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FirstNano CNT Growth Furnace Recipe Development
in Stanford Nanofabrication Facility

Abstract

In February 2015, a FirstNano "EasyTube 3000" Carbon Nanotube (CNT) growth furnace was installed in the SNF cleanroom featuring a high level of automation and process control built into an easy-to-use software environment. The purpose of the tool is to grow horizontally aligned or unaligned single-walled carbon nanotubes, and is capable of vertical forest CNT growth if future users desire it. This report summarizes the efforts to create a turn-key solution for carbon nanotube growth in the Stanford Nanofabrication Facility (SNF). We 1) define a wafer-scale sample preparation process using tools entirely sourced from the Stanford shared facilities, 2) demonstrate the consistency and turn-key capability of the furnace by growing CNTs successfully every single time for more than two dozen growth repetitions, and 3) explore the catalyst deposition, catalyst pretreatment and growth condition parameters that will lead to higher average densities for our wafer-scale growths.

Motivation

Single-walled Carbon Nanotubes (CNTs) are strong candidates for applications in high performance and energy efficient electronics, monolithically heterogeneously integrated computing architectures, and sensor networks or biological interfaces. Specifically in VLSI electronics a 10x improvement in energy-delay-product, a metric of energy efficiency and performance, is projected to occur for systems on the sub-7nm technology node based on transistors with semiconducting CNT channels. Uniquely, the low-temperature CNT transfer decouples high temperature growth from temperature-sensitive device processing thereby enabling logic to be placed at multiple levels of a monolithically integrated circuit and to co-exist with other low-temperature device or memory technologies in future heterogeneous architectures. CNTs also make great sensors, and are being considered as possible electrical interfaces to biological materials such as cells or neurons. The leading materials platform for these applications are horizontally aligned single-walled carbon nanotubes that are grown in a chemical vapor deposition (CVD) process. The preferred growth technique is the perfectly aligned parallel arrays of CNTs on Quartz substrates, before transfer to the device fabrication substrate. The SNF will now have this capability.

CNT Growth Mechanism, Sample Preparation and Growth Process Overview

The aligned CVD growth process for Single-walled carbon nanotubes has been used in various forms for more than a decade, and the mechanisms involved have been studied extensively across a range of substrates, catalyst materials, carbon sources, and growth conditions in hundreds of publications. Here, we summarize the key mechanisms involved in horizontally aligned CNT growth.

A cartoon of these mechanisms alongside a growth example is shown in Figure 1. First, a thin film (2-4Å) of metal (Can be Fe, Ni, Cu, Co, etc… we use Fe) is deposited by evaporation in a lithographically patterned catalyst region. During evaporation the film grows as sub-monolayer islands of metal according to Volmer-weber mechanism. These islands are annealed at high temperatures in the presence of hydrogen and coalesce into the nanoparticles with diameters of a few nanometers. Next, at high temperature a carbon containing gas (CH_4, C_2H_6O, C_3H_8O, etc...) decomposes catalytically at the catalyst nanoparticle into the reactant carbon gas species. This reactive carbon species coats the nanoparticle morphology to form a hemispherical CNT end-cap through either a direct surface assembly (Vapor-Solid mechanism) or subsurface diffusion into the nanoparticle bulk before precipitating out and forming a surface assembly (Vapor-Liquid-Solid mechanism). This end-cap is then extended by the addition of subsequent carbon blocks into a longer tube of carbon thereby building the CNT. The structure of the carbon nanotube is partially determined by the catalyst particle size, and is randomly distributed between the possible CNT chiralities to give approximately 2/3rds fraction semiconducting CNTs and the rest metallic. Growth mechanisms to enhance the purity of the semiconducting CNT fraction by direct chiral selective growth or selective metallic CNT removal exist and may be introduced in future evolutions of this tool's process. Finally, when grown on certain substrates (Quartz, Sapphire, a few others) the CNTs interact with the crystal lattice which imparts an angle-dependent Van der Waals force on the CNT along certain crystal lattice directions. For ST-cut Quartz, this aligns the CNT along the [100] plane.
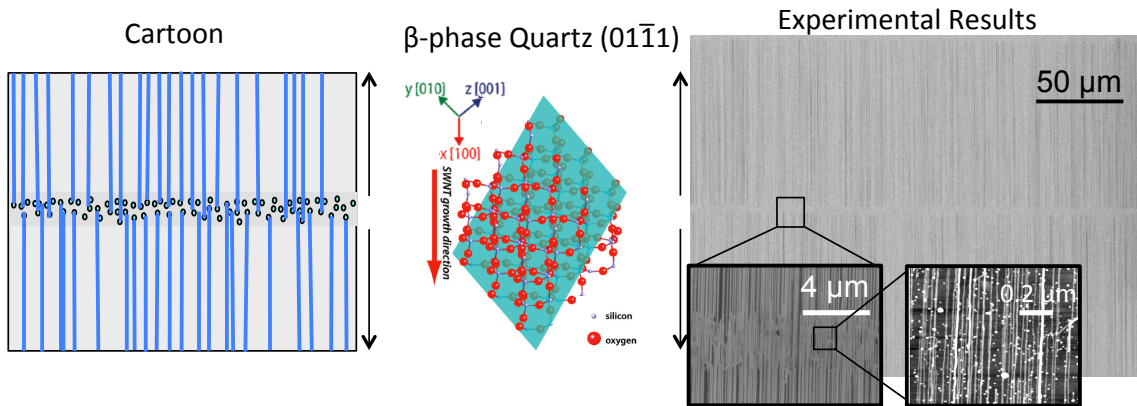

Figure 1: Growth Mechanism cartoon and experimental example. (Quartz crystal lattice citation: A. Rutkowska, et. al. 2009)

Sample Preparation

The sample preparation process has been re-defined in this project, and is summarized in Figure 2. The fabrication details are contained in this paragraph, and in a process run-sheet that will be distributed during training. The 100mm quartz substrates wafers used are single-side polished ST-cut Quartz with an angle of 42°45' sourced from Hoffman Materials, LLC. First the quartz is solvent-cleaned then annealed in Thermco 4 at 900°C for 8 ½ hours using the recipe "4SLO900". Details on the operating the anneal recipe are in Appendix 1. Next, evaporate 3Å of Iron at a slow rate of 0.1Å/s on an un-patterned quartz substrate. This thickness and rate value may change based on future

process improvements. (Note: We recommend users do not use Innotec for catalyst evaporation due to the lack of a crystal monitor reading before the shutter opens and deposition begins. Catalyst evaporation can be done for labusers two wafers at a time by Tom Carver in the SNSF flexible cleanroom for a fee. An evaporator owned by the Prof. Philip Wong group is also commonly used for catalyst by affiliated students). Use SVG coat track 2 to spincoat Shipley 3612 resist 1µm thick without an HMDS vapor prime and without an edge bead removal. Use ASML to pattern your catalyst stripes (we typically use a 4um wide stripe with a pitch of 100um) all over the wafer with dose ~40 mJ/cm^2 to avoid overexposing the isolated narrow photoresist lines. Develop the photoresist using develop program 3 in SVG Develop tracks 1 or 2. Inspect the pattern quality under a microscope before moving to the next step. Next, etch the exposed Iron in diluted HCl:H20 1:1 at WBGen or WBFlexCorr for 30 seconds before rinsing in 2 DI water baths for 3 minutes each then blow dry with a N2 gun. Finally strip the photoresist in 2 clean acetone baths for ~10 minutes each, before rinsing with IPA and blow drying with a N2 gun. Inspect again under a microscope and there should not be any resist residue or particles. The sample is now ready for growth in the FirstNano CNT CVD Growth Furnace.

