PROCESS FOR AGGREGATION OF MICRON-SIZED PATTERNS OF VERTICALLY ALIGNED CARBON NANOTUBE FORESTS

by

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ABSTRACT

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Carbon nanotube forests condense when they are saturated with a solvent and then dried. While larger features readily condense into patterned features, smaller features require more delicate shrinking conditions and are highly dependant on temperature, solvent type, solvent vapor density, and heating rate. Through optimization of these parameters, nanotube forests can be successfully densified so that they maintain their original patterns, simply becoming thinner and denser. Shrinking micrometer-scaled features allow us to use larger patterns to create extremely small features up to one hundred times smaller than the original features.

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Thank you Sterling. Thank you ORCA. Thank you Dr Davis. Thank you David.

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Chapter 1

Introduction

1.1 History

In 1965 Gordon E. Moore, the co-founder of Intel predicted for the semiconductor industry that the density of semiconductor components on integrated circuits was going to increase exponentially [1]. He later clarified this prediction by saying that every two years the density of semiconductor components would double. Since then, the semiconductor industry has successfully maintained the rate set forth by this prediction. Because of it's founder's vision, Intel has been at the forefront of this push.

Most semiconductor processing uses photolithography to create thin film patterns and thus create semiconductor devices. In photolithography, first a thin film is deposited on a sample. Then a photosensitive polymer called photoresist is spin-coated onto the first thin film. A previously designed and created mask is placed on top of the sample, and shined light through the mask. In the areas where the light hits the sample, the photoresist is chemically changed. Then the sample is rinsed with a base, which removes the part of the photoresist that was exposed, leaving the photoresist that wasn't chemically altered through exposure. After that patterns can be etched in our original thin film. Finally, the remaining photo resist is dissolved, leaving patterns in the original film.

Photolithography processes easily make features as small as a few hundred microns. But to create smaller scales each step requires more expensive equipment and more difficult processing. Semiconductor firms have spent billions of dollars building equipment to create smaller and smaller features. Currently the cost of photolithographic equipment for a single factory is half a billion to one billion dollars [2]. These machines are able to produced features as small as 70 nm [3]. As feature size in semiconductor devices becomes even smaller, eventually another solution may need to be found to overcome this prohibitive processing expense.

Carbon nanotubes (CNT) are one of the technologies being explored to extend production techniques into the micron and nanometer scale. Nanotubes are structures made entirely of carbon. The carbon atoms are linked together in a hexagonal pattern that forms what looks like a sheet curled up into a tube. Single walled nanotubes are generally about 1 nm across, but can be hundreds of microns long. Depending on the amount of twist of the nanotubes (the chirality), the nanotubes can have either conductor or semiconducting properties. Nanotubes have an extremely high specific strength– 48,000 kNm/kg compared to high-carbon steel's specific strength of 154 kNm/kg. CNT's have been shown to have extremely high field emission properties [4]. Due to all these properties, carbon nanotubes are quite a hot topic and many potential applications are being researched [5].

Nanotubes are often grown from iron catalysts. As a carbon-based gas flows through a heated furnace, the carbon reacts with the thin layer of iron deposited on the substrate and a nanotube starts to grow. These nanotubes can be grown in 'forests' with all the nanotubes growing essentially perpendicular to the substrate [6].

