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The Effect of Growth Parameters on the Height and Density of Carbon Nanotube Forests

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THE EFFECT OF GROWTH PARAMETERS ON THE HEIGHT AND DENSITY OF CARBON NANOTUBE FORESTS

by

Robert W. Call

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Physics

Approved:

Tsung-Cheng Shen Major Professor	David Peak Committee Member
D. Mark Riffe Committee Member	Mark R. McLellan Vice President for Research and Dean of the School of Graduate Studies

UTAH STATE UNIVERSITY
Logan, UT

2012

ABSTRACT

The Effect of Growth Parameters on the Height and Density of Carbon Nanotube Forests

by

Robert W. Call, Master of Science

Utah State University, 2012

Major Professor: Dr. Tsung-Cheng Shen
Department: Physics

Carbon nanotube forests (CNTFs) are grown using an injection chemical vapor deposition method. Images of CNTFs are taken using a scanning electron microscope and are used to measure their height and density. Growth parameters are systematically varied to determine their effect on the height and density of CNTFs. Investigations of CNTF density as a function of distance from the growth substrate reveal that diffusion can be a limiting factor on CNTF growth. Our findings indicate that height and density are related and that each growth parameter has multi-dimensional effects.

(44 pages)

PUBLIC ABSTRACT

The Effect of Growth Parameters on the Height and Density of Carbon Nanotube Forests

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Rolled-up graphene sheets, known as carbon nanotubes, are grown in vertically aligned arrays called carbon nanotube forests (CNTFs). CNTFs make extremely dark surfaces. They are being investigated for use on space crafts as calibration surfaces and to protect optical sensors from unwanted signals. These CNTFs are grown by injecting a precursor consisting of a metal catalyst particle and a hydrocarbon component into a furnace at high temperature (~700°C). This study investigates the influence of several different growth parameters on the final height and density of the CNTF. Height and density influence the absorbance of the surface at different wavelengths.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. T. C. Shen, for his tremendous patience and direction on this project, as well as my committee members, Dr. David Peak and Dr. Mark Riffe. This work was funded by the Space Dynamics Laboratory, a part of the Utah State University Research Foundation. I would also like to thank the USU College of Science, Department of Physics, and School of Graduate Studies for providing me with scholarships and a fellowship that allowed me to conduct this research.

Robert W. Call

CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

INTRODUCTION

In modern materials research, some of the most promising candidates for application in technology are different low-dimensional forms of carbon whose properties differ dramatically from those of amorphous bulk carbon. One of these structures is a hollow cylindrical shape known as a carbon nanotube. Carbon nanotubes (CNTs) were first grown by Ijima in 1991[1] and since then have been intensely researched because of their interesting electrical, mechanical, and optical properties.

A carbon nanotube can be thought of as a graphene sheet that has been rolled into a cylinder. The specific structure of a CNT is important because it dramatically affects its properties. First of all, there are single-walled and multi-walled CNTs. CNTs can differ in their chirality (the angle at which they have been rolled), radius, and length. They can also be grown in arrays or bundles. All of these factors can affect their properties and thus need to be controlled during the growth process.

The property of interest in this study is the emissivity of CNT arrays. From Kirchoff's law, we know that emissivity is equal to absorptivity. Figure 1 shows the emissivity of a single-walled CNT array compared to three other commercially available black surfaces. The array has significantly better emissivity than the other surfaces and therefore, it is a much better absorber. In fact, it is almost a perfect black body.[2] Low-density vertically aligned CNTs, also called carbon nanotube forests (CNTFs), have been shown to have a total integrated reflectance of less than 0.045% for optical wavelengths, which is nearly 35 times lower than the NIST certified reference for optical reflection, and less than 0.2% for mid-to-far-IR wavelengths.[3]

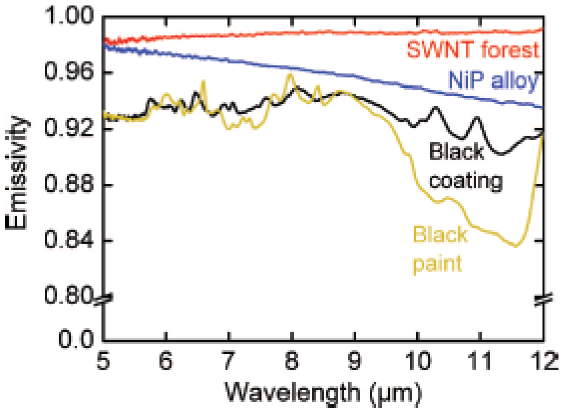


FIG. 1. Emissivity of a single walled carbon nanotube array (SWNT) compared to other commercially available black surfaces.[2]

Existing black surfaces are only absorptive for a particular range of wavelengths. We want to develop a method to grow CNTFs for as broad a range of wavelengths as possible. We expect the geometries of CNTF would play a part in the range of absorbed wavelengths from the basic theories of light interacting with matter. The height and density of CNTFs can be controlled by the various parameters of the growth process. There are three common methods for growing CNTs: arc-discharge, laser ablation, and chemical vapor deposition. Of the three methods, chemical vapor deposition (CVD) has been the most popular one because of its simplicity and commercial potential.

Chemical Vapor Deposition

Several variants of CVD are used to grow CNTs, but they all have the same basic process. The biggest difference is in how the catalyst is deposited on the growth substrate. In deposition CVD, the catalyst is deposited onto the substrate by sputtering or evaporation. Particles are formed by depositing a thick layer on the substrate and then etching it or depositing a thin layer (~.1 nm) and allowing it to clump into particles.

During injection CVD, the predeposition of the catalyst is skipped and instead the catalyst, generally in the form of a metallocene, is dissolved into a solvent.[4] This liquid precursor is injected into a hot reactor where it quickly evaporates. Pyrolysis of the metallocene allows the metal catalyst atoms to deposit on the substrate and diffuse around to form catalyst particles. For this study we use injection CVD with a mixture of ferrocene and xylene as the precursor.

The CVD process generally starts by flowing an inert gas through the reactor tube to displace unwanted gasses. This continues while the reactor is heated to approximately 700°C. The liquid precursor is injected into the reactor where it evaporates and the inert gas carries the gaseous precursor to the growth substrate. Unwanted byproducts from the growth reaction are pushed out of the reactor by the carrier gas. Other gasses might also be fed into the reactor: hydrogen is necessary and water vapor can also be useful.[5] The specific gasses and their concentration in the reactor are critical in controlling the growth.

CNT Growth Mechanism

There are two growth mechanisms for CNTs: base and tip growth.[6, 7] During base growth, hydrocarbons react with the metal catalyst particles on the substrate. Carbon atoms dissolve into the catalyst and precipitate at crystal edges. The carbon eventually completes a ring around the catalyst particle and new carbons react with the particle and push up old growth.[7]

During tip growth, the catalyst particle does not remain anchored to the substrate. Instead the carbon rings growing around it eventually push the particle to the top of the CNT.[6] The process continues with short lengths of CNT growing from the catalyst particle that then squeeze the catalyst to the top of the tube. Another possibility is that new catalyst lands on existing CNT and reacts with incoming carbon from that position.[8] The actual growth mechanism is determined by the binding strength of the catalyst particles to the substrate. In this project, evidence suggests base growth is the growth mechanism.

One of the principal challenges for continuous growth is the build-up of amorphous carbon on the catalyst particles. Eventually the amorphous carbon can cover a catalyst and stop the growth from that particular particle. The problem can be reduced by injecting a small amount of an oxidizing agent to burn off the amorphous carbon or by using injection CVD where fresh catalyst particles are continuously being deposited on the substrate.[5]

Another challenge to the base growth mode is the diffusion of the catalyst and fractions of hydrocarbon molecules on the substrate. The diffusion rate of Fe catalyst on the substrates is the major factor for the density of the CNTF. If the diffusion rate into the substrate is too high, the catalyst particles can diffuse into the substrate. This makes CNT growth on metals extremely difficult. For example, Fe catalyst particles can diffuse 35nm into a copper substrate in one second at 700°C.[9]

If the diffusion rate is too low and the nucleation rate is high enough, the CNTF could become more and more dense. Eventually it could reach the point that it inhibits the diffusion of the precursor molecules through the forest and, for a base growth system, that would terminate the growth. This condition is known as diffusion limited growth. Li et al., claim that this effect is negligible, but we find that it is an important factor to determine the saturation height of the CNTFs.[7]

Sustained Growth with Injection CVD

Ideally, a continuous growth state can be established inside the reactor leading to linear increases in height with time. In order to obtain this state in injection CVD, the nucleation rate of new catalyst particles on the substrate must match the death rate of the older catalyst particles. The nucleation rate is tied closely to factors such as precursor concentration, injection rate, and volume, as well as CNTF density and height. Those factors determine the total number of catalyst atoms that arrive at the surface to form particles.

Other factors must also be taken into account, for example, the rate at which the metallocene breaks apart. That is controlled by the reactor temperature and the composition of gasses in the reactor. The composition of gasses in the reactor can also contribute to the lifetime of the catalyst particles and thus affect the required flux of new catalyst particles.

