1 to 740 deg C
set zone 2 to 800 deg C
turn zone 1 on
turn zone 2 on
wait until zone 1 temperature > 738
deg C
wait for 5 min

' Growing CNTs
set ethylene to 150 sccm
turn ethylene on
wait for 12.5 minutes
turn ethylene off
turn zone 2 off

'Delamination Process
wait 5 minutes

' Shut down

turn hydrogen off
turn zone 1 off
set helium to 920 sccm
wait 10 minutes
set helium to 100 sccm
wait until zone 1 temperature < 180
deg C
turn helium off
turn log off
```

Figure 2-1: Comparison of Ansari growth scripts from before and after furnace setup move in the summer of 2013. Zone 1 refers to the furnace and zone 2 the preheater. Sccm is standard cubic centimeters per minute. Apostrophes mark commented lines.

2.1 Changes to the Growth Script

Figure 2-1 shows a comparison of the growth script used before and after the equipment was moved from Building 37 to Building NW14 in the summer of 2013. There are differences in where some commands are written, but the significant changes are in the temperature set point for the furnace (zone 1) and the Ethylene flow rate during growth. The new script sets the furnace to grow at 10°C lower than previous because as can be seen in Figure 2-2, the maximum temperature reached in the center of the tube had increased by approximately 10°C. Ceramic insulating endcaps were purchased for the furnace to flatten the temperature profile, but were not implemented in any experiments because it was only necessary to grow a few samples at a time, and because we were unclear as to how significant a difference it would make in the temperature profile.

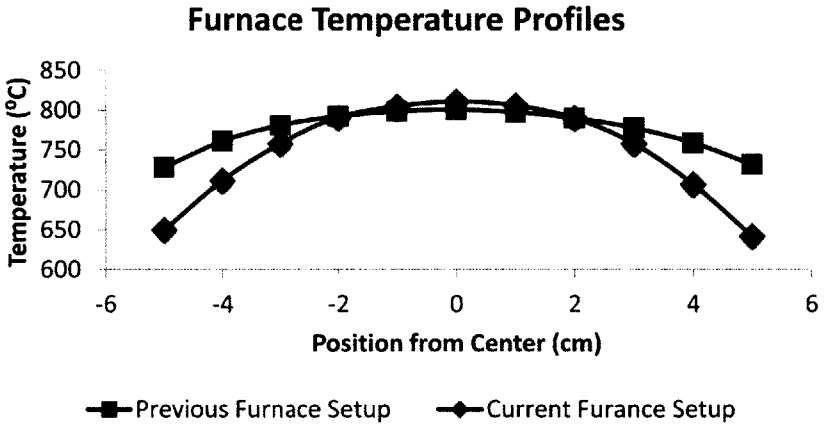

Figure 2-2: Temperature profile of the growth furnace measured via thermocouple, compared before and after the furnace was moved.

Before the move to the fume hood in NW14, the gas lines downstream of the furnace were under constant suction, such that there was always gas flowing downstream. Without knowing how strong this suction was, or how significant of an effect it had on gas flow rates, ethylene flow rate during growth was investigated. Results are show in Figure 2-3, and the average forest heights were 590um, 743um, and 625um for 50%, 75%, and 100% (from original) Ethylene flow. Despite the small sample size, forests grown with 75% Ethylene flow were more likely to be taller, and showed the

most promise for achieving consistently tall growths.

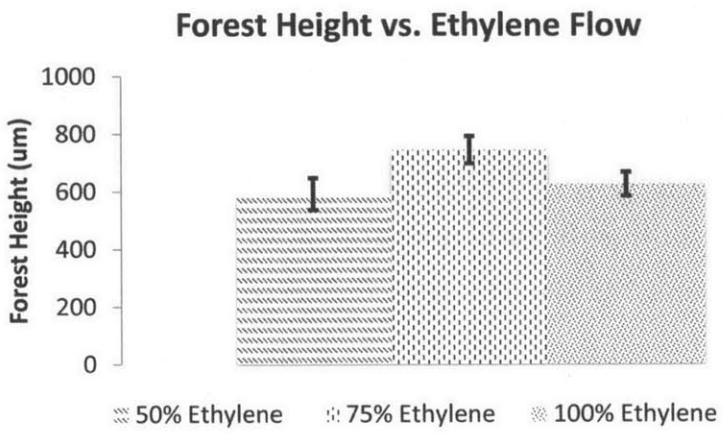

Figure 2-3: Comparison of different Ethylene flow rates during growth. Average forests heights were 590 um, 743 um, and 625 um for 50%, 75%, and 100% Ethylene flow.