A deeper discussion of the sample preparation evolution and troubleshooting is located in Appendix 2.
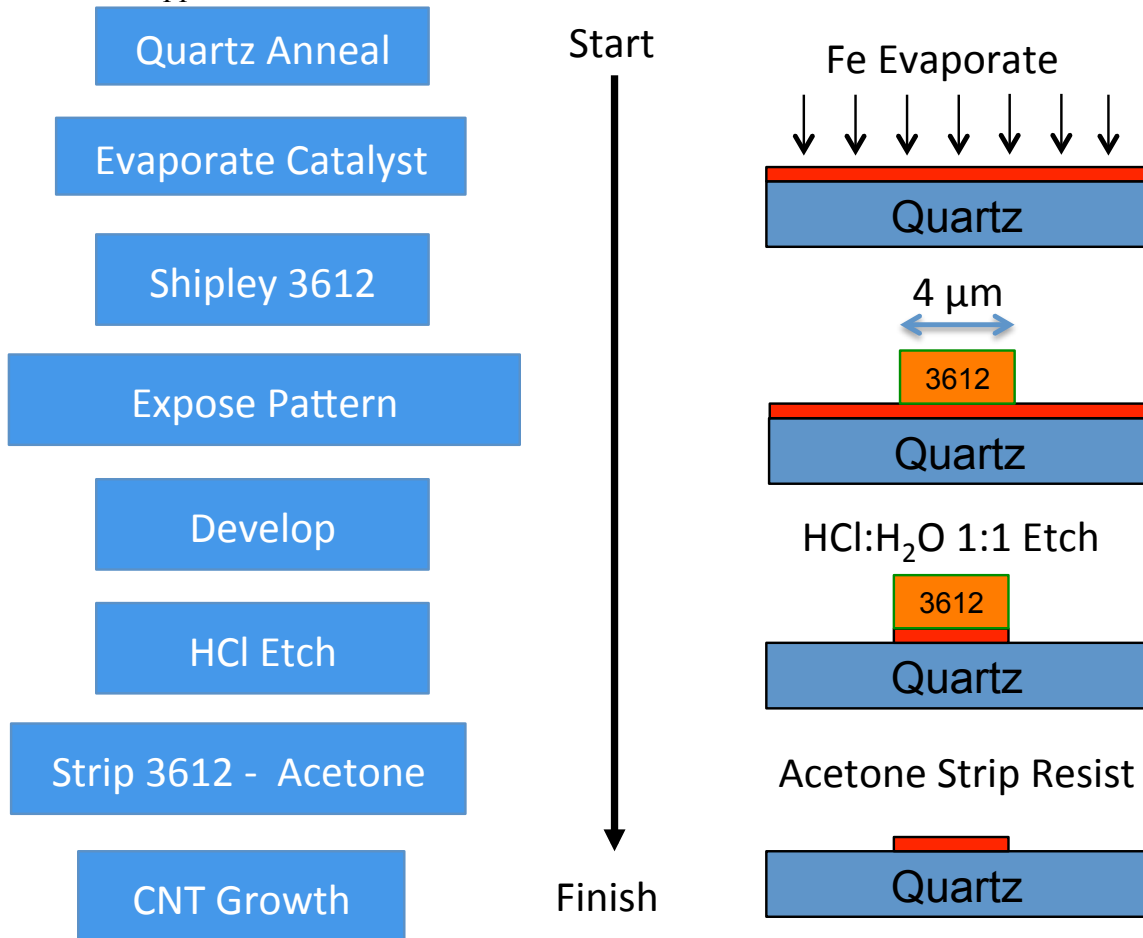

Figure 2: Sample Preparation Process Flow

CNT CVD Growth Procedure

The CVD growth procedure has four distinct phases as shown in figure 3: 1) Calcination, 2) Reduction, 3) CNT Growth, and 4) Cool-down. A brief description of the important steps for each phase is as follows. Calcination is the first phase of growth in which oxygen flows into the tube while the temperature ramps up to 620°C to clean any carbon contamination off the furnace sidewalls or sample and to oxidize the Iron into Iron oxide if it wasn't already. Between ~550°C and 620°C the temperature is increased very slowly in low pressure atmosphere to maintain low thermal mass and uniform temperature to prevent the quartz substrate from cracking as it transitions from α-β phase at ~573°C. Reduction is the 2nd phase of growth in which hydrogen flows into the tube as the temperature increases from 620°C to the growth temperature of 865° and continues as the tube stabilizes for an additional 10 minutes. This phase reduces the Iron oxide into elemental Iron and the Iron then coalesces into a nanoparticle. Possible improvements to the reduction phase being are scrutinized such as optimizing the pressure, temperature, and times to tune the catalyst nanoparticles as described in the recipe development section. Next, the CNT growth phase introduces the flow of carbon containing gas, typically methane or ethanol, for about 30 minutes alongside hydrogen at atmospheric or reduced pressure and is when the CNTs actually begin to grow. Finally, the cool-down phase stops the methane flow and cools down the furnace in Hydrogen or Argon ambient taking care to slowly cool near the phase-change temperature.