We intend to optimize these conditions by using scanning electron microscopy (SEM) images of CNTFs to measure the height and density of CNTFs grown under different conditions. By taking the ratio of the density near the bottom and top of the CNTF, we can determine if the rate of creating new catalyst particles is too high (ratio>1), too small (ratio<1), or almost right (ratio~1). As long as the initial density is not too high, a growth with a ratio near one should be close to being sustainable. This measurement will be referred to as the density ratio.

BACKGROUND

While the mechanical, electrical, and optical properties of CNTs and CNTFs are extremely useful, they are also a challenge to engineer. The different parameters of the growth process must be carefully controlled to produce CNT/CNTF with the desired properties for a particular application. In some cases, attributes such as chirality, purity, and diameter are important; but in this study, the chief concerns are density and length as indicators of sustainable CNTF growth. The principal growth parameters affecting density and length are the substrate, temperature, precursor composition and injection rate, and the composition of the growth chamber atmosphere.

The following is a brief review of the effect of these different growth parameters as found in CNT literature. Interpreting the results of CNTF experiments has proven to be difficult because a change in a single parameter has multiple effects on the growth. For example, increasing the amount of hydrogen in the reactor will help breakdown hydrocarbons faster to fuel CNT growth. Conversely it has been shown that hydrogen has an inhibiting effect on CNT growth.[10, 11]

Previous CNTF work is often based on looking at one change in a CNTF's final properties due to a variation in a growth parameter, such as final length, CNT thickness, distribution, or impurity. We have found the effects of changes in growth parameters are multi-dimensional and that, in particular for injection CVD, length and density are interdependent. Another problem with comparing work done by different groups is that small differences in the experimental setup can lead to large differences in the final results. Because of these factors, the results from previous studies can differ greatly and are occasionally contradictory. Following this review, Table 1 provides a simplified explanation of the effects of these parameters for reference.

Substrate

Quartz, sapphire, and silicon were used as growth substrates in this study. The growth substrate is important because it dictates the diffusion of catalyst particles on the surface. High diffusion rates of the catalyst on the substrate cause small catalyst particles to group together on the substrate surface and form larger ones. Catalyst particles can also diffuse directly into the substrate. These actions result in a decrease in density and can also cause an increase in CNT diameter. The result of differences in diffusion is that for each substrate, there will be different optimal growth conditions for obtaining sustained CNTF growth.

Occasionally a desired substrate is simply not suitable for CNTF growth. For example, metals are problematic substrates because the metal catalyst particles tend to diffuse into the bulk at high temperatures. A simple solution to this problem is to deposit or grow a diffusion barrier on the surface of the substrate, such as titanium oxide or aluminum oxide.[9] Silicon has a similar problem with CNTF growth, but it is resolved by growing an oxide layer on the surface. Cao et al. found that CNTF growths are dependent on the thickness of the oxide layer.[12]

Growth Temperature

Higher temperatures will increase the diffusion rate of the catalyst, both on and into the substrate. A higher diffusion rate can lead to a lower density and a larger average catalyst particle size. This in turn influences the density and diameter of CNTs, as discussed previously.[10, 13]

Higher growth temperatures also enhance the pyrolysis of hydrocarbons. Instinctively this would seem beneficial to the growth rate, because more carbon would be available per unit of time. However, Patole et al. found that the increased pyrolysis actually served to decrease CNTF growth rate because of the deposition of pyrolyzed carbon on the catalyst particles.[14]

Precursor Composition, Injection Rate, and Volume

The concentration of the metallocene in the precursor is important for a number of reasons. It is a control on the size of the catalyst particles. A lower concentration results in smaller catalyst particle size because of the scarcity of metal atoms.[10] This scarcity also points to lower CNTF densities, but this is more difficult to confirm because density is also closely coupled to the precursor injection rate. These two parameters combined are extremely important in obtaining a flux of catalyst particle on the surface that leads to sustained growth in injection CVD. Thus, they must be carefully optimized with respect to each other.

If the metallocene concentration is reduced, but the injection rate of the precursor is increased, the flux of metal atoms onto the substrate could remain approximately the same over a set amount of time. However, the quantity of available hydrocarbons would increase, which might enhance the synthesis of polyaromatic hydrocarbons (PAHs). Both the metallocene concentration and the precursor flow rate contribute to the density of the CNTF.

Since the catalyst particle lifetime is often limited to a few minutes, there must be a constant new supply of catalyst particles for growth to continue. The metallocene concentration and precursor flux must be optimized so the flux of new catalyst onto the substrate matches the death rate. If the flux is too high, the density of the CNTF will slowly increase until it is too dense to allow diffusion. In this experiment, we also found that higher precursor injection rate requires a higher concentration of hydrogen in the system to prevent the formation of PAH. If the catalyst flux is too low, the forest density might not be sufficient to create a dark surface.

The volume of the precursor is important because it determines the total amount of catalyst and carbon in the system. In an ideal sustained growth, additional precursor would lead to a linear increase in CNTF length, while keeping the density constant. Generally, the precursor volume will be kept constant in these experiments, while focusing on the effects of the injection rate and metallocene concentration.

Growth Atmosphere

Another solution to the problem of sustained growth is associated with the mixture of gasses in the growth chamber. Gasses, like oxygen and hydrogen, can play important roles in the growth process. Hydrogen can help break down carbon rings, but it can also inhibit CNT formation.[10] Oxygen can burn off the amorphous carbon on the catalyst particles and thus extend their lifetime, but it can also oxidize the catalyst particles to render them inactive. Oxygen can be introduced by water vapor, air, or pure oxygen gas.[5, 14, 15] These gasses can be helpful in CNTF growth, but they must be carefully controlled and optimized to obtain sustained growth.

Table 1. Effects of injection CVD growth parameters.

Substrate	Affects density
Temperature	Affects density and growth rate
Catalyst Concentration	Affects density
Precursor Injection Rate	Affects density and pyrolysis
Precursor Volume	Affects height
Atmosphere	Affects pyrolysis and growth rate

EXPERIMENT

Sample Preparation

Sample surfaces are cleaned prior to growth to remove surface impurities. All substrates are first placed in an acetone bath and sonicated for 30 minutes. The process is repeated with a bath of isopropyl alcohol. They are stored in closed pyrex dishes until they are used.

Two substrate types had extra steps in their preparation. Quartz substrates were also etched in a 10% HF solution for twenty seconds. Several different times were tested for etching ranging from 0 – 60 seconds. Twenty seconds gave the best results.

Silicon substrates are not suitable for direct CNTF growth. Therefore, a thicker layer of oxide was grown on silicon samples before growth.

Procedures

An injection chemical vapor deposition method was used for this study. Figure 2 shows a diagram of the experimental setup. There are three main parts to the setup: the injection apparatus, the growth reactor, and the vacuum equipment.

The injection apparatus is pictured in Figure 3. A Swagelok fitting is used to connect the syringe to the apparatus. A 0.25 inch diameter tube guides the precursor to the injector head. In the injector head, the precursor is vaporized and mixed with the carrier gasses.

The injector head fits inside a quartz tube that is used as the reactor for CNT growth. The tube is placed in a Thermolyne single-zone split-tube furnace to be heated