2.2 Growth Time

The 12.5 minute growth time has been shown to yield 1mm tall forests, and therefore has had no reason to change. It also stands to reason that flowing Ethylene for longer times should result in taller forests, because of the influx of Carbon with which to form CNTs. Figure 2-4 reveals that this is not the case. Not only does the longest growth time not yield any 1mm tall forests, which could be explained by those growths being 2nd or later growths, but all three cases grew shorter forests. It has been shown that abrupt forest termination can occur when individual CNTs are pulled away from their catalyst particle by surrounding CNTs [26, 27], and it is a possible explanation for why longer growth times don't result in taller growths. For time considerations, there was no good reason to change the growth script to use a longer growth time.

2.3 The Complications of Studying Water

Preliminary tests of water during growth were performed using a rudimentary water bubbler system connected to a He mass flow controller. Adding water during growth

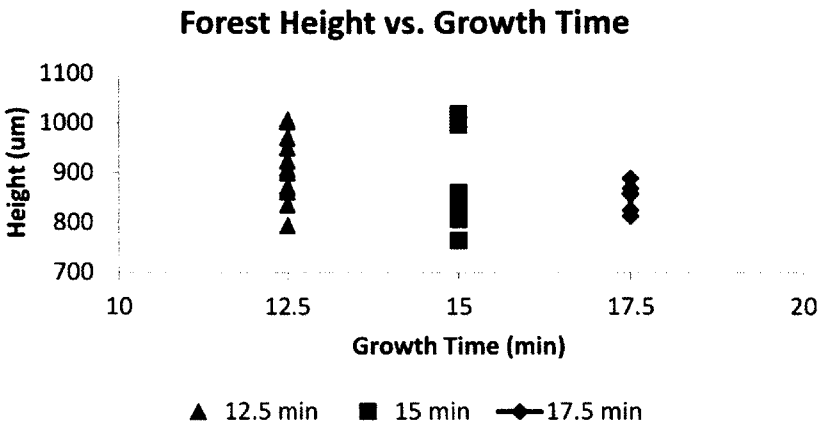

Figure 2-4: Forest heights of batches grown for 12.5, 15, and 17 min.

could recreate the environment of first of day growths, leading to significant gains in height over multiple growths in a day. However, the results showed no relationship between heights of forests grown with and without water. Limitations on drawing conclusions from this study come from a small sample size, and the current furnace setup which does not allow for testing of water effects on growth. Water added during growth has been shown to dramatically increase the height of forests [17], but with a method of adding O_2 gas to create water vapor that is more accurate and controlled. First-of-day growths and the literature suggest that the controlled addition of water to growth would increase forest heights, and it will be necessary to build a more precise and controllable system to realize these gains.

Chapter 3

Experimental Approach

3.1 Experimental Setup

Herein is a description of the experimental equipment, procedures, and CNT forest characterization.

3.1.1 Furnace and Gas Setup

CNT forests are grown in a Chemical Vapor Deposition (CVD) furnace in a 22mm diameter "1 inch" quartz tube, with a preheater furnace, shown in Figure 3-1. Helium, Hydrogen and Ethylene (C_2H_4) gas tanks are connected via stainless steel tubing, and led to a mass flow controller (MFC). The furnace and preheater are located inside a fume hood because of possible high temperature, high pressure interactions with Hydrogen and Ethylene gases. The downstream end of the furnace leads to a bubbler with mineral oil, which acts as a physical measure of gas flow through the system, and an indicator of pressure changes. The flow of gases and furnace and preheater temperature are controlled via Ansari software.