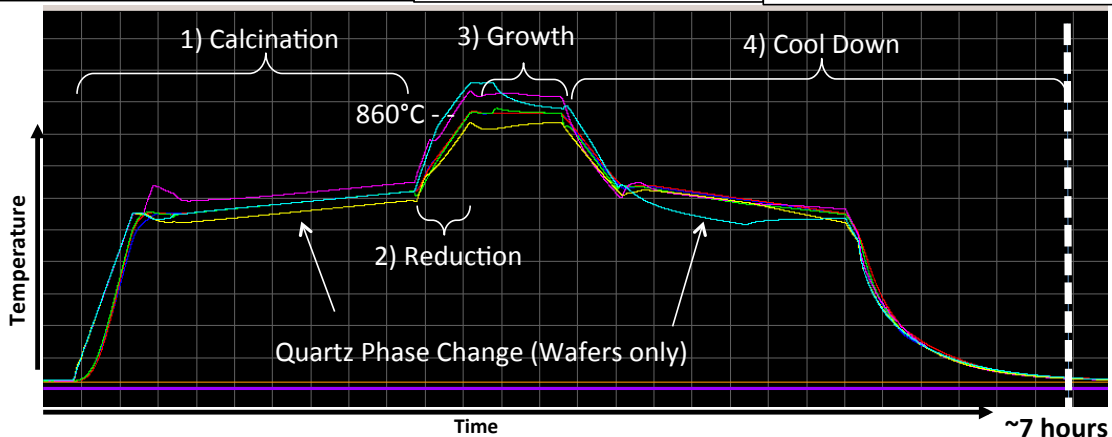| Phase 1: Calcination	Phase 2: Reduction	Phase 3: Growth
• Slow ramp at phase change to prevent cracks. • Cleans carbon contamination • Oxidizes Fe Catalyst • O_2 diluted in Ar up to 620°C • Variable Pressure	• Anneals Fe film into nanoparticles. • H_2 ambient 620–860°C • Low pressure ~120 Torr	• H_2 and CH_4 ambient 860°C • Low Pressure ~ 315 Torr • Grows CNTs for 30 Min.
		Phase 4: Cool Down • H_2 ambient 860 – 300°C • Ar ambient 300 – 100°C • Slow ramp to prevent cracks

Figure 3: Growth Temperature vs. Time plot illustrates the four phases of growth.

Growth Furnace Stability

With an un-optimized recipe, we had an opportunity to grow more than two dozen times on pieces from the same reference wafer while our other efforts focused on resolving the sample preparation issues. The results were encouraging, with CNT growth every time. As shown in Figure 4, the quality of the growths were binned into groups: "good" with

density ~1 CNT per μm, "OK" with density 1 CNT per several μm, and "Bad" with 1 CNT per 10's of μm. Of 24 sequential growths 19 were good, 4 were OK and 1 was bad. The bad growth was investigated and discovered to be caused by human error loading an incorrect and incomplete recipe that was written for testing only. The OK growths were clustered together with unknown cause. The effect of performing tube cleaning (1050°C for 1 hour in O2 ambient) to remove carbon contamination on growth results was investigated and no correlation was found to the "OK" growths, however this lack of correlation is not enough to rule out that some other furnace condition was not responsible for the change in results so our process monitoring continues.

With this early success record we will claim that the FirstNano CNT Furnace is stable with consistent results. The turn-key operation concept is validated, so future users only need to load their sample and an established recipe before pressing start. Finally, by establishing a baseline growth result on a reference sample we have created a methodology for evaluating whether any future sample failures are due to the furnace or sample problems - historically a major challenge for evaluating any inconsistent results.
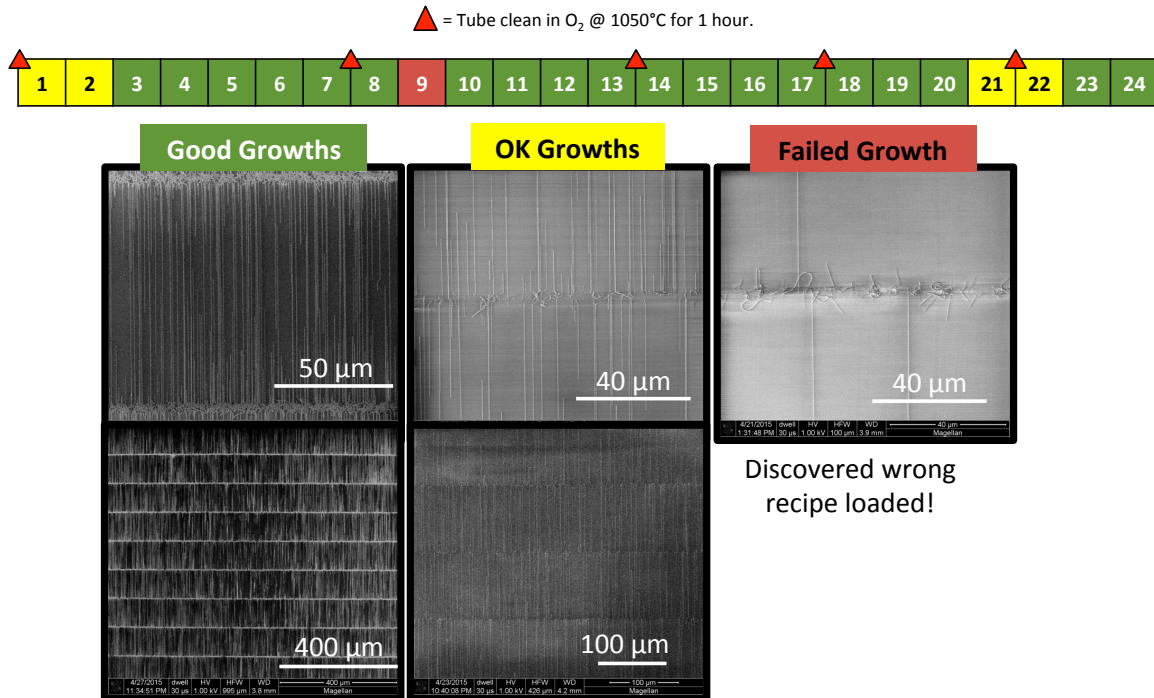