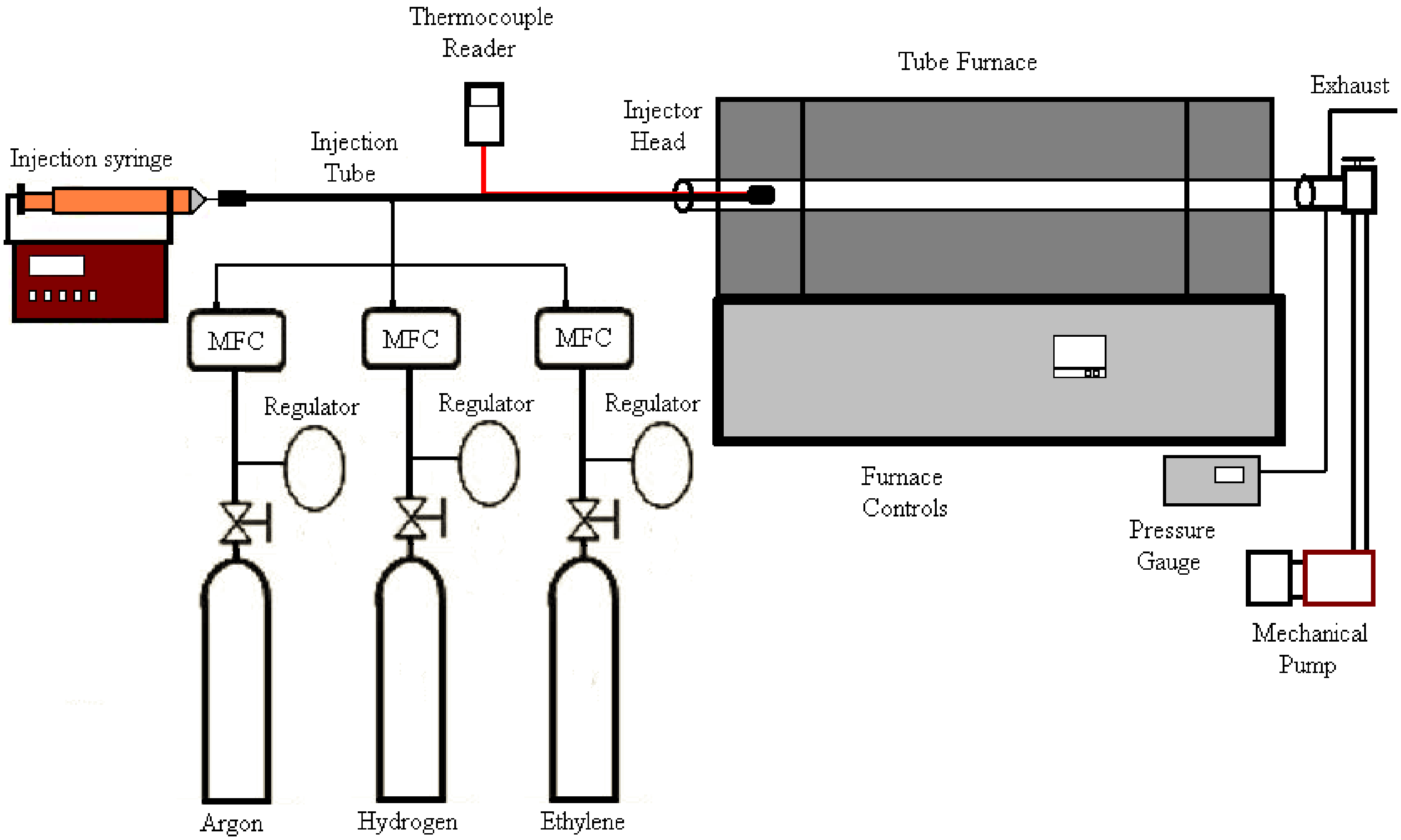


FIG. 2. Experimental setup for injection chemical vapor deposition.

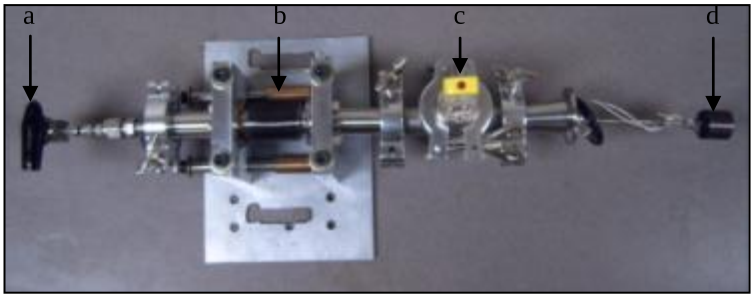


FIG. 3. Injector assembly. a) precursor injection attachment; b) injector head control; c) thermocouple attachment and gas injection connectors; d) injector head.

with the samples positioned approximately nine inches from the center of the tube. Prior to heating, the tube is evacuated to approximately 3×10^{-2} torr (pressure measurement is made with a Varian XGS-600 gauge) to reduce contaminants. After evacuation, the tube is backfilled with argon to greater than atmospheric pressure. The flow of argon is maintained at 50sccm with a mass-flow controller (MFC) to reduce the impurity entering the system.

The furnace is then heated to the desired growth temperature. When the injection head temperature reaches 150°C, the gas flow is altered to have the desired composition for the experiment, while the total gas flow rate is maintained at 100sccm. When the injection head reaches 170°C, the approximate evaporation temperature of the precursor, the precursor solution of ferrocene and xylene is injected into tube by the syringe pump. After the growth, the gas flow is maintained until the furnace temperature reaches 300°C.

Height and Density Measurements

CNTF samples were imaged using a scanning electron microscope. Length measurements were made using low-magnification side-view images of the CNTF. An example of such an image is shown in Figure 4. None of the CNTFs had a constant height across the entire sample. Thus, multiple images were used for each sample to obtain the range of heights, rather than using a single height measurement for each CNTF.

Density measurements are estimated by calculating the percent of each image that is covered by CNT. Percent coverage measurements were made using an image processing program called ImageJ. For each measurement, multiple small regions in the area of interest were chosen to be analyzed. The use of smaller regions was necessary because of brightness gradients across the image.

For each region, a line profile is used to characterize the CNT coverage. Next, a histogram of the region is obtained with ImageJ. The histogram and plot profile are

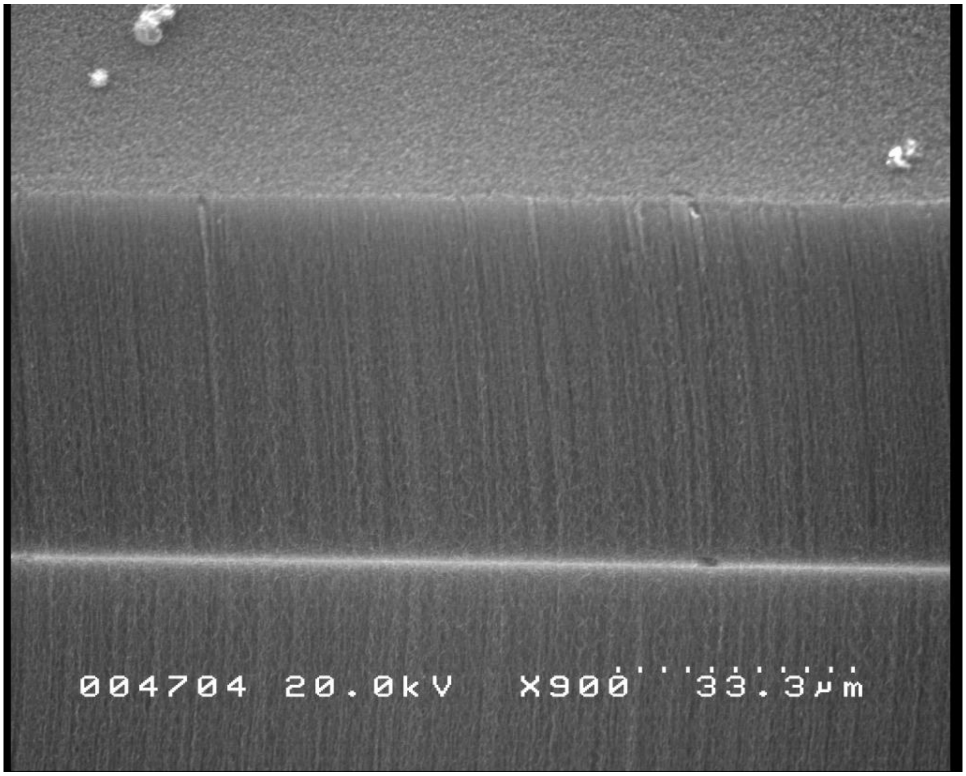


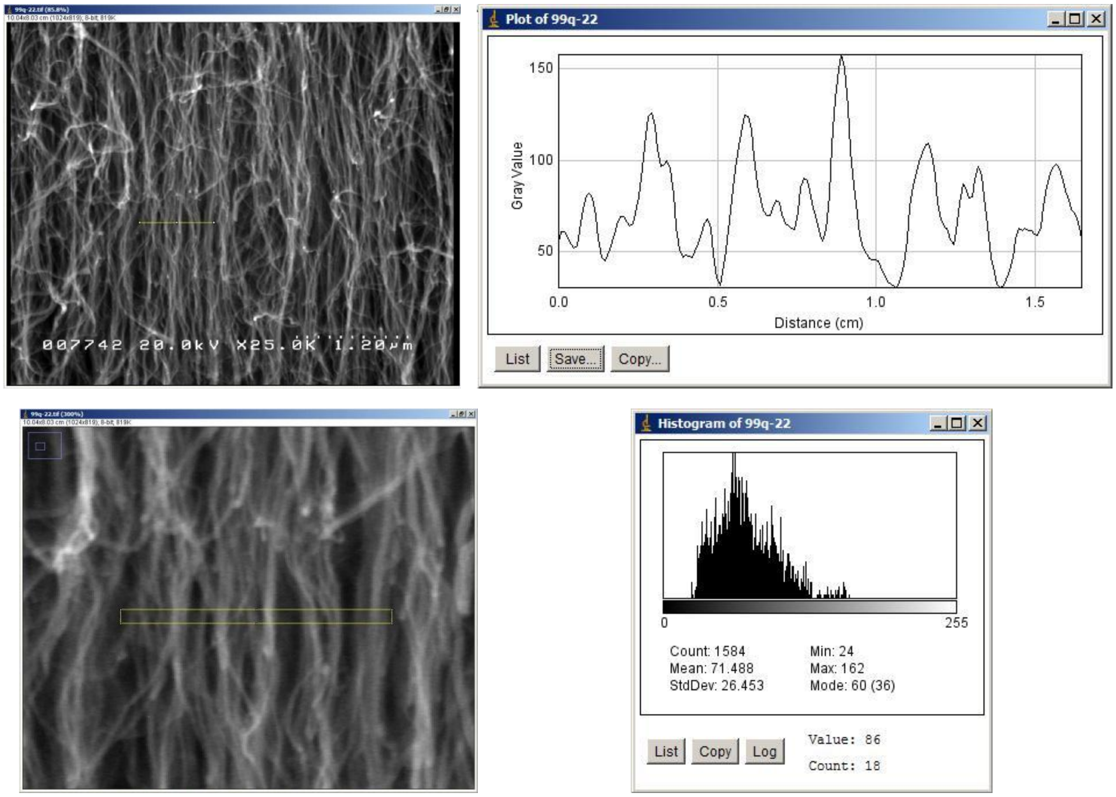
FIG. 4. Side view of CNTF growth for height measurement. Sample 76Q-08.

loaded into a Mathcad document, which plots them both and can apply a threshold to the histogram delineating the difference between covered and uncovered pixels. Thresholds are determined by zooming into the region of interest and doing small line profiles through areas that are uncovered in the region being measured. The maxima of the profiles in these regions are used to set the thresholds.