3.1.2 Sample Preparation

A catalytic layer of 1 nm Fe/10 nm Al_2O_3 is electron beam deposited onto the 500nm layer of protective oxide layer of [100] Silicon wafers, serving as the substrate for CNT

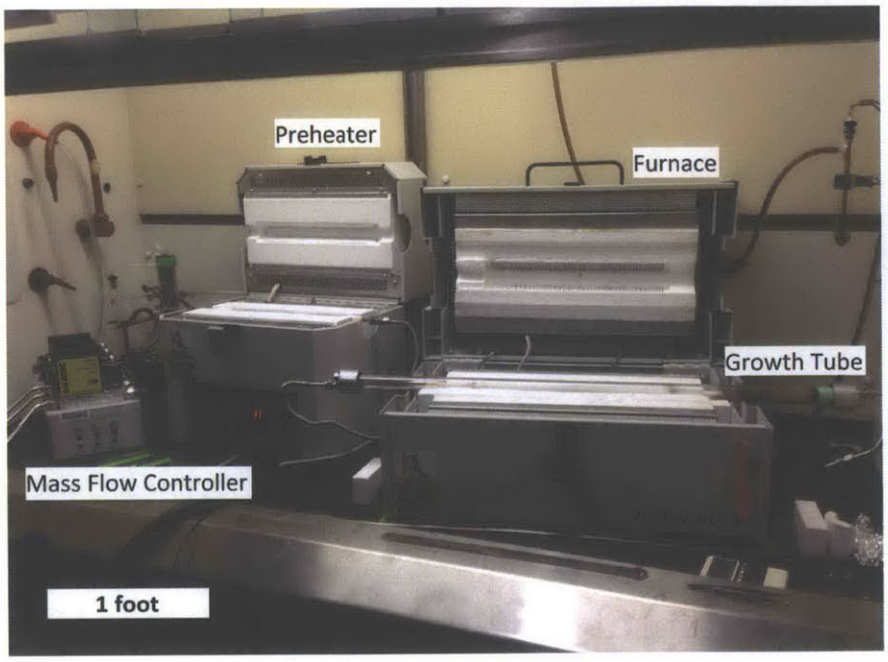

Figure 3-1: Picture of fume hood setup.

forest growth. 1 cm x 1 cm chips are cleaved from the wafer by scratching notches into the wafer surface and three-point bending the wafer. Wafers are procured and processed by several members of Necstlab, and then are shared amongst those growing forests.

Chips are then cleaned using Scotch brand tape, to remove dust and broken wafer bits from the surface. Three chips are placed 1cm apart in a quartz boat procured from Finkenbeiner, as shown in Figure 3-2. The entire boat is placed in the quartz growth tube, and maneuvered to the center via a stainless steel rod. The growth tube always remains in the same location relative to the furnace, and the sample boat is placed so that the sample chips are at -1cm, 1cm, and 3cm as measured from the center of the furnace. Once positioned, the growth tube is connected to the gas lines, and the furnace and preheater lid is closed.

3.1.3 Ansari Growth Script

The Ansari growth script has five phases. First, the ambient air is flushed out of the system with He, then the furnace and preheater are turned on and allowed to ramp to

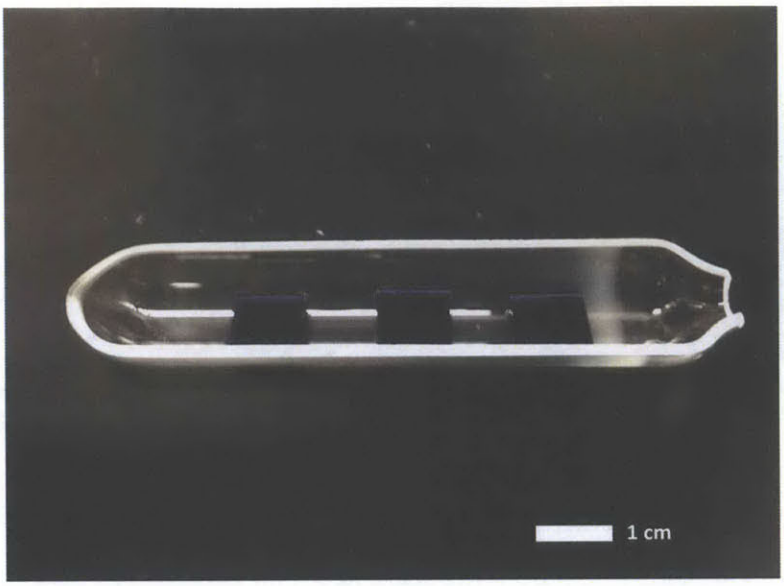

Figure 3-2: Finkenbeiner quartz boat with three samples loaded. Chips are 1cmx1 cm, and are placed 1cm apart.