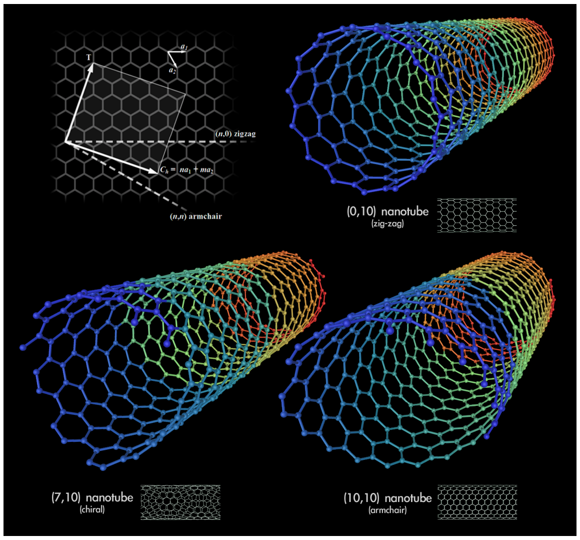

Figure 1.1 .Graphic of nanotube structures. Image from wikipedia.org

Nanotube forests are not dense. Even though they look solid and substantial, they are more of a gel-like consistency. They can easily be damaged, and often are with misguided tweezers. This is a potential drawback to using nanotube forests. One way to make the forests stronger is to make them denser through causing the individual tubes to stick together. This process is called nanotube aggregation. This creates densely packed aligned nanotube material [7]. This process is often used to created nanotube foams [8] [9] [10] [11] and patterns [12] [13]

It is commonly known that many fibrous materials exhibit clumping properties. Paint brushes that have gotten wet and then dry often have bundles of bristles that clump together. CNT's exhibit this same aggregation properties [14]. This bundling allows us to create intricate patterns from larger-featured patterns.

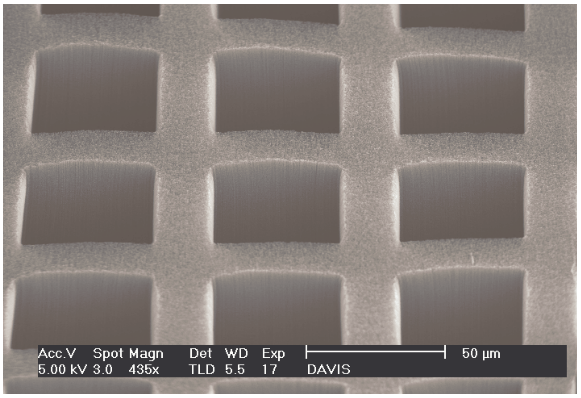

Figure 1.2 Large patterned nanotube forest before aggregation.

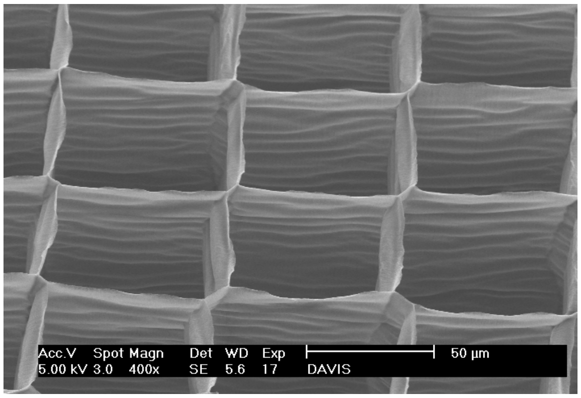

Figure 1.3 Large patterned nanotube forest after aggregation.

1.2 Previous Work

Previous research has shown that 20-100 micron sized features in patterns of vertically aligned carbon nanotubes can be aggregated into much smaller features within the same patterns (Fig 1.2,1.3). In this paper aggregation refers to nanotubes sticking together within a particular nanotube forest.

These patterns were made using photolithography to deposit patterns of iron catalyst and then using a chemical vapor deposition (CVD) process to grow the nanotubes. After this was done, the nanotube forests were aggregated by exposing them to vapor and then allowing the vapor to condense on the forests. When the condensed

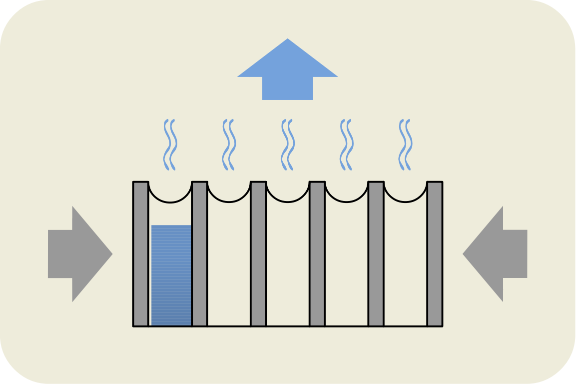

Figure 1.4 Representation of nanotube forests before aggregation.

