

CARBON NANOTUBE SHEET SYNTHESIS IN NITROGEN ENVIRONMENT AND
FLEXIBLE CNT SHEET STRAIN SENSOR

by

Ye Il Choi

APPROVED BY SUPERVISORY COMMITTEE:

Dr. Gil S. Lee, Chair

Dr. Lawrence J. Overzet

Dr. Jeong-Bong Lee

Dr. Chadwin D. Young

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Dedicated to my wife,

Karen Eunbee Choi

For her endless love and support.

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YE IL CHOI, BS

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Ye Il Choi, PhD
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Supervising Professor: Dr. Gil S. Lee

This thesis focuses on the potential of mass-production of spin-capable carbon nanotubes (SCNTs), which produce carbon nanotube sheets (CNTSs). A CNT forest (CNTF) that satisfies the specific conditions, such as CNT diameter, distances between CNTs, and shapes, are available to produce CNTS via Van der Waals interaction between each CNT. To understand and be able to control those factors, the morphology of the metal catalyst (Fe) was studied. The CNTs were synthesized with the chemical vapor deposition (CVD) method at 780 °C. First, the thickness of the Fe film was controlled, using the electron beam deposition method. Samples were deposited with 1.5, 2.0, 2.5, 3.0, and 3.5 nm of Fe, then the samples were annealed in H₂. After the annealing process, the Fe layer formed nanoparticles (NPs) with diameters of 16.91±1.88, 19.79±1.18, 23.28±5.42, 24.47±4.54, and 26.78±2.27 nm, respectively. The samples with 1.5, 2.0, and 2.5 nm produced SCNTs while others produced CNTF that were not spin-capable. The catalyst morphology and the synthesized CNTs are examined with atomic force microscopy (AFM) and scanning electron microscopy (SEM). Secondly, the H₂ exposure time was controlled to change the NP sizes at the annealing process. After annealing 20, 40, and 60 s

of H₂ exposure time, the annealed NPs with diameters of 16.45 ± 2.2 , 16.88 ± 3.99 , and 34.41 ± 5.79 nm. The samples that were exposed to H₂ for 20 and 40 s produced SCNT, but the one under 60 s produced non spin-capable CNTs. The results conclude that both initial Fe thickness and the H₂ annealing duration affect the growth process of the catalyst NP. Simply by controlling the initial deposition or the annealing process, it is possible to produce SCNT and CNTS in a repeatable fashion.

The production cost needs to be reduced for the mass-production to be possible. The conventional CVD system requires inert environment. However, relatively expensive gases, such as He and Ar are used in many studies. To solve this problem, we have replaced the inert gas with the N₂ gas. The catalysts annealed in N₂/H₂ and He/H₂ are examined thoroughly via AFM. The CNTs from each environment were taken under SEM and TEM to study their physical properties. The average densities of the particles and the CNTs from N₂ and He exhibited very similar results. In addition, the TEM images show that the thickness and the number of the walls from either environment do not show much difference from each other. The IV characteristic also suggests that the CNTs from either environment can be interchangeable. With the experimental results, using N₂ as the carrier gas for the spin-capability of CNTF is a notable discovery for mass-production and commercialization.

Finally, CNTSs grown in an N₂ environment were used as a sensing material for strain sensors. The resistances were measured for the devices. To find the relationship between the number of the CNTSs and the resistance and sensitivity, 2, 4, 6, and 8 layers of CNTSs were deposited on a flexible polymeric slab. The eight layers of CNTSs under 20% strain resulted in a sensitivity of 15.4%. After applying strain for 50 cycles, the resistance changes and sensitivity were very

consistent after the first few cycles. The sensitivities were 4.00, 8.44, 11.14, and 15.40% for 2, 4, 6, and 8 layers of the CNTSs in the device, which depicts that the relationship between the sensitivity and the number of the CNTS is linear.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	v
ABSTRACT.....	vi
LIST OF FIGURES.....	xiii
LIST OF TABLES.....	xvi
CHAPTER 1 INTRODUCTION	1
1.1 Introduction to Carbon Nanotube (CNT)	1
1.2 Structure of Single-wall CNT and Multi-wall CNT	2
1.3 Different Methods of CNT Synthesis.....	7
1.3.1 Arc discharge	8
1.3.2 Laser ablation.....	9
1.3.3 Chemical vapor deposition	10
1.4 Introduction to CNT Forest and CNT Sheet	12
1.4.1 Carbon nanotube Forest	12
1.4.2 Carbon nanotube sheet and yarn	14
1.4.3 Conditions to synthesize CNTS.....	17
1.4.4 Spinning grades definition	20
1.5 Motivation and research goals	22
1.5.1 Controlling the catalyst morphology	23
1.5.2 Replacing He with N ₂	23
1.5.3 Flexible strain sensor with CNTS synthesized in N ₂ for motion detection	24