the final growth temperature. During this time, H_2 is flowed to reduce the naturally occurring oxidation on the Fe catalyst layer, so that it can anneal and Ostwald ripen into catalyst particles. De-wetting of the Fe layer is assisted by the layer of Al_2O_3. The growth phase begins when Ethylene, the source of carbon, is turned on. The preheater assists in the heating up of the gases, allowing the hydrocarbons to pre-crack and be ready to decompose onto the wafers. The next phase is the easy delamination step, where Ethylene is cut, but H_2 is left on to eat away at the roots of the CNTs. The final phase is cool-down, when the furnace and preheater are shut down. Cool-down runs concurrently with the easy delamination step. He continues to flow until the furnace cools down to <200°C, and the forests can be removed anytime thereafter.

3.1.4 Growth Cool-down Profiles

Four different growth cool-down procedures were implemented to study the effects of post-growth CNT kinetics. All four procedures used the basic growth script detailed above, with the removal of the H_2 post treatment easy delamination step. In the baseline growths, the preheater and furnace were shut down at the end of the growth phase, but were not opened until five minutes had been allowed to pass. This five

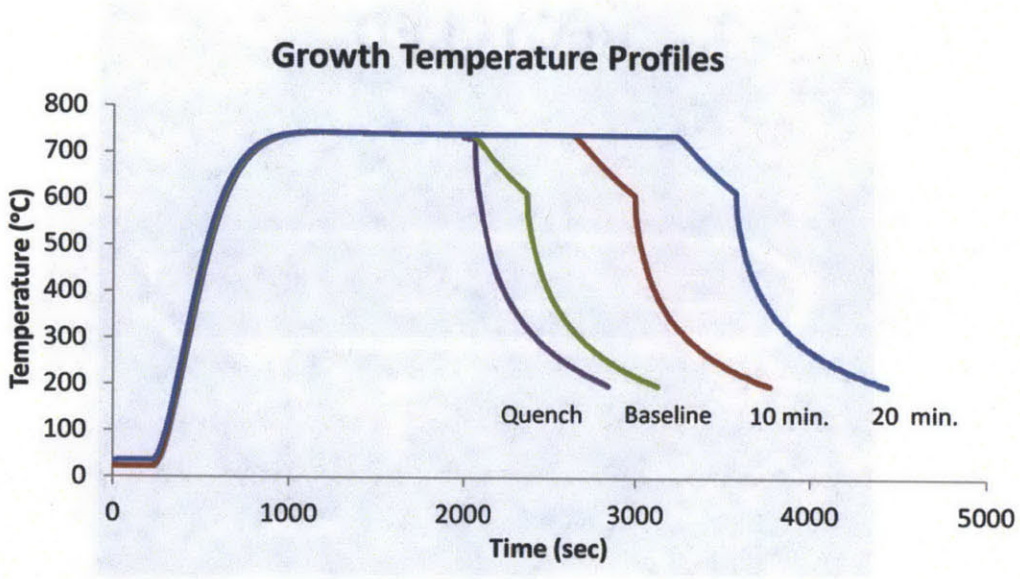

Figure 3-3: Comparison of baseline, quench, and two deforestation cool-down temperature profiles.

minutes allowed the furnace to cool down to approximately 630°C. In the fast cool down quenched growths, both preheater and furnace lids were opened immediately after the growth phase was over, and the quartz growth tube was removed from the furnace and allowed to cool in the ambient fume hood temperature. In two deforestation growths, both preheater and furnace were left at temperature for 10 and 20 minutes, before being allowed to cool under the same procedure as the baseline growths. Figure 3-3 shows the comparison between each growth temperature profile. The quench cool-down condition will show forest height at as close to 12.5 minutes of growth time. The extra change in slope evident in the baseline and two deforestation steps is the five minute slow cool-down period where the preheater and furnace were turned off but were not opened.

It should be noted that these measured temperature is the set-point taken from the thermocouple built into the furnace lid, and is therefore not a direct measure of the temperature of the quartz grow tube or the samples within. It can be assumed that the quenched growth cool-down profile within the reference frame of the samples would be significantly faster. Likewise, the baseline and deforestation cool-down profiles would probably be slower, as the growth tube is still resting in close proximity to the large hot mass that is the furnace. With these considerations, it is the relative difference

in cool-down profile that is most important. The baseline and deforestation growths have identically cool-down profiles so that the time effect of annealing the samples can be investigated. The baseline growths are the most similar to current growths for comparative purposes.