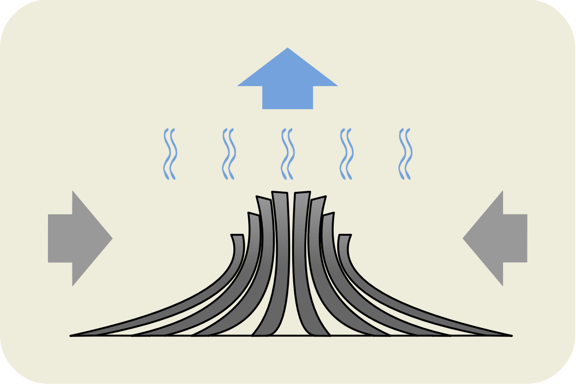

Figure 1.5 Representation of nanotube forests after aggregation.

vapor was evaporated, the tubes within the forests were aggregated. The aggregation caused the lines of nanotubes within the pattern clump in on themselves and become thinner, but the integrity and structure of the pattern was still maintained. [15]

First the nanotubes are wet with a solvent. (Fig As the solvent evaporates from the substrate, the surface tension will try to keep the solvent wetting the nanotubes instead of lowering the level of the solvent. This will cause a horizontal force that pushes the nanotubes in as the solvent continues to evaporate. The nanotubes get pulled closer together until the solvent is completely evaporated away, leaving nanotubes aggregated together.

However, when I tried to do this same process on patterns of nanotubes in smaller dimensions (i.e., on the order of a few microns instead of tens or hundreds of microns) nothing happened. The nanotube structures didn't aggregate. In this paper I present research on the effects that different parameters in the aggregation process have on the aggregation of smaller nanotube forest dimensions. I have also developed a process in which can take these smaller nanotube forests which have been grown in patterns and aggregate them, so that features within the patterns will shrink up to 1000 times. This may have potential to create nanometer-scale patterns without the prohibitive cost.

Chapter 2

Materials and Methods

The vertically aligned carbon nanotube forests were grown on a silicon surface that was prepared according to the following procedure:

The following were carried out under class 10 clean room conditions.

1-A 4-inch silicon wafer was coated with 30 nm of alumina using an Denton Vacuum E-beam Evaporator.

2-AZ3312 photoresist was spun onto wafer at 3000 rpm for 60 seconds.

3-The photoresist-coated wafer was baked on a hotplate for 60 seconds at 9030 °C C.

4-A pattern was transferred onto the wafer by exposing the photoresist through a glass mask in a Karl Suss Mask Aligner for 5 seconds on hard-contact mode with a 10 second hard contact delay and a 40 micrometer contact distance.

5-The exposed photoresist was removed through developing it for 40 seconds in developer solution (AZ300MIF)

6-The wafer was then rinsed in deionized water for 1 minute, and dried with N_2

7-A 2 nm iron layer was deposited onto the wafer with the WHAT TYPE??????evaporator

8-The remaining photoresist was removed by immersing the wafer in 1165 solvent and sonicating the immersed wafer for 15 minutes

9-The 1165 solvent was removed by rinsing it with acetone for one minute and then with isopropyl alcohol for one minute

After this process, the wafer is ready for further processing. Nanotube forests were grown with the following Chemical Vapor Deposition (CVD) Process.

1-The sample is placed in a water-cleaned quartz tube furnace.

2-To anneal the iron film the furnace is heated to 75030 °C C while flowing 69 milliliters/second of Argon gas and 500 milliliters/second of Hydrogen gas.

3-When the furnace had reached the desired temperature, 700 milliliters/second of ethylene (C_2H_4) was flowed for 5 seconds.

All work described in this paper used the previously described process.