Figure 4: Growth stability results

Growth Recipe Improvements

Having demonstrated the stability of the CNT Furnace with a recipe based off a legacy process we set out to improve the average CNT density through process improvements. Past experience has informed us that the catalyst deposition, pretreatment and the CVD growth condition are very important in achieving the best results. As shown in figure 5, an experiment in which the evaporated catalyst thickness was varied by 0.5Å on four samples between 2Å and 3.5Å resulted in dramatic density effects between 1 CNT per 30 μm and 15 CNT per μm. This motivates us to begin our efforts by focusing on characterizing the evaporated catalyst thickness and the pretreatment condition.
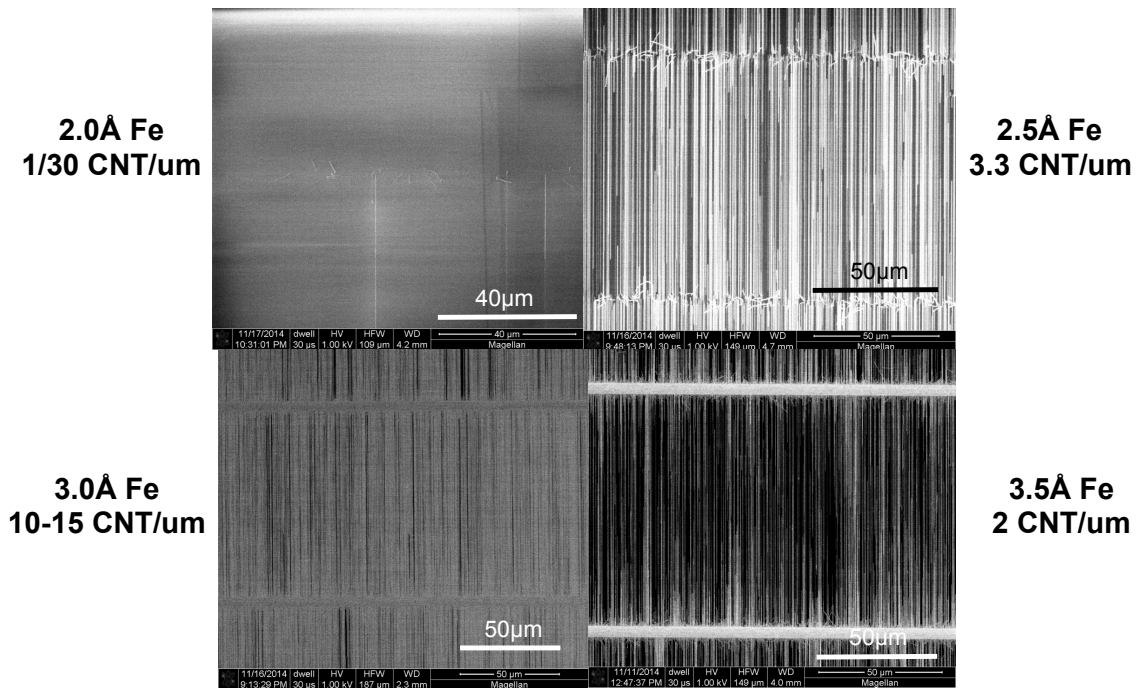
Figure 5: Past results showing growth density sensitivity to catalyst condition. These samples were all grown in a non-SNF CNT furnace at the same time.

Catalyst Pretreatment Study

During the reduction pretreatment preceding CNT growth, hydrogen reduces patterned Iron oxide sub-monolayer film to catalytic metallic Iron nanoparticles. Our hypothesis for the lower density growth seen with the legacy recipe is that the catalyst was not prepared optimally to yield CNTs from the nanoparticles we generated, which is confirmed by AFMs shown in Appendix 3. Therefore we designed a pretreatment study to systematically investigate the relationship between nanoparticle size and density to the pretreatment pressure, temperature and time. Samples were prepared with the thickness values indicated in table 1 through evaporation from the SNC vendor at 0.1Å/s, the minimum rate possible with that tool, for better control over the thickness. These samples were left un-patterned for ease of AFM characterization.

Rate	Iron Evaporation Thickness			
	2.0 Å	2.3 Å	2.6 Å	2.9 Å
0.1 Å/s	X	X	X	X

Table 1: Thickness Values and nanoparticle densities from pretreatment study.

As a baseline the initial pretreatment was done using legacy recipe values and then compared to an anneal that was 30 minutes longer. As shown in Figure 6 AFMs with adjoining table 2 summarizing catalyst density, there was no clear difference in nanoparticle density of NPs between different catalyst thicknesses and an obvious decrease in density for longer anneal time. This is consistent with the mechanism of Ostald ripening, in which generally claims during annealing larger particles get larger and smaller particles get smaller due to thermodynamic equilibrium favoring large particles.

For an unknown reason, the 2.9Å film failed to yield appropriate NPs each time and it is assumed that this has nothing to do with the very slight film thickness difference so that sample was dropped from future study.
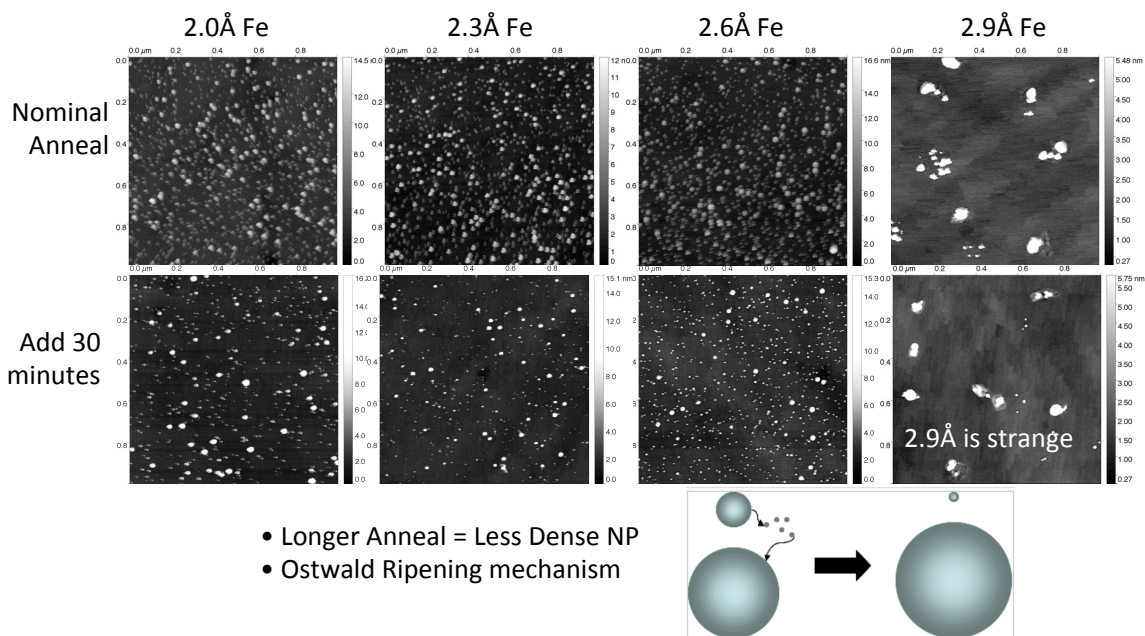

Figure 6: Results from baseline pretreatment study, and Ostwald ripening illustration (Ostwald ripening image citation: Wikipedia article "Ostwald Ripening")

NP Density (NP/μm)	Catalyst Thickness		
	2.0Å	2.3Å	2.6Å
Nominal Anneal	893	828	885
+30 Minutes	491	444	733

Table 2: Baseline pretreatments results.