CHAPTER 2 CATALYST CONTROL TO ACHIEVE SPIN CAPABLE CNT FOREST SYNTHESIS	25
2.1 Introduction.....	25
2.2 Experimental.....	26
2.2.1 Substrate.....	26
2.2.2 Chemical vapor deposition	27
2.2.3 Fe film thickness variation.....	28
2.2.4 Annealing time variation.....	29
2.2.5 Equipment.....	29
2.3 Result and Discussion.....	31
2.3.1 Effects of Fe Film Thicknesses.....	31
2.3.2 Effects of Different H ₂ Annealing Duration	37
2.4 Conclusion	43
CHAPTER 3 SPINNABLE CARBON NANOTUBE FOREST SYNTHESIS IN A NITROGEN ENVIRONMENT	45
3.1 Introduction.....	45
3.2 Experimental.....	47
3.2.1 Substrate preparation	47
3.2.2 Catalyst annealing process and SCNT synthesis in N ₂ environment.....	47
3.2.3 Comparison of the SCNTs synthesized in N ₂ and He.....	49
3.3 Result and Discussion.....	50
3.3.1 Effect of H ₂ annealing duration on the CNT areal density	50
3.3.2 Effect of H ₂ annealing duration on the catalyst areal density	57
3.3.3 Characteristics of CNT forests synthesized in N ₂ or He.....	61

3.4 Conclusion	67
CHAPTER 4 CHARACTERISTICS OF FLEXIBLE STRAIN SENSOR USING CARBON NANOTUBE SHEET SYNTHESIZED IN N ₂	68
4.1 Introduction.....	68
4.2 Experiment	70
4.2.1 CNTS synthesis.....	70
4.2.2 Sensor fabrication	70
4.2.3 Strain test	71
4.3 Result and Discussion.....	72
4.3.1 Number of CNTS layers and resistance.....	72
4.3.2 Cycle tests and hysteresis test	74
4.4 Conclusion	76
CHAPTER 5 SUMMARY AND POTENTIAL FUTURE WORK	78
5.1 Summary and Conclusion	78
5.2 Potential Future Research	80
5.2.1 What has already been done	80
5.2.2 Future Works	81
APPENDIX VARIATIONS OF CVD SYSTEMS.....	82
Vertical Chemical Vapor Deposition System.....	82
Horizontal CVD system with slidable Furnace	83
Horizontal CVD system with retractable magnetic arm.....	84
REFERENCES	85

BIOGRAPHICAL SKETCH	98
CURRICULUM VITAE	99

LIST OF FIGURES

Figure 1.1 Illustration of hexagonal crystalline of ideal graphene by Armano et al.[32].	2
Figure 1.2 Illustration of a) SWCNT, b) DWCNT, and MWCNT from ref [34].	3
Figure 1.3 Illustration of the honeycomb structure carbon structure and the chirality of CNT by Prasek et al. [39].	5
Figure 1.4 Graphite structure illustrated by Khan et al.[41]	7
Figure 1.5 Simple Schematic of the arc discharge chamber.	9
Figure 1.6 Schematic of the laser ablation chamber.	10
Figure 1.7 A simple schematic of conventional CVD system.	11
Figure 1.8 Illustration of CNT growth process by Azam et al. [51]	13
Figure 1.9 A SEM image of CNT forest and the alignment of the CNTs.	13
Figure 1.10 CNT growth mechanism explained by Zhang et al. [59].	15
Figure 1.11 Images of a) CNTS produced from CNT forest, b) SEM images of CNTS pulled from CNT forest, and c) schematic of CNTS forming from CNTF.	16
Figure 1.12 SEM image of CNT yarn produced by Zhang et al.[61].	17
Figure 1.13 A SEM image of an example of CNTs grown in aligned but curly fashion.	19
Figure 1.14 Schematic of CNT grades. The grades were labeled depending on the behavior that the CNTF exhibited.	21
Figure 2.1 Diagram of CVD process with the mobile furnace.	28
Figure 2.2 CVD process for a) regular CNT growth process and b) annealing process without the growth of CNTs.	30
Figure 2.3 The SEM (a-e) and AFM (f-j) images of CNT forests grown from a,f) 1.5, b,g) 2.0, c,h) 2.5, d,i) 3.0, and e,j) 3.5 nm of Fe films.	32
Figure 2.4 Raman spectroscopy results for each Fe film thicknesses (a-e) and f) the plot of I_D/I_G ratio.	33

Figure 2.5 Plot of Average NPs diameters (black) and the average areal density (red) calculated from the diameters. The qualities of the CNTFs are also shown in the boxes: blue for spin-capable and red for not spin-capable.	34
Figure 2.6 TEM images of the CNTs that are grown from Fe film thicknesses of a) 1.5, b) 2.0, c) 2.5, d) 3.0, e) 3.5 nm, and f) plot of average diameter with respect to the film thickness.	37
Figure 2.7 The SEM (a-c) and AFM (d-f) images of the CNT forest and the catalysts annealed for a,d) 20, b,e) 40, and c,f) 60 s.	39
Figure 2.8 Raman spectrums of CNTs that were annealed for a) 20 sec, b) 40 sec, c) 60 sec and d) plot of the defect ratio.	40
Figure 2.9 Plot of average NP diameter (black) and the average areal density (red) in respect to the H ₂ annealing time.	41
Figure 2.10 TEM images of the CNTs from annealing duration of a) 20, b) 40, c) 60 seconds, and d) the plot with respect to the average CNT diameters.	43
Figure 3.1 Diagram of CVD chamber and CNT synthesis process for the new furnace.	49
Figure 3.2 SEM images of CNT forests that were synthesized in N ₂ (a-f) and He (g-l) environment with different H ₂ annealing time; a,g) 20 s, b,h) 40 s, c,i) 60 s, d,j) 80 s, e,k) 100 s, f,l) 120 s.	52
Figure 3.3 CNT volume density