Determining the correct threshold is difficult because the focus and contrast of the images are imperfect. These problems lead to the CNT images having a fuzzy area surrounding each tube. When multiple CNT overlap, the fuzzy areas of the different tubes are superimposed causing bright regions where no CNT actually exists. In fact, these areas can be even brighter than actual CNTs. To compensate for this, two different thresholds are used for each region. One threshold eliminates almost all pixels that are falsely covered. The other threshold maintains all the CNT that are obviously real. Unfortunately this results in a higher error in the measurement.

After the thresholds are set, the Mathcad sheet uses them to perform percent coverage calculations for each region. The resulting percent coverage measurements are averaged to determine the percent coverage of the area. The standard deviation of the mean of those measurements is the range shown in the images. Figure 5 has an illustrated set of steps for calculating percent coverage, and the Appendix has a copy of the Mathcad sheet used for the calculations.

This method results in significantly higher error in the density measurement, but it appears to be the most accurate of the methods we have tested. The measurements of the percent coverage will be used to describe the density of the CNTF. The density ratio will be a ratio of the percent coverage at the base and the tip of the CNTF.



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Count: 1584     Min: 24
Mean: 71.488    Max: 162
StdDev: 26.453  Mode: 60 (36)

Value: 86
Count: 18
```

FIG. 5. Illustrations for the steps used to calculate density of CNTFs with ImageJ. Top left: draw a line in the desired region. Top right: plot the line profile to make sure average brightness does not increase. Bottom left: zoom in on region and box in region around line. Bottom right: create a histogram of that region.

RESULTS AND DISCUSSION

The following is not a comprehensive review of every experiment in this study. Only experiments investigating the effects reviewed in this paper are discussed.

Substrate

Quartz and sapphire substrates were studied extensively. Silicon was only given a cursory examination. Generally, two or three substrates went through the growth process simultaneously. Thus, the only differences in their growth parameters were their distances from the injector head and a small temperature gradient due to the difference in distance from the center of the furnace. The only other concern is the possibility of a shadowing effect due to one sample being thicker than another. We attempted to minimize that problem by spacing substrates sufficiently.

Growths on quartz substrates tended to be longer and less dense than growths on sapphire substrates. This seems to suggest sapphire substrates have a lower diffusion coefficient for the catalyst particles than the quartz. A lower diffusion coefficient causes the catalyst particles to move around less on the surface, leaving them smaller and less spread out. It also allows fewer particles to diffuse into the surface. That is why CNTFs grown on sapphire have a higher density than those grown on quartz.

The lower height can be explained through carbon conservation. Both the quartz and the sapphire substrates had roughly the same number of carbon atoms available for growth per unit area. Since the sapphire had more (but smaller) catalyst particles on the surface, the carbon on the sapphire was used to supply many more CNTs than the carbon on the quartz. In short, sapphire substrates used the available carbon to form many short CNTs, while the quartz substrates used the available carbon to form fewer long CNTs. Figure 6 illustrates the difference in height between CNTFs grown on quartz and sapphire at the same temperature.