Next the pressure was changed from 1 Torr to 760 Torr in steps of ~250 Torr to evaluate whether pressure was a significant factor in catalyst pretreatment. Pretreatment values shown in table 3 were chosen to explore the sensitivity of NP density and size to the pressures during annealing. The density and size of the 2.3Å film's nanoparticles were quantified with the help of a semi-automatic matlab script and results in the histogram shown in figure 7 with nanoparticle density shown in table 3. This result is excellent, and confirms that there is a strong relationship between nanoparticle size and density that we can tune with pressure. In addition the 1 Torr case highlights a previously unknown mechanism of annealing we would strongly avoid in the future: at 1 Torr the catalyst is largely gone regardless of film thickness possibly due to vaporization cause by the elevated vapor pressure of the nanoparticles compared to bulk iron at elevated temperature or by rampant surface diffusion. Either way, it was standard practice for the

legacy growth recipe to pump to base pressure (~30 mTorr) between flowing Oxygen and hydrogen combustibles, with hydrogen flow beginning at the base pressure. As just discovered, this was exposing the catalyst to a potentially bad pretreatment condition. To avoid this issue there is now a transition purge with Argon until the desired pressure is reached before flowing Hydrogen that begins the reduction and coalescing of the nanoparticles.

Pressure (Torr)	NP Density (NP/µm²)	NP Size Mean (nm)	NP Size STD (nm)
1	2	3	N/A
250	1141	1.7	0.51
500	816	2.1	0.27
760	674	4.2	2.25

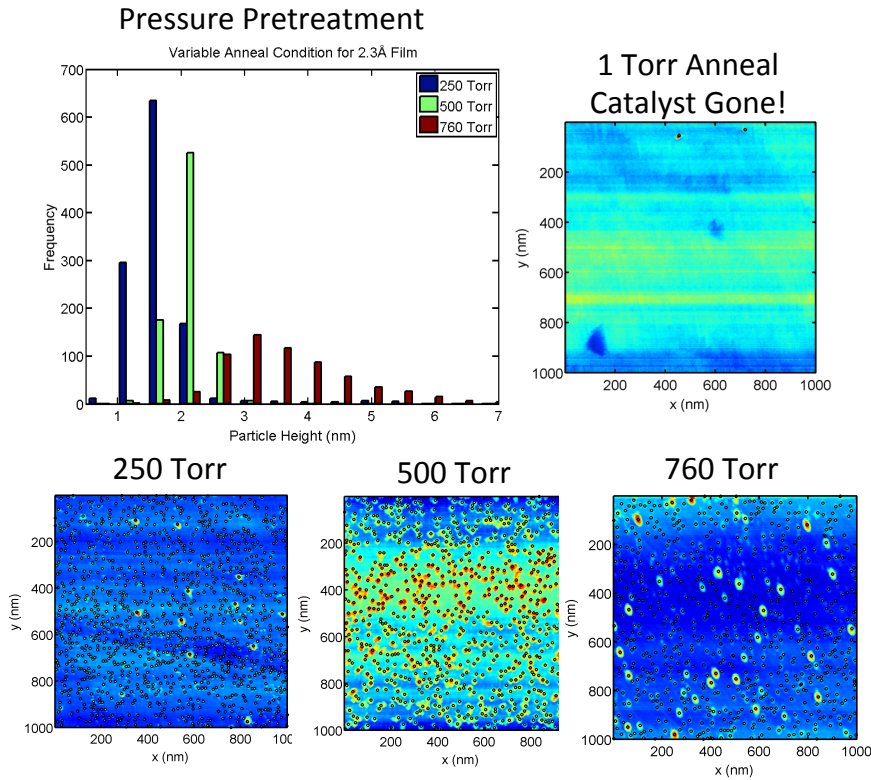Table 3: Pressure values and results

Figure 7: Pressure pretreatment results

This pretreatment strategy was carried through to CNT growth with good results. Patterned catalyst regions were created on pieces from the same wafer as the pieces used in the pre-treatment study, and the same pretreatment recipes were used with the addition of a 30 minute growth phase with methane flowing. The results are shown in Figure 9, where the 2.6Å sample went from almost no growth with 250 Torr pretreatment to good growth at 500 Torr and weaker growth at 760 Torr due to the changing catalyst morphology. This is supports our hypothesis that CNT growth can be optimized by controlling catalyst morphology.
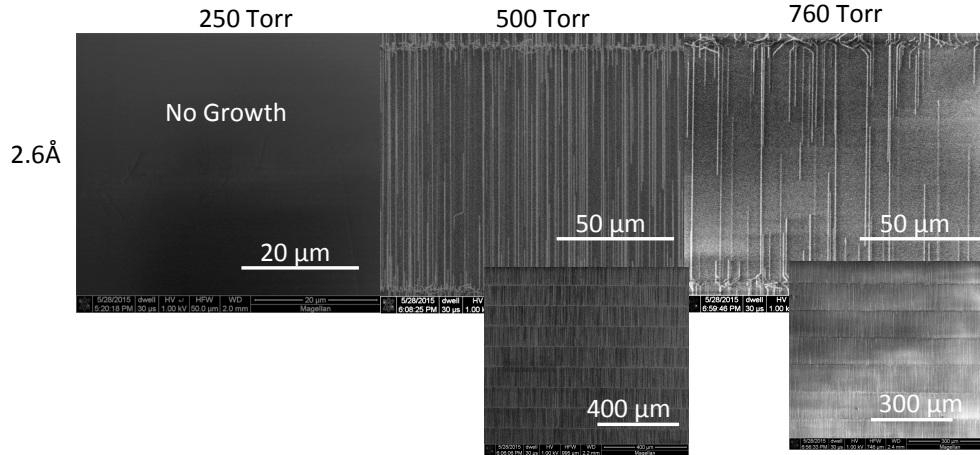
Figure 8: Pressure Pretreatment Growth Results

Another catalyst study was performed varying the temperature at which H2 is introduced to the CNT furnace while preserving the temperature profile of the growth, therefore the anneal time was also coupled as shown in Appendix 4 table 1 and figure A4-2. The nanoparticle morphology results were not quantified in as much detail as the pressure pretreatment, but the detailed AFM image in figure A4-3 clearly shows the morphology changes significantly. To see the effect on growth the study was repeated on patterned pieces and the result was significant between the 550°C and 860°C anneal, with the 860°C anneal being superior and approaching 5 CNT/um near the catalyst stripe. Due to the complexity caused by changing temperatures and pressures when H2 is introduced early in growth, the temperature at which the H2 is introduced is now strategically fixed 860°C for a future experiment that will be limited to the film thickness, pressure, and time.

Next Steps:

The furnace start-up goal is for turn-key wafer-scale growth recipe with densities reproducibly at around 5 CNT/μm. We are confident that through one or two more iterations of tuning the catalyst film thickness, H2 anneal pressure and time that the catalyst will be suitably optimized for this goal. Then the focus should turn to other important growth parameters such as the growth phase pressure and partial pressure of CH_4 and H_2, the growth time, and the growth temperature. In addition the tool supports ethanol growth recipes that have historically have given even better growth yield than methane. For wafer-scale growth the uniformity is of great concern and will be derived from the uniformity of the catalyst film during evaporation. And finally, the tool maintenance and cleaning procedures are being defined for stable operation. Table 4 shows the progress towards our overall growth goal.