3.1.5 Growth Schedule

To study the effect of first-of-day vs. subsequent growth heights, three growths of a single condition were grown in a row. On average, six growths were done a day, with a maximum of nine growths in a day. Each batch of three growths was followed by a tube bake-out, so that the growth tube would be clean for the subsequent batch.

3.2 Forest Height Measurements

Forest height measurements were performed using an optical microscope at 20X magnification and a moving z-stage. The base of the CNTs could be identified by focusing on the edge of the wafer, where there is a thin region of wafer surface without CNT growth. Then the forest height could be calculated by incrementally moving the z-stage until the forest top comes into focus. Each sample was measured in two corners and in the center. Measured forest heights are accurate to +/- 10um, between the 5um focal depth of the 20X magnification lens and drift in the z-stage gears.

Chapter 4

Results and Discussion

Forest height measurements between all four growth types are shown in Figure 4-1 and Figure 4-2 by position in the growth tube. As was expected, each condition shows significant variance between shortest and tallest growth, and a simple conclusion about the effects of cool-down cannot be constructed. Figure 4-3 shows a direct comparison between the average forest heights by growth position and cool-down condition. Figure 4-4 compares the average heights of first-of-day growths, all growths, and all but first-of-day growths. Figure 4-5 compares the average heights of forests by position in the growth tube. All error bars show standard deviation in forest height.

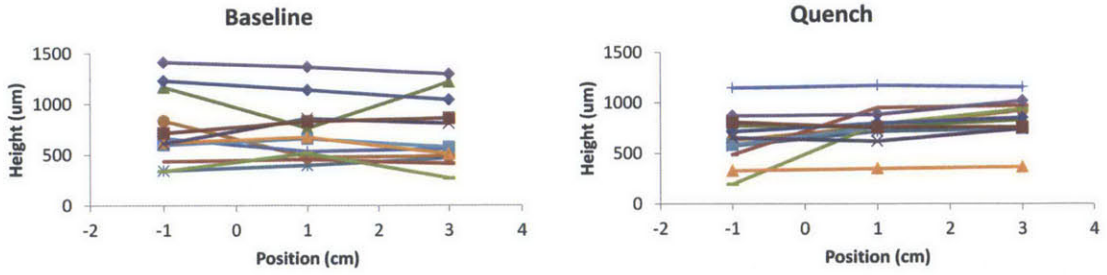

Figure 4-1: Plot of all forest heights by chip placement for baseline and quench growth types. Forests of each growth are connected to show variability.

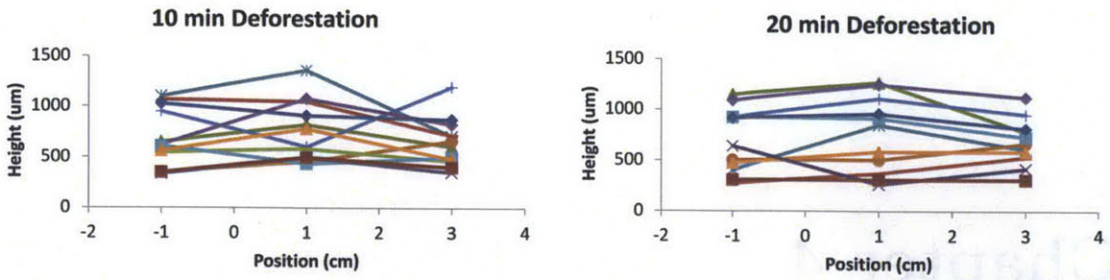

Figure 4-2: Plot of all forest heights by chip placement for both deforestation growth types. Forests of each growth are connected to show variability.