In the aggregation of the nanotube forests, the following general process was used. However, to examine the effects of different variables, segments of the process were varied.

1-The silicon chip with nanotubes grown on it was placed on a temperature-controlled stage.

2-An environmental chamber into which the gas flow was controllable was placed over the sample.

3-The temperature-controlled stage was lowered to the desired temperature

4-When the desired temperature was reached, nitrogen was sent through a bubbler filled with solvent (ethanol or dichloroethane) and piped through the environmental chamber.

5-The solvent vaper that the nitrogen gas carried was allowed to condense on the nanotube forests.

6-The temperature-controlled stage was then heated up to room temperature and the sample was removed.

The aggregated nanotube forest samples were then analyzed with a Phillips SG300 S-Feg Scanning Electron Microscope (SEM) on the ultra high resolution mode. Most of the images were taken with the sample at a 30 °C tilt from vertical.

Chapter 3

Results and Conclusion

As part of my study of the aggregation of nanotubes, I varied different aspects of the aggregation process to determine the effects of each variable. Ultimately, a method for controlled aggregation of nanotube forest patterns was found. The solvent type, solvent vapor concentration, and condensation temperature were all varied. The time allowed for the condensation to occur was also drastically reduced. The results of these variations were analyzed and a process to create extremely dense, thin nanotube walls from larger nanotube patterns was created.

Each of the samples started out as rows of nanotube forests that were between 15-20 μm tall. (Fig 3.1)

3.1 Solvent

Ethanol was the main solvent used in the experiment. However, I also tried using dichlorethane as the aggregating agent. I cooled the stage on which I placed the silicon chip down to 730 °C C, and followed the entire aggregation process. Figs 3.2 and 3.3 show the SEM images of the two samples. The image of the nanotubes aggregated

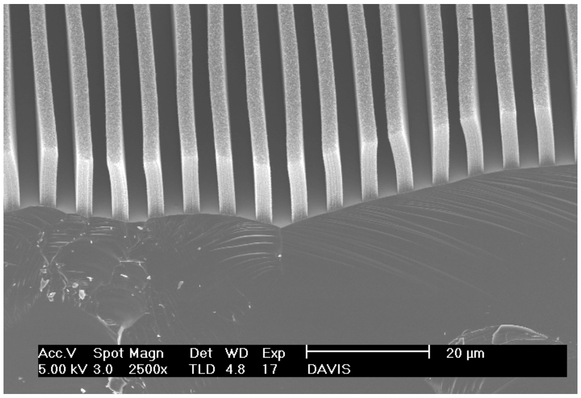

Figure 3.1 Patterned nanotube forests before aggregation. Image taken with a 30 degree tilt.

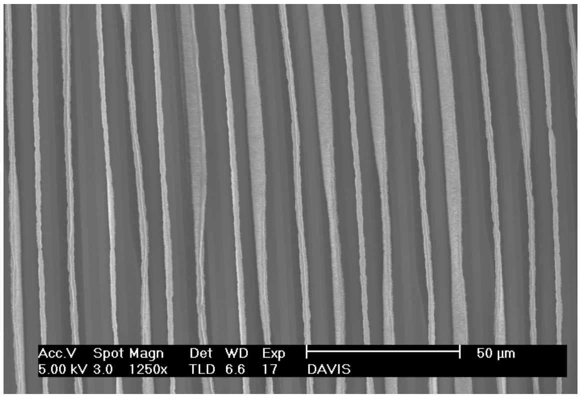

Figure 3.2 Ethanol-induced aggregated nanotube forest.

with ethanol (Fig 3.2) shows the nanotubes within the pattern aggregating to each other. This causes the lines of the pattern to be thinner. Some lines have been ripped up and are aggregated to the adjoining lines so the original pattern is not maintained. In the case of the nanotubes aggregated with dichloroethane (Fig 3.3), the lines do not exhibit substantial aggregation within themselves, but the lines themselves aggregate to each other. Once again the original pattern is not maintained.