Tracking Progress	Metric
Achievements to-date	1-2 CNT/μm on pieces
Tool startup objective	~5 CNT/μm on 100mm wafer
Broader research objective	>15 CNT/μm on 100mm wafer

Table 4: Tracking progress.

Summary

In this report we summarize the startup for the FirstNano CNT Growth Furnace located in SNF. The key growth mechanisms are described using both cartoons and actual examples. The sample preparation procedure is defined and a broader discussion of the sample preparation development process is included in Appendix 2. We then demonstrate the stability of the CNT growth furnace with turn-key operation of this furnace resulting in more than two dozen growths that each successfully grew CNTs. This resulted in a strategy using reference samples for furnace stability monitoring, which has historically been very difficult to isolate. Finally, the initial work toward improving the growth results are described in detail with density improvements shown by tuning reduction pressure, temperature, and time. The next steps include a final optimization of the reduction phase, a CVD growth condition optimization, and wafer-scale uniformity characterization.

Appendix
Appendix 1: Quartz Annealing in Thermco 4

This recipe will cool the furnace down to 400°C for loading. It will ramp up to 900°C as slow as 1°/min near the phase change at 573°C. Then it will hold at 900°C for the user defined 8.5 hours annealing in O2 and a small amount of H2 ambient before cooling down with a similar slow rate near the phase change temperature.

Load recipe as follows:
1. Load recipe 4SLO900 into Thermco 4 (Tube #2) with "oxtime" of 8 hours 30 minutes.
2. When you press start (1st time) the recipe will begin cooling from 800°C to 400°C and hold. Wait ~4 hours. You may boat out the tube early for faster cooling.
3. The door will open after you press start (2nd time). You can open the door early to accelerate the cool down.
4. Load your wafers in the boat 8-12" from the baffle on the left. Ensure the wafer flat is directed towards the front upper groove and not touching the boat to prevent quartz wafer cracking. Press start to close the door (this is the 3rd time you have pressed the start button).
5. Once the door closes it will stabilize temperature and purge the tube for 10 min with N2.
6. The tube will now start Lo O2 flow and start heating to 900c at a rate of 2°C/min from 400-500°C, 1°C/min from 500-600°C, and 2°C/min from 600-900°C.
7. After stabilizing at 900c the tube will hold for the "oxtime" you entered. This is a 'wetox' recipe and has some hydrogen flowing into the chamber.
8. After the oxtime the tube will start to cool back to 400c at a rate of 2°C/min from 900-600°C, 1°C/min from 600-500°C, and 2°C/min from 500-400°C.
9. Once it reaches 400c it will hold until told to go to the next step.
10. Press start (4th time) to open the tube. Unload wafers. Press start again to close the door.

11. Load 800 anneal recipe in order to return tube to standby state. Press "Start" (5th time)

Appendix 2: Sample Preparation Process Development and Troubleshooting

As shown in Figure A2-1a, a legacy CNT growth sample preparation procedure used a bi-layer photoresist stack (LOL2000 beneath Shipley 3612) for patterning the catalyst stripe before evaporation and liftoff of the catalyst metal film. The purpose of the LOL is to serve as an under-cutting layer that prevents sidewalls developing at the edge of the pattern during evaporation. This process was stable for years and served as the starting point for this project. However, a previously un-seen issues in which any substrate that used LOL2000 for liftoff would not have catalyst or CNTs on after growth as shown in Fig A2-1 left AFM. On the other hand, wafers without LOL2000 would consistently grow CNTs without this issue as shown in the Figure A2-1 right AFM and SEM, though sidewall issues prevent this approach from being suitable to move forward as shown in Fig A2-1 height profile. This consistent issue forced us to troubleshoot, focusing on the key differences between the two wafers.

Two differences exist: first the LOL2000 has the potential to leave residue between the evaporated film and the substrate surface, and second the stripping of the LOL2000 in the developer MF-26A could have some undesired effect on the catalyst. Our early efforts focused on the reducing the potential presence of LOL2000 residue, so we attempted to 1) reduce the temperature and duration of the LOL bake (usually 30 minutes at 235°C in an oven), 2) Increase the develop time, and 3) implement an oxygen plasma de-scum before evaporation. Each of these efforts failed to resolve the observed issue, and a reference piece that never saw LOL2000 grew well in each growth confirming the furnace stability. Therefore we focused on the possible effects of MF-26A reacting with the iron catalyst by taking a sample with catalyst patterned using Shipley 3612 only (the sample never had seen LOL2000) and dipped it in MF-26A as if we were stripping off an LOL layer. To our great surprise, this reproduced the issue and caused the sample to fail - while a reference piece grew well in the same growth. Our skepticism required us to reproduce this two more times before we were confident that the issue was the MF-26A, despite our long experience with this chemical being used to strip LOL2000 before CNT growth. We attribute the issue to the 2% concentration of the strong base TMAH, which is known as a surfactant for Iron and other metals, contained in the MF-26A potentially dissolving the Iron film.