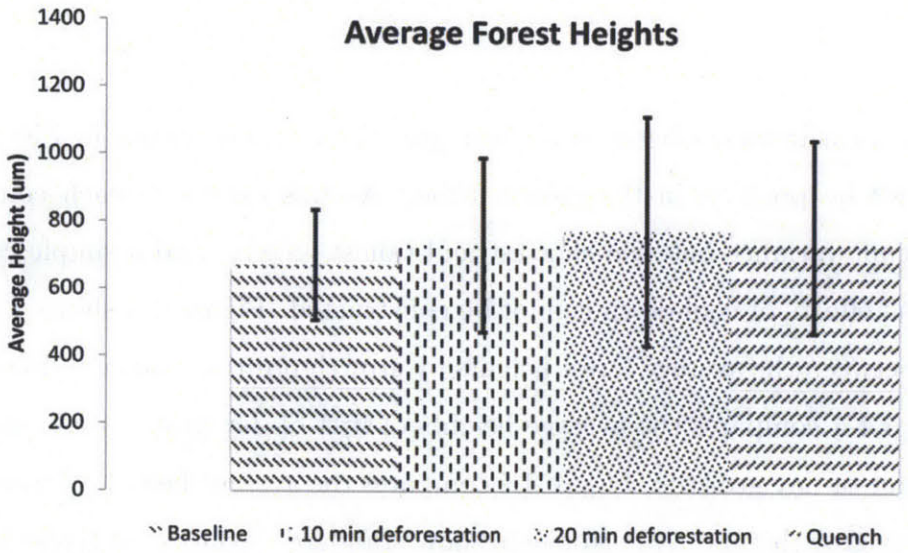

Figure 4-3: Average forest heights between the four cool-down conditions.

4.1 First-of-Day Growths

Figure 4-4 shows that first-of-day growths grow consistently taller forests than any subsequent growths, even between different cool-down conditions. However, there is only one first-of-day growth per growth condition, compared with latter growths per condition. It is then understandable that the range of heights between 3 samples in 1 growth is significantly smaller than the range between 24 samples.

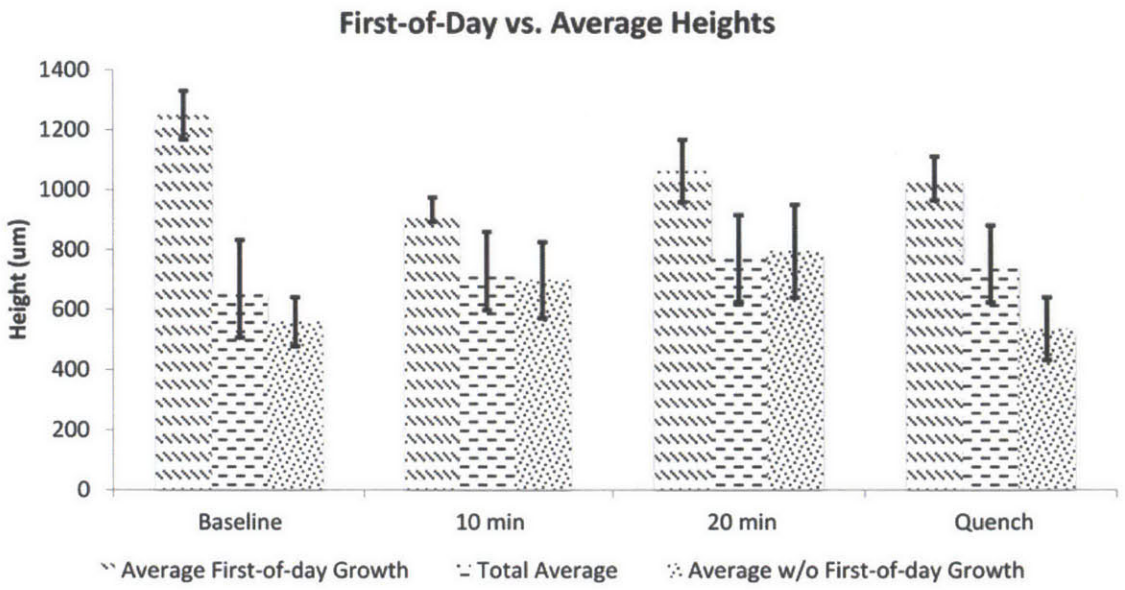

Figure 4-4: Comparison of forest height averages with and without first-of-day forests.

4.2 Effects of Post Growth Cool-down

From an understanding of CNT forest growth mechanics and kinetics, a forest held at high temperature without a renewing carbon source would find it favorable to decompose. Catalyst particles can "eat" away at CNTs, similar but opposite to the process of CNT growth. But this deforestation effect is not evident in any of the four cool-down types. Although the main goal is to grow tall forests, it would be easier to see the effect of the different cool-down conditions if the first-of-day growths (the most significant contributor to height variability) were discounted. The standard deviation between non-first-of-day growths in Figure 4-4 show that there is no significant correlation between cool-down conditions.