Another set of experiments was done on silicon substrates with different thicknesses of oxide. Earlier work by Cao et al. showed CNTF growth on silicon could be controlled by varying the surface oxide thickness. They report variation in CNTF growth until the oxide reaches 50 nm and then no significant changes.[12] We experimented with oxides many times thicker than Cao et al. and found significant variation in the resulting CNTFs. Figure 7 shows that with increasing thickness the tips of the forests became denser. We also found that for growths with the same experimental

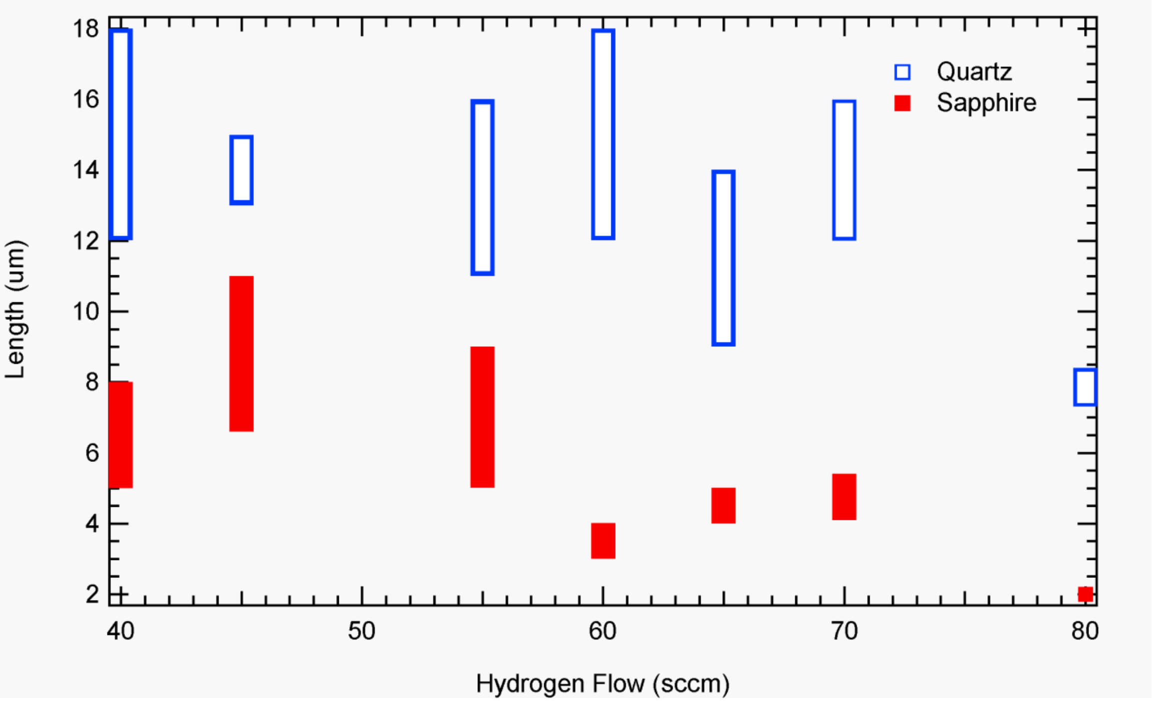

FIG. 6. Comparison of heights of CNTFs grown on quartz and sapphire.

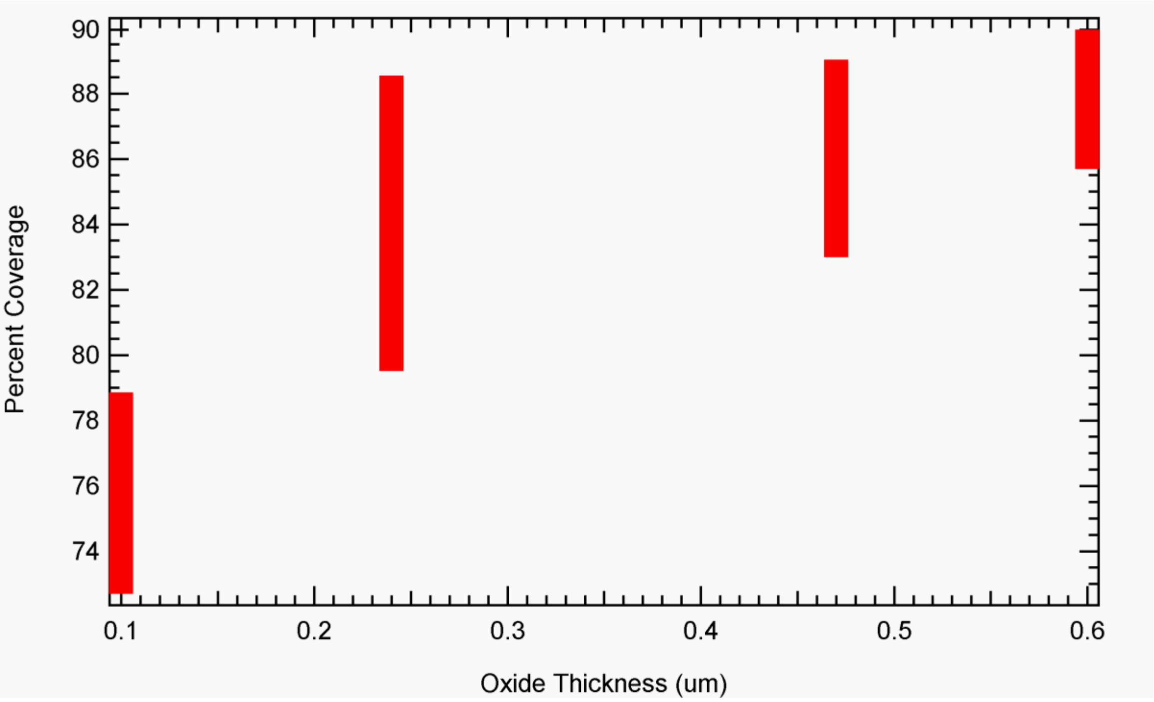

FIG. 7. Percent coverage of CNTF tips vs. oxide thickness. 0.6μm is actually bulk

parameters except oxide thickness, CNFT height increased with oxide thickness.

Temperature

Two temperatures were compared in this study, 700°C and 760°C. We expected that the 760°C growths would have longer CNTF growth than the 700°C growths because the higher temperature would encourage the hydrocarbons to break down faster and thus provide more carbon to be used in the growth. Figures 8 and 9 show the difference in CNTF heights on quartz and sapphire, respectively, at the two different temperatures. It is easy to see that CNTFs grow higher at the higher temperature.

In the experiments represented in Figures 8 and 9, the total volume of precursor was constant for each run. Thus, the hypothesis that the higher temperature would make more carbon available to grow CNT is borne out. There is a difference in the injection

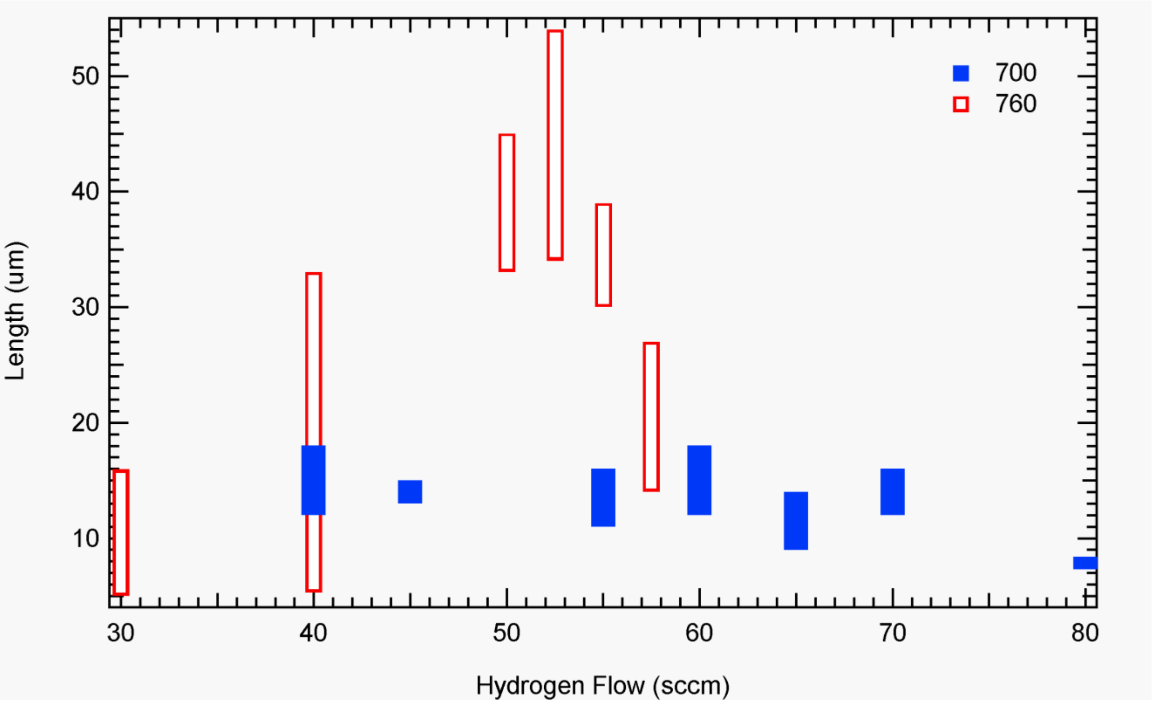

FIG. 8. Heights of CNTF grown on quartz at different temperatures.

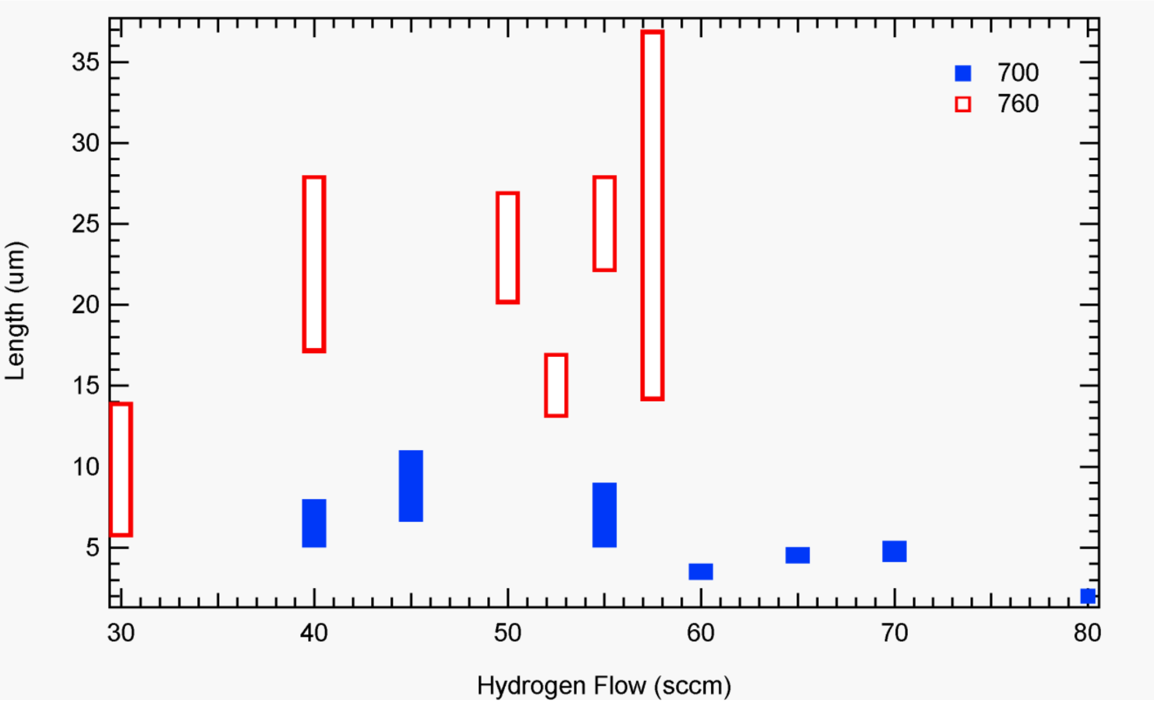

FIG. 9. Heights of CNTF grown on sapphire at different temperatures.

rate between these growths. At 700°C, the injection rate was 2 ml/hr, and at 760°C the injection rate was 4 ml/hr.

Increasing the injection rate increases the flux of carbon and catalyst onto the substrate. Our results show that at the same temperature, a higher injection rate leads to denser, but not higher, CNTFs. Thus the change in injection rate is not responsible for the large change in final height, so the temperature must be responsible for the difference.

The temperature difference also influenced the density ratio (base density/tip density) of the CNTFs. Forests grown at the higher temperature tended to have lower density ratios, which indicate there was greater variation in the density between the tip and the base for higher temperatures growths. A closer look showed the variation in density was entirely due to variation at the base. Tip densities were almost the same irrespective of temperature.

Precursor Concentration and Injection Rate

We also tested the effects of increasing the precursor concentration in the growths. For sample 108Q, a 3% precursor concentration was used. We predicted this growth would be significantly more dense than the growth at 1.5%. Figure 10 illustrates the difference in the densities between the two growths. On average, the 3% growth appears approximately 10% more dense than the 1.5% growth. Apparently, the in-diffusion might play a role in the catalyst nucleation rate.

Investigating the density as a function of distance from the substrate reveals some interesting features of CNTF growth. Consider the plot of 75Q in Figure 11. Notice near the tip of the CNTF, the density remains constant. This is a common feature of many of

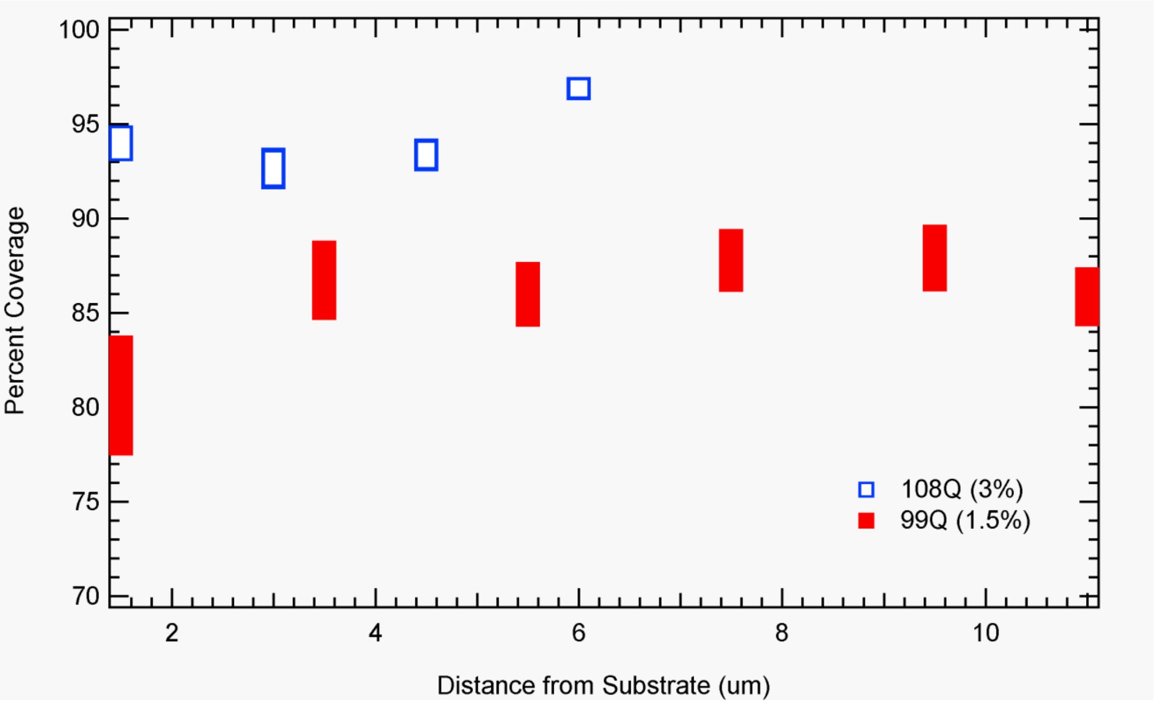

FIG. 10. Density vs. distance from substrate for different catalyst concentrations.