Possible solutions to this issue are shown in Figure A2-2 and include 1) Stripping the LOL2000 using a different chemical such as RemoverPG, 2) Stripping LOL2000 using a different technique such as a remote plasma ashing that would not damage the quartz surface, 3) avoid liftoff together entirely by evaporating catalyst as a blanket film everywhere then using patterning to remove the catalyst from unwanted regions, and 4) do the blanket evaporation with an extra remote plasma step to ensure any un-wanted photoresist residue is removed before growth. All four potential solutions were implemented, and all four succeeded in resolving the issue as shown in Figure A2-3. We chose to proceed using solution #3 as described in the main text due to its simplicity, however tool users have the option of choosing liftoff or evaporation as both will work equally well.
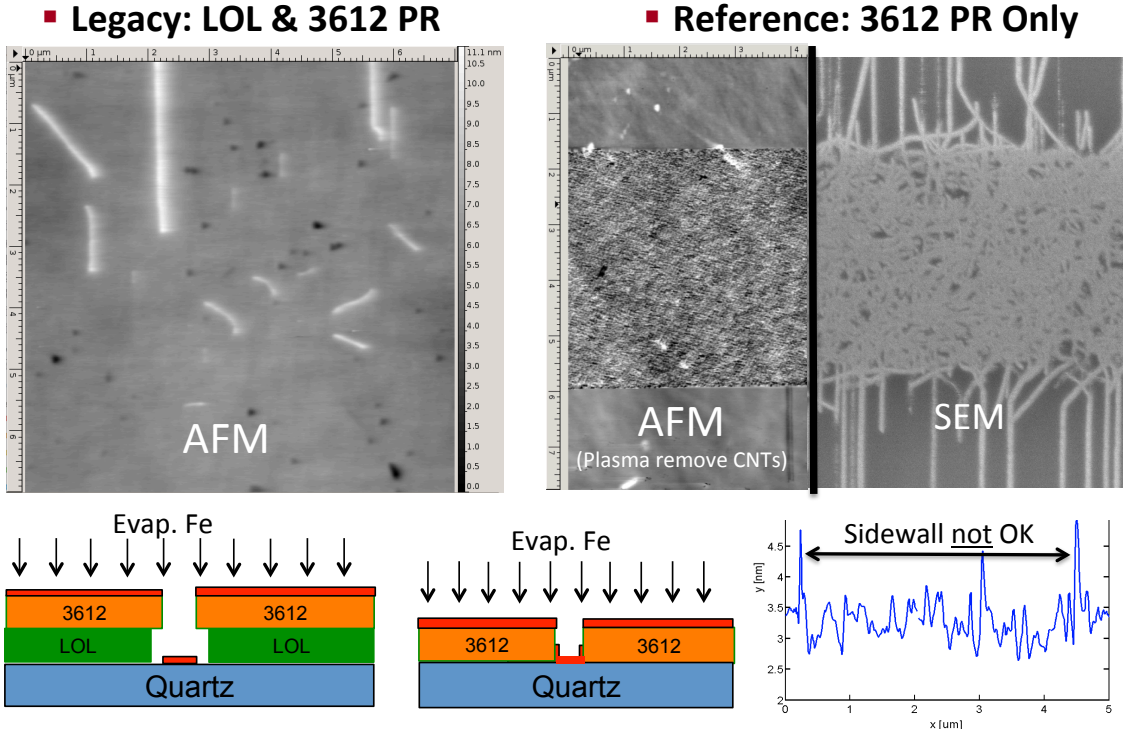
Figure A2-1: AFM and SEM showing reproducible missing catalyst in samples with LOL2000 undercut layer vs. samples using 3612 only where the catalyst remains but sidewall issues make it unsuitable.
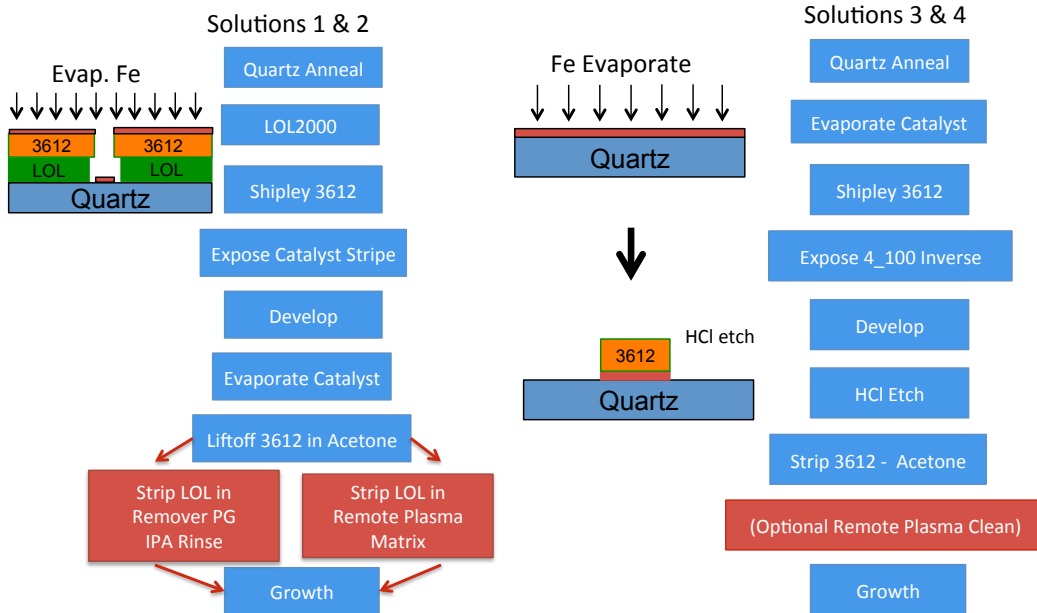

Figure A2-2: Processing options for solving the MF-26A issue include liftoff where the LOL2000 is stripped through another means, or blanket evaporation and then patterned etch.
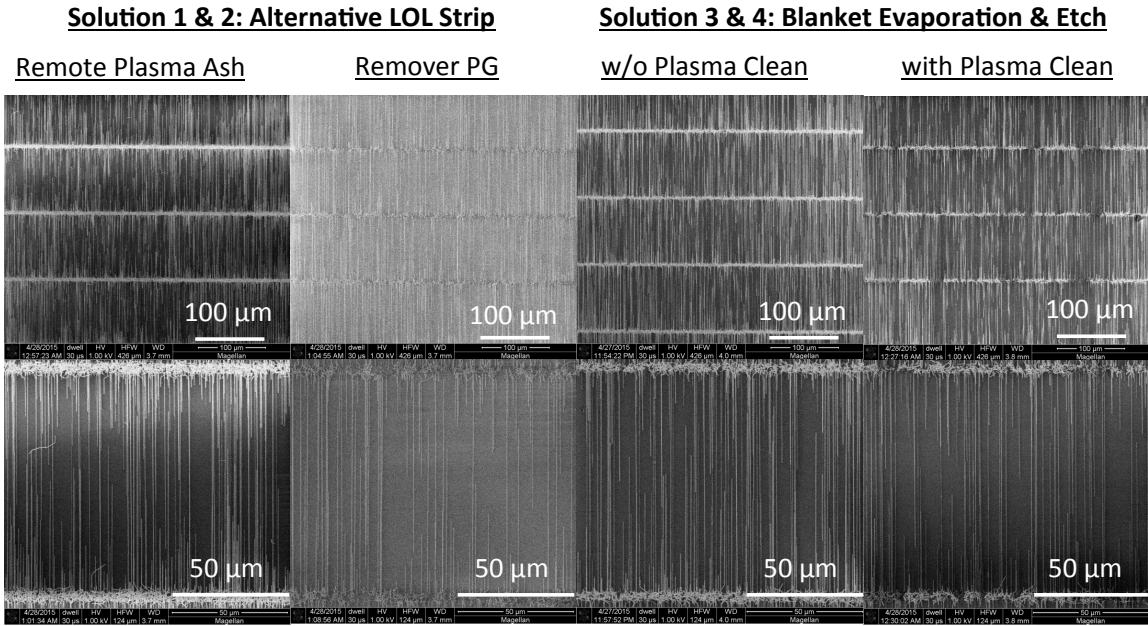
Solution 1 & 2: Alternative LOL Strip   **Solution 3 & 4: Blanket Evaporation & Etch**

Remote Plasma Ash   Remover PG   w/o Plasma Clean   with Plasma Clean

Figure A2-3: All four solutions succeeded.