In all the following aggregations I used ethanol as my solvent because the ethanol led to aggregations within the lines rather than between the lines

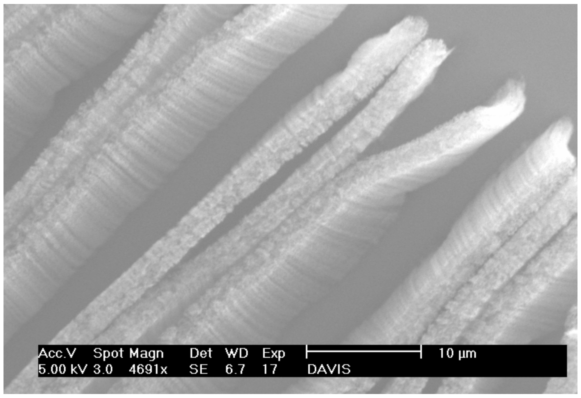

Figure 3.3 Dichloroethane-induced aggregated nanotube forest.

3.2 Solvent Vapor Concentration

Originally large patterns of nanotube forests were aggregated through a passive evaporation then condensation technique. During this process, the nanotubes were placed in the presence of a dish of solvent. The nanotubes were cooled to encourage condensation, but the solvent was allowed to evaporate passively. This created a low vapor concentration within the environmental chamber. With this technique, the large patterns pictured in Fig 1.3 were aggregated. However, when this same technique was applied to small-featured patterns no aggregation occurred. I then used a bubbler to distributed solvent particles into the air of the environmental chamber. Two separate bubblers were used in the project. The first was simply had an open-ended pipe in the solvent. Nitrogen was then piped through it, producing large bubbles that carried vapor with them. This increased the solvent vapor concentration within the environmental chamber compared to that of the passive evaporation method. The second bubbler had a Styrofoam cap on the end of the pipe. When nitrogen was piped through it, small bubbles were produced. These small bubbles carried much more vapor with them, so this produced the highest solvent vapor concentration within the environmental chamber. The solvent density images will be displayed in

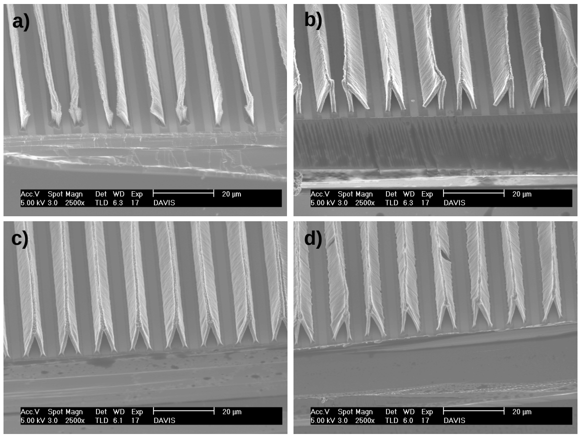

Figure 3.4 Nanotube forests aggregated at varying temperatures: a)1 °C, b)2 °C, c)3 °C, d)4 °C

the temperature variation section.

3.3 Condensation Temperature

The silicon chips were mounted on a variable temperature stage. To change the condensation parameters, the temperature of the stage was varied. The stage temperature was varied between 230 °C and 1530 °C . Figs 3.4-3.7 show the products of the various temperature variations. The nanotubes cooled down to about 730 °C created the thinnest features with the least inter-line aggregation. I was unable to control the rate at which the nanotubes were heated up after their cooled condensation, so it is possible that the critical variable is not the temperature to which the nanotubes were cooled. The critical variable could be the time in which it takes to evaporate off the sample