The most likely explanation for why some of the deforestation forests are taller than the baselines is that while the Ethylene source was stopped, there was still enough Ethylene and Carbon byproducts remaining in the tube for the forests to keep growing. This theory not only explains the increase of 20 um in height between quenched and baseline growths, but also the 140um increase in between baseline and 10 minute deforestation growths, and the 100 um increase between 10 and 20 minute deforestation growths. The significant increases in height between each condition are

relative to the amount of time samples spent at elevated temperatures post growth. It is possible that the Carbon debris deposited on the growth tube is a significant source of post growth carbon, which in turn could explain why first of day growths do not follow a similar trend. With less Carbon debris accumulated during the first growth, there would be significantly less Carbon available. It is also possible that catalyst involvement with CNT growth is affected by the height of the forest, as a function of Carbon diffusivity through the forest.

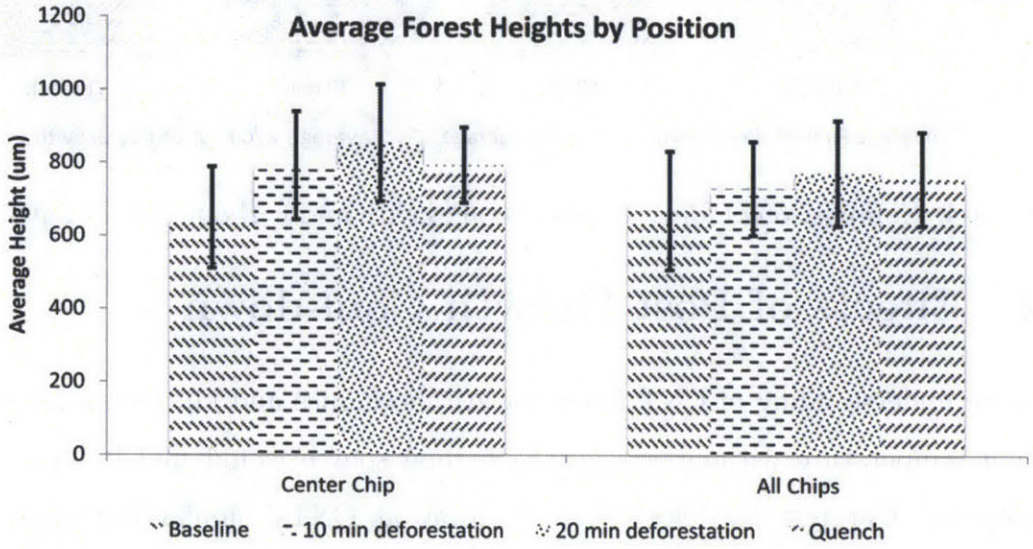

Figure 4-5: Average forest heights between the four cool-down conditions.

The increases in height seen in the deforestation conditions are correlated to furnace temperature, as shown by Figure 4-5. Forest in all sample positions from baseline and quench growths grew similarly tall, unlike the case of the deforestation growths. The center chips in the two deforestation cases grew taller than average, which indicates a positive correlation between increased temperature and the continued growth of CNTs without Ethylene flow. This supports the theory that the Carbon deposits in the growth tube substitutes as the Carbon source for growth.

Growing forests with the "deforestation" cool-down condition may be a small trick to growing taller forests, but is not a sustainable approach for consistency. At the very least, we have confirmed that deforestation effects do not apply under our growth conditions.

4.3 Conclusions and Future Work

First-of-day growths grown with any cool-down condition continue to yield the tallest forests, although subsequent longer "deforestation" growths yield forests taller than any other condition. This suggests that the most significant contributors to CNT forest growth studied here are related to conditions in the growth setup at the beginning of the day. Experiments from other laboratories strongly suggest that humidity is an integral piece, and future work should strive to recreate first-of-day conditions multiple times in a row. The new mass flow controller that is currently being built with a water sensor and controller will be instrumental to furthering our knowledge of how water can influence CNT forest growth. The key to consistent growths may be as simple as pre-humidifying the growth system.

It would also be interesting to see how furnace temperature at the start of growth affects repeatability. Due to time constraints the forests in this study were grown before the furnace reached ambient temperatures. If less variability is found in growths started at ambient temperature, then catalyst annealing time would need to be more strictly controlled. Ideally forest height variability depends on water in the system before growth, which can be artificially recreated, and controlled annealing time, which can be easily accomplished with a new growth script. While these changes would require more time per growth, the time and cost savings may be a positive tradeoff.

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