our samples. It suggests that at the beginning of the growth, the catalyst nucleation is at least equal to if not greater than the death rate. Closer to the substrate, there is a very obvious change (decrease) in CNTF density. Since the precursor injection rate is constant, that means the nucleation rate of the catalyst particles decreases with longer diffusion distance in these experiments.

In fact we found that with increasing concentration, which results in an increase in CNTF density; the height of the forests decreased as shown in Table 2. We speculate the reason for the change in height is diffusion limited growth. The CNTF growth with 7.2% ferrocene concentration precursor exhibits particles on the tops of the nanotubes in the forest (see Fig. 12) that are not observed in low-concentration growths. We believe these particles are pyrolyzed carbon that were unable to diffuse to the bottom of the forest and react with the catalyst.[15]

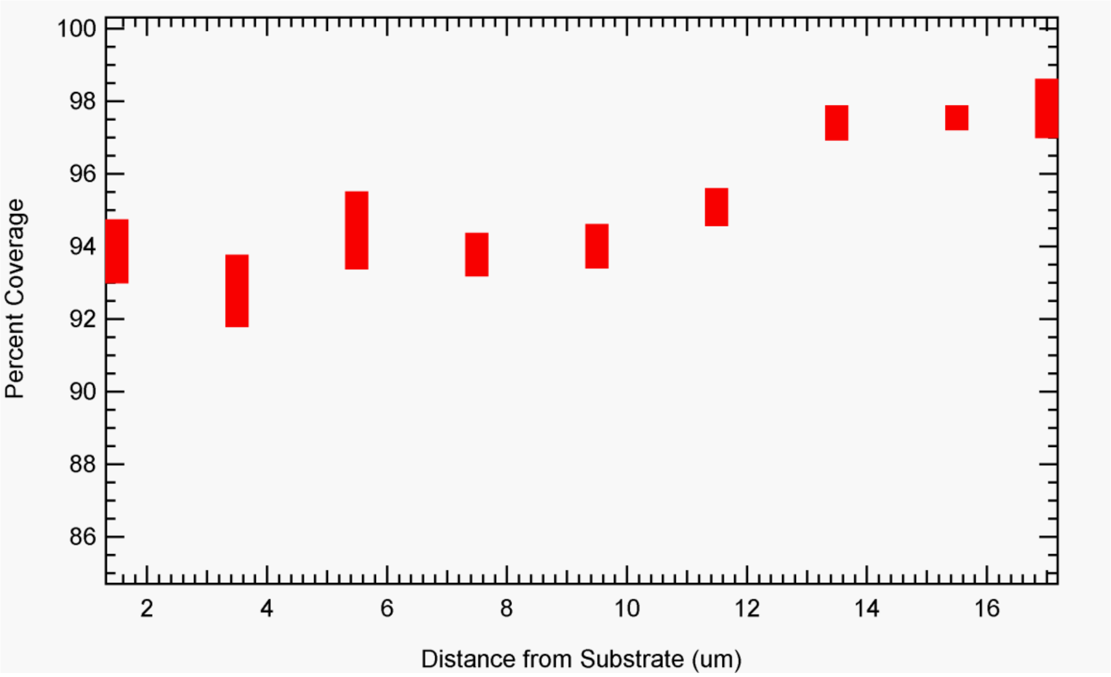

FIG. 11. Density vs. distance from substrate. Sample 75Q.

In another experiment, a small amount of 7.2% concentration precursor was injected into the reactor, followed by 20 minutes of ethylene flow. In this instance no

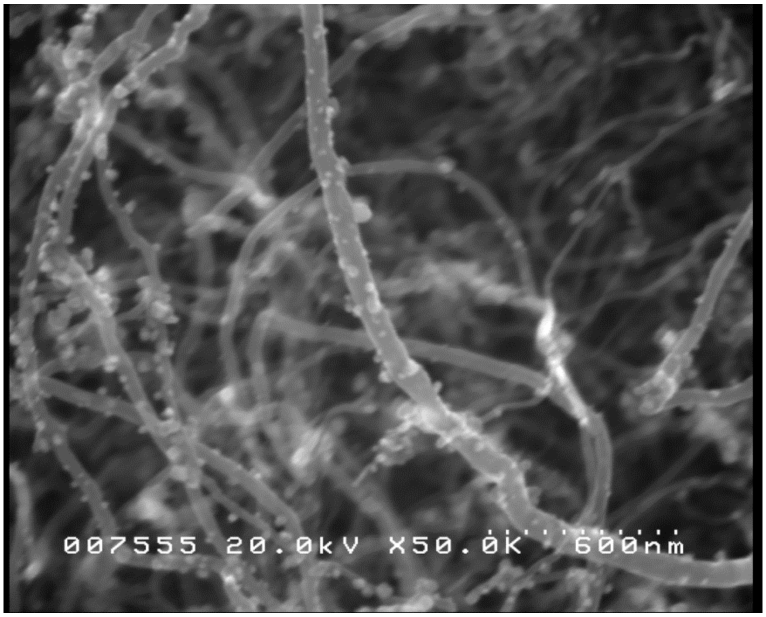

FIG. 12. Image of CNTs with pyrolyzed carbon. Sample 107Q-05.

particles appeared and the forest grew to 8-11 µm. It appears the small ethylene molecules were able to do what the large xylene molecules were not able to do, i.e., diffuse through the CNTF and react with the catalyst on the substrate. This gives us cause to think what we see here is an instance of diffusion limited growth.

Table 2. Comparison of increasing ferrocene concentration vs. CNTF length.

Ferrocene Concentration (mol %)	**Length (µm)**
1.5	12-18
3	10
6	5-7
7.2	1-2

Growth Atmosphere

One of the major findings of interest in this study is the optimal amount of hydrogen to use in CNTF growth. Hydrogen studies were done at 700°C and 760°C. Table 3 shows the results for the samples grown for the hydrogen study on quartz.

For the 760°C experiments on quartz, the optimal amount of H_2:Ar was found to be 52.5:47.5 sccm, while at700°C the H_2/Ar ratio remained reasonably constant across a range of hydrogen flows from 40 to 80 sccm. Figure 13 shows the plot of density ratios to hydrogen flow for each set of experiments. Figure 8 shows the plot of CNTF height to hydrogen flow for both temperatures on quartz substrates.

The results for growths on sapphire in this experiment are in Table 4. (Note: all growths used .1 ml precursor.) They show a similar trend to that found for quartz, though the optimal amount of hydrogen is not as obvious in the 760°C data (see Fig. 9). In this case the optimal amount of hydrogen is approximately 57.5 sccm, different from the optimal flow for quartz. For 700°C, the growths are all fairly consistent across the range of hydrogen flows. Hydrogen is necessary in this growth system because without it, the cyclopentadienyl radicals from ferrocene form PAH instead of decomposing into methane and other smaller molecules, which is the feedstock for the CNTFs.

On the other hand, too much hydrogen has generally resulted in shorter CNTFs with a less consistent density. We believe the reason has to do with the formation of the catalyst particles. In a separate set of experiments, we tested copper substrates that were annealed for different times in different conditions. Copper samples annealed in argon formed crystal faces on their surfaces, but samples that were annealed with a small amount of hydrogen in the reactor did not form crystal faces. Similarly we believe too much hydrogen inhibits the formation of the crystalline iron catalyst particles.

Table 3. Results of hydrogen study on quartz substrates.

Growth	**Temp(C)**	**Percent Ferrocene**	**Rate (ml/hr)**	**Ar (sccm)**	**H_2 (sccm)**	**Height (μm)**	**Density Ratio**
84	700	1.5	2	50	50	16-23	