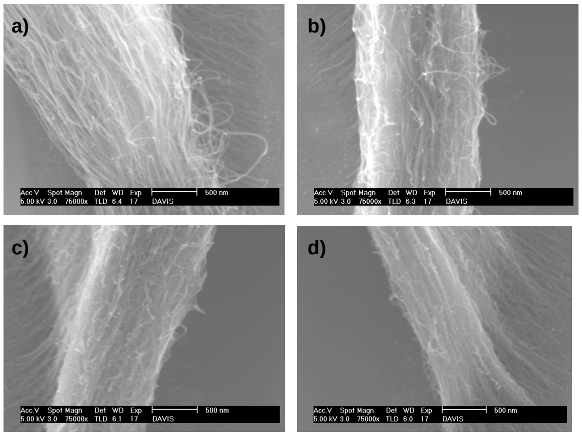

Figure 3.5 Close up of the same samples as above. a)1 °C, b)2 °C, c)3 °C, d)4 °C

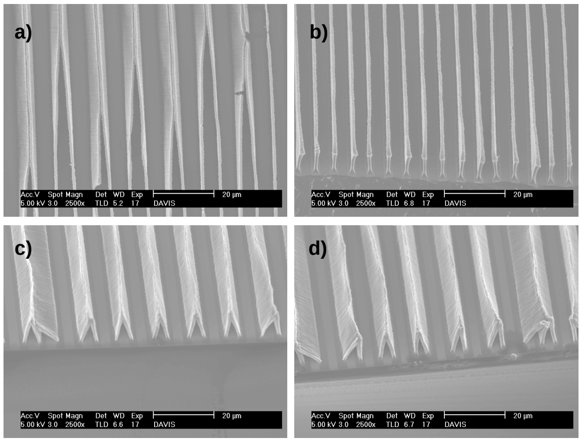

Figure 3.6 Nanotube forests aggregated at varying temperatures: a)7 °C image taken from above, b)7 °C signal taken at 30 ° from vertical, c)11 °C, d)12 °C.

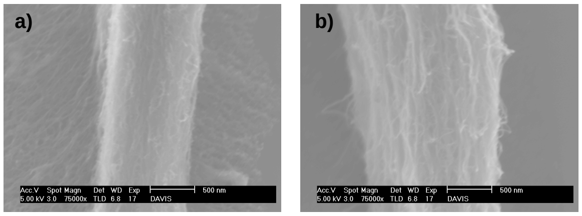

Figure 3.7 Close up of the same samples as above. a)7 °C, b)12 °C.

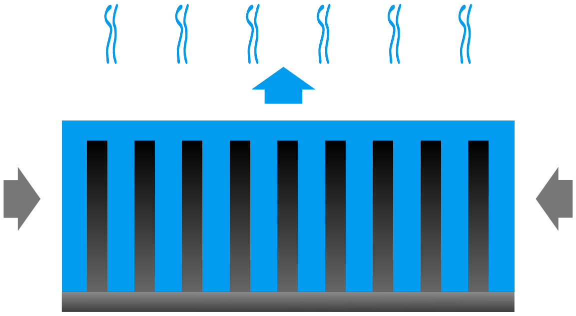

Figure 3.8 Diagram of aggregation between nanotube features.

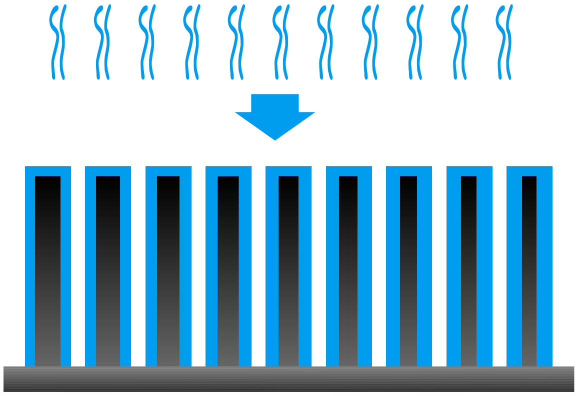

Figure 3.9 Diagram of aggregation only within nanotube features

3.4 Condensation Time

The previous nanotube aggregations were all done over an extended length of time so that the entire wafer was covered with the solvent. But these all resulted in significant inter-line aggregation. As Fig 3.8 shows, this is probably due to the solvent evaporation causing forces between the lines as well as within the lines. But as Fig 3.9 shows, if the solvent isn't allowed to completely fill in the gap between the lines, this will reduce the forces between lines and reduce the inter-line aggregation.