Appendix 3:

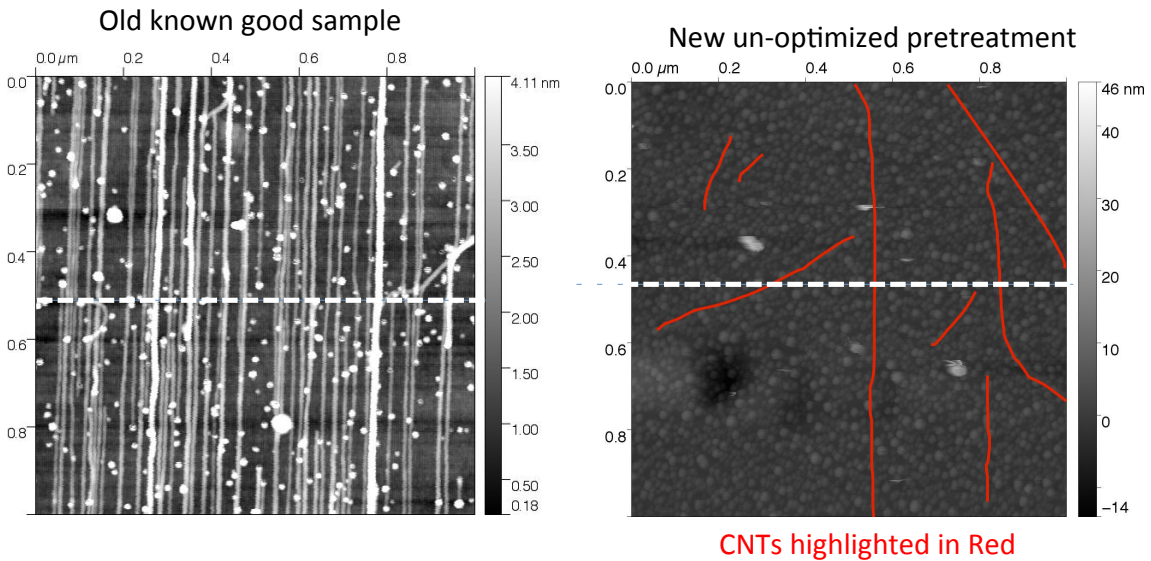Old known good sample

New un-optimized pretreatment

CNTs highlighted in Red

Figure A3-1: "Known good" old sample vs. un-optimized catalyst example from initial runs.

Appendix 4:

H₂ Initiation Temperature	
T_1 (°C)	25
T_2 (°C)	550
T_3 (°C)	864

Table A4-1: Conditions chosen for H2 Anneal temperature introduction sweep.
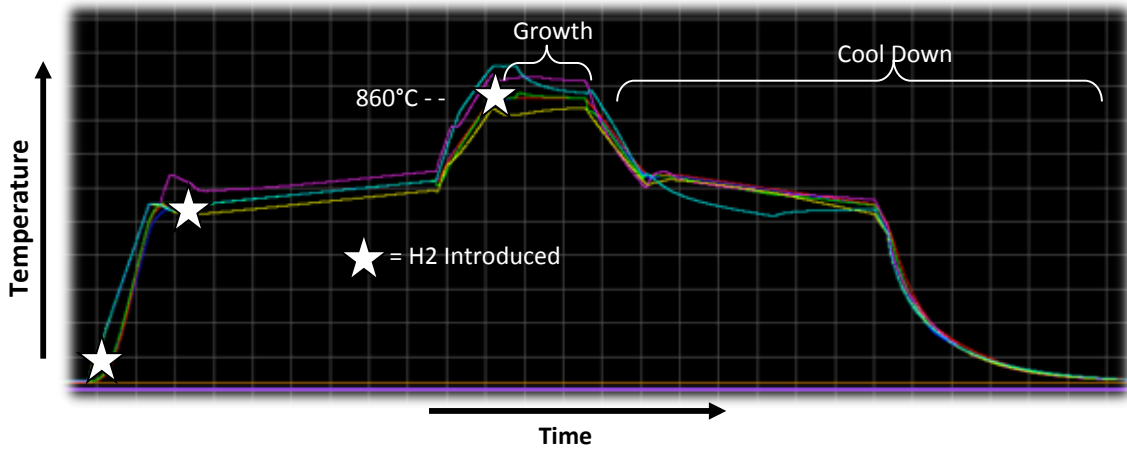
Figure A4-2: Temperature profile with H2 introduction points indicated.

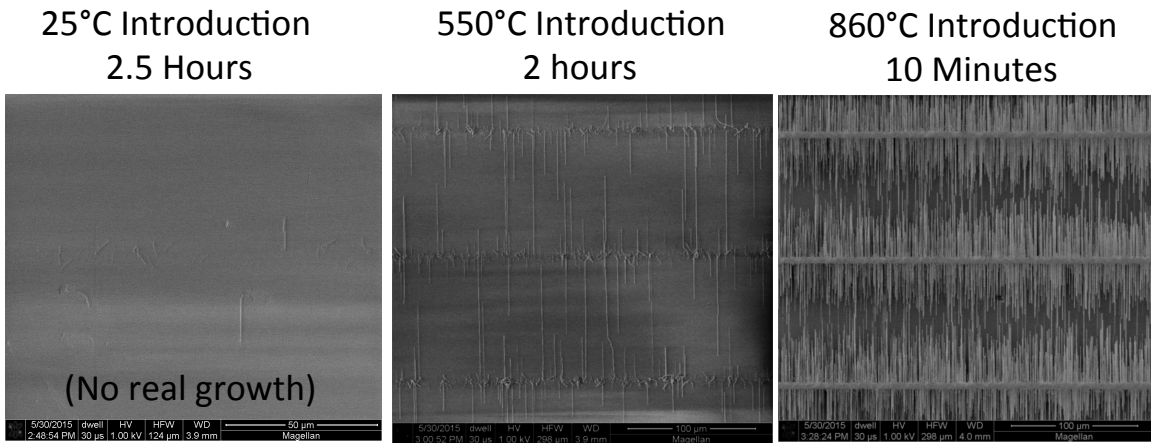| 25°C Introduction 2.5 Hours	550°C Introduction 2 hours	860°C Introduction 10 Minutes

Figure A4-3: SEM results for growth after 25°C Introduction, 550°C H2 introduction and 864°C H2 introduction with approximate anneal times noted.