97	700	1.5	2	60	40	12-18	
98	700	1.5	2	35	65	9-14	
99	700	1.5	2	45	55	11-16	.92-1
100	700	1.5	2	55	45	13-15	.95-1
101	700	1.5	2	40	60	12-18	
102	700	1.5	2	30	70	12-16	
103	700	1.5	2	20	80	7.3-8.4	
91	760	1.5	4	70	30	5-16	
92	760	1.5	4	50	50	33-45	.8-.9
93	760	1.5	4	60	40	5.3-33	
94	760	1.5	4	45	55	30-39	.85-.97
95	760	1.5	4	42.5	57.5	14-27	.84-.92
96	760	1.5	4	47.5	52.5	34-54	.93-1

Table 4. Results of hydrogen study on sapphire substrates.

Growth	Temp(C)	Percent Ferrocene	Rate (ml/hr)	Ar (sccm)	H_2 (sccm)	Height (µm)	Density Ratio
84	700	1.5	2	50	50	4-5	
97	700	1.5	2	60	40	5-8	
98	700	1.5	2	35	65	4-5	
99	700	1.5	2	45	55	5-9	
100	700	1.5	2	55	45	6.6-11	
101	700	1.5	2	40	60	3-4	
102	700	1.5	2	30	70	4.1-5.4	
103	700	1.5	2	20	80	2	
91	760	1.5	4	70	30	5.6-14	
92	760	1.5	4	50	50	20-27	
93	760	1.5	4	60	40	17-28	
94	760	1.5	4	45	55	22-28	
95	760	1.5	4	42.5	57.5	14-37	
96	760	1.5	4	47.5	52.5	13-17	

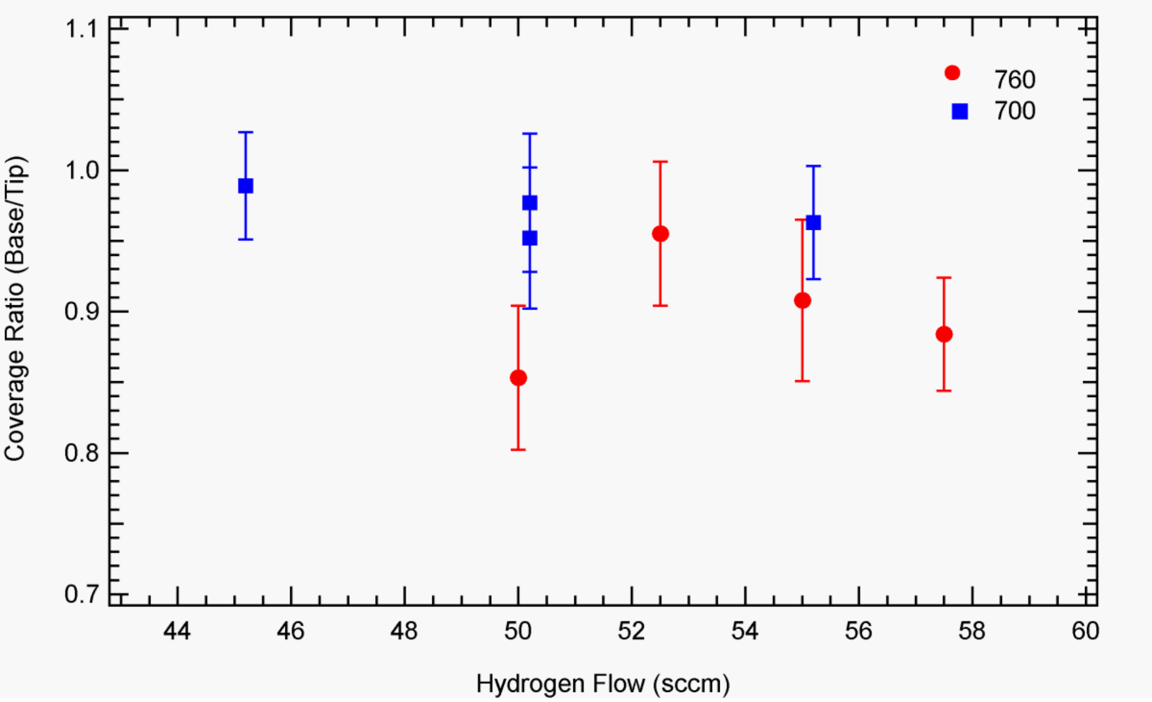

FIG. 13. Comparison of density ratio for CNTFs grown at different temperatures as a function of hydrogen flow.

CONCLUSIONS

In these experiments, an injection chemical vapor deposition method was used to grow CNTFs on different substrates. The effects of five growth parameters were studied to discover their influence on CNTF height and density. The parameters of interest were the substrate, temperature, ferrocene concentration, precursor injection rate, and the composition of the reactor atmosphere.

The substrate is important in determining the diffusion rate of the catalyst particles. Quartz and sapphire were the principal substrates, but silicon was also tested. CNTFs grown on quartz were longer and less dense than growths on sapphire. This implies the catalyst particles are more spread out on the quartz substrate. It also implies, via conservation of carbon, there are more individual catalyst particles on sapphire than there are on quartz. That is why we believe the diffusion coefficient of the iron catalyst on quartz is higher than that of the iron catalyst on sapphire.

On silicon, the thickness of the oxide layer was found to be important in determining the height and density of the CNTF. Our results run contrary to a previous work done by Cao et al. who claim that significant changes in CNTF stop for oxide thicknesses greater than 50nm.[12] We find for much thicker oxides (hundreds of nanometers thick), there is significant variation in the height and density of CNTFs.

The two growth temperatures compared in this work were 700°C and 760°C. CNTFs grown at the higher temperature are significantly longer and less dense than those grown at the lower temperature. A probable reason for this is the higher temperature enhances the breakdown of the hydrocarbons and thus, provides more carbon for the

CNTF to use as it grows. Equally important is that the high temperature promotes diffusion leading to less dense CNTFs, which also helps the growth to be longer.

Precursor concentration and injection rate are closely related to the flux of incoming catalyst particles and thus they influence density of the CNTF as a function of distance from the substrate. It is found that higher concentrations result in higher density CNTFs. In some cases, the density became so high it inhibited diffusion of hydrocarbons to the surface causing the termination of CNTF growth. However, higher injection rates were needed at higher temperatures to achieve an optimal concentration. This could help counteract the increased death rate of the catalyst particles and the increased rate of catalyst diffusing into the substrate.

The optimal amount of hydrogen for long CNTFs with more consistent densities was studied. The optimal hydrogen composition changed with growth temperature and substrate. For lower temperatures the growth is not as sensitive to the hydrogen concentration as in the high-temperature cases.