To prevent solvent building up between the lines, I used a cyclic method with a constant environmental chamber solvent vapor density. I cooled the sample down to 7 °C , then immediately heated it up to 12 °C, down to 7 °C, up to 12 °C, and so forth.

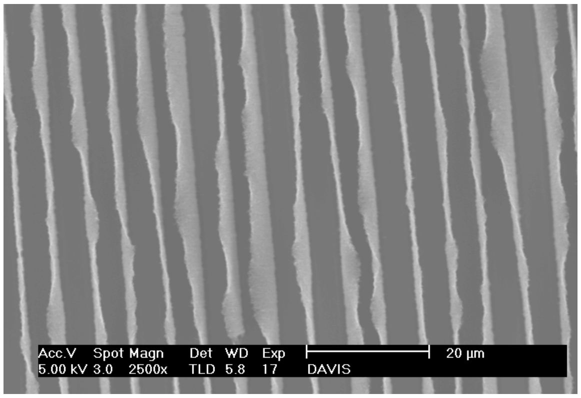

Figure 3.10 Aggregated nanotubes with cyclic method. Image taken from above

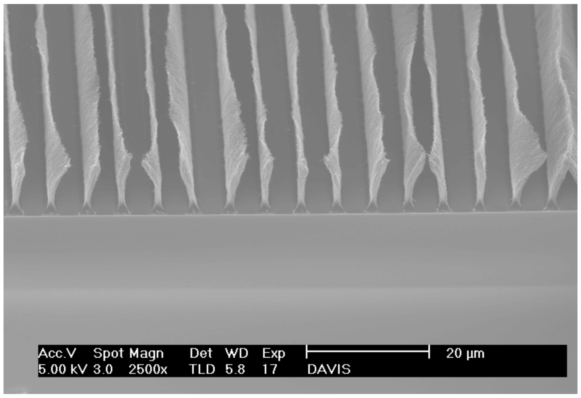

Figure 3.11 Aggregated nanotubes with cyclic method. Image taken at 30 °from vertical

As suspected, Figs 3.10-3.12 show that this cyclic method with small condensation time produced thin aggregated lines with no inter-line aggregation. The aggregated lines were smaller than the original lines by a factor of 50 percent.

3.5 Conclusion and Future Work

I analyzed the effects that solvent, solvent vapor concentration, condensation temperature and condensation time have on nanotube forest aggregation. In general, I found that high solvent vapor concentration done at 7 °C produces the densest patterns with

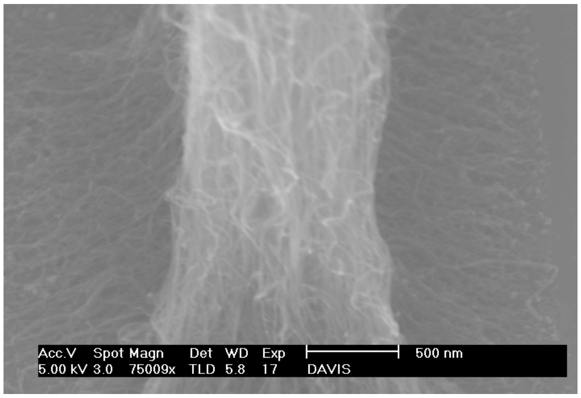

Figure 3.12 Close up of aggregated nanotubes with cyclic method.

the most aggregation within the pattern lines rather than between the pattern lines. I also found that it's possible to minimize forces between pattern features by using extremely short, repeated condensation times that only create thin layers of solvent on the nanotube forests.

In the future, it would be interesting to look more closely at the effects of changing the solvent has on the nanotube aggregation by performing more experiments with dichloroethane as well as other solvents. I would also be informative to do further studies to see increasing the number of cycles with extremely short condensation times would increase the amount of aggregation within the lines of nanotubes and create even thinner lines.

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