The two properties we focused on were the density and height of CNTFs. In these experiments, we have found the height and density of forests grown with injection CVD are interconnected. They are connected by the diffusion of catalyst and carbon feedstocks through the forest and by the relationship between the nucleation rate of new catalyst and death rate of old catalyst.

Diffusion-limited growth has previously been considered and rejected in injection CVD growth of CNTFs.[7] Our experiments consistently showed with a base growth mode, the CNTF was less dense near the substrate than at its top. This observation has held through a large range of variation in the growth parameters. We believe this effect is due to two contributing factors. One is that the nucleation rate of new catalyst particles is lower than the death rate of catalyst particles. The other factor is that unlike ethylene or methane, the ferrocene and xylene molecules used in this study do not diffuse well through tall, dense CNTFs unless they have very low density. This effect was most obvious in the experiments using the 7.2% precursor. We think it probably has some influence in other growths, as well, but in those cases the difference between the nucleation and the death rates might be the most important factor.

In the work done by Li et al., a mixture of ferrocene dissolved in xylene was also used.[7] However, they still conclude their growth was not diffusion limited in disagreement with our result. An important difference is the precursor used by Li et al. only had 1.3% (mol %) catalyst concentration. Our experiments included precursor with significantly higher catalyst concentrations.

Another explanation for the disagreement is we were measuring different things when we talk about density. In this work we measure percent coverage of our images. Li et al. used reflection high-energy electron diffraction (RHEED) to measure the average center-to-center distance between aligned CNTs.[16] A potential issue with that method is that they were only able to measure the center-to-center spacing for aligned samples. We have observed that CNTs near the substrate are less aligned than CNTs at the tip of the forest (another indication of the change in density) thus measuring the change in density across a single forest might be difficult for the RHEED method. Below, Figure 14 is an illustration of our current understanding of the effects of growth parameters on CNTF height and density.

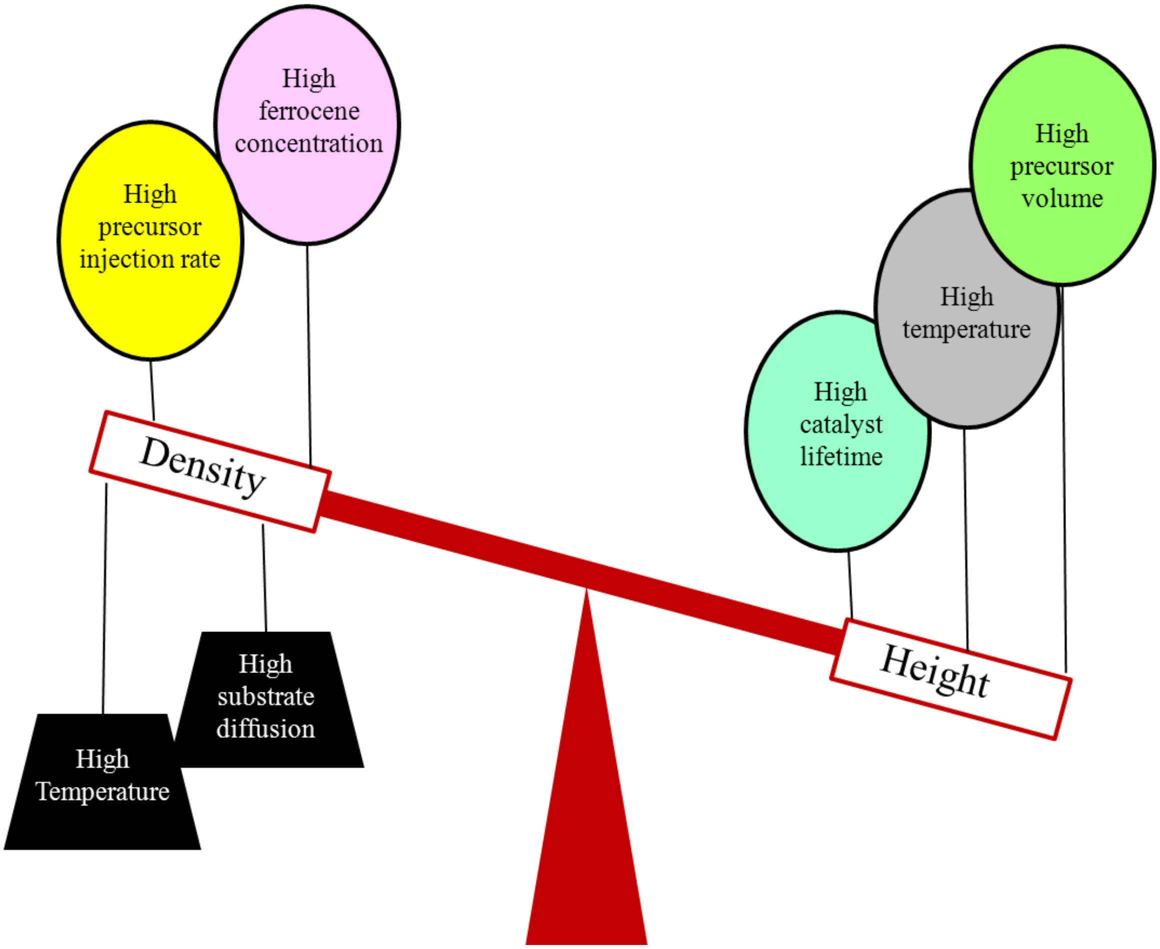

FIG. 14. Illustration of the effects of growth parameters on CNTF height and density.

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APPENDIX

Mathcad sheet used for calculating percent coverage

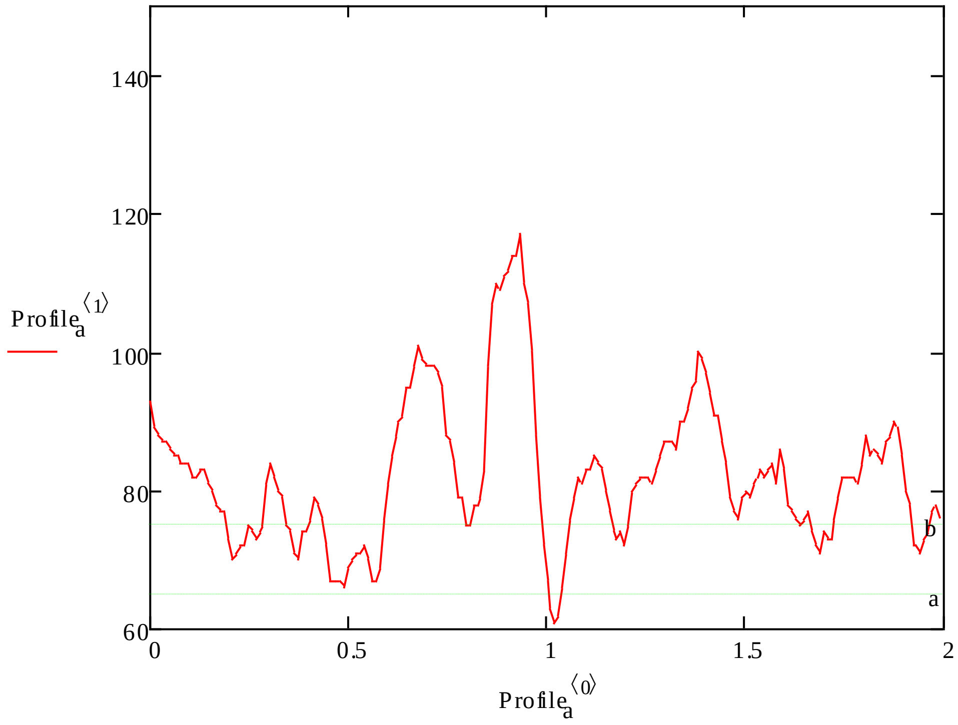
Input the original profile.

$\text{Profile}_a :=$

	0	1
0	0	93
1	0.01	89
2	0.02	88
3	0.029	87
4	0.039	87
5	0.049	86
6	0.059	85
7	0.069	85
8	0.078	84
9	0.088	...

Plot original profile and set thresholds with a and b.

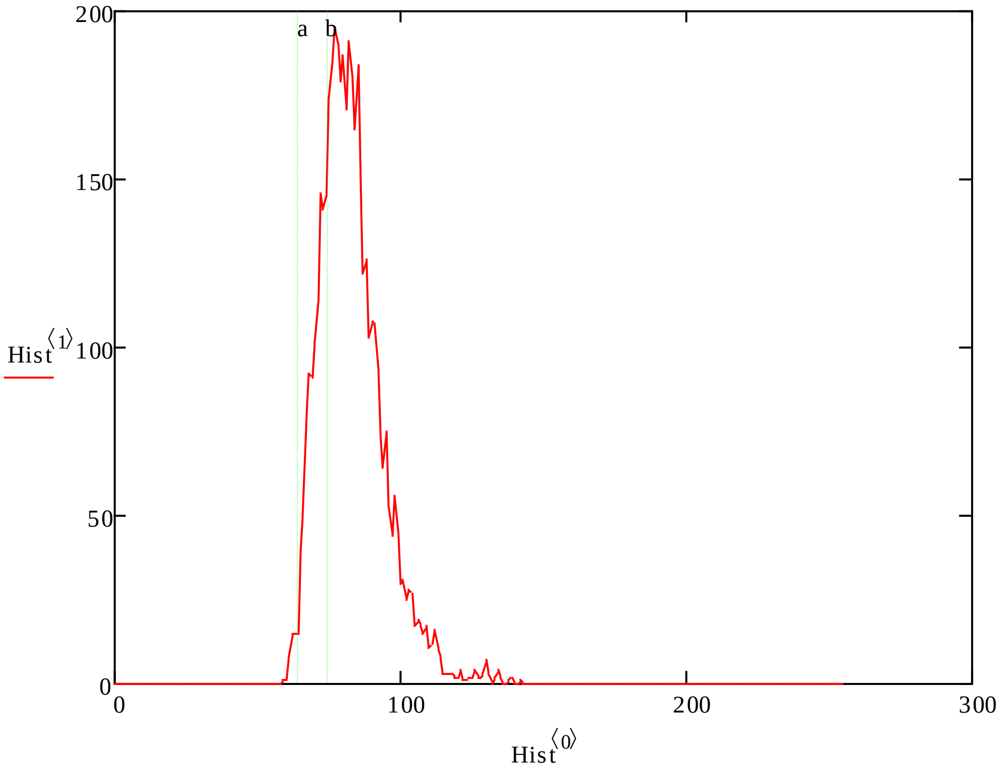
Looks like $a := 65$, and $b := 75$.



Input histogram of region.

Hist :=

	0	1
0	0	0
1	1	0
2	2	0
3	3	0
4	4	0
5	5	0
6	6	0
7	7	0
8	8	0
9	9	...



Calculate the percent coverages for thresholds a and b.

For threshold a:

$n := 0..a-1$ $\quad\quad$ $j := a..\mathrm{length}\left(Hist^{\langle 1\rangle}\right)-1$

$pixel := Hist^{\langle 1\rangle}$

$Covered := \sum_{j} pixel_j$ $\quad\quad$ $Not := \sum_{n} pixel_n$

$\frac{Covered}{Covered + Not}\cdot 100 = 98.81$ $\quad\quad$ $a = 65$

For threshold b:

$n := 0..b-1$ $\quad\quad$ $j := b..25$

$pixel := Hist^{\langle 1\rangle}$

$Covered := \sum_{j} pixel_j$ $\quad\quad$ $Not := \sum_{n} pixel_n$

$\frac{Covered}{Covered + Not}\cdot 100 = 77.143$ $\quad\quad$ $b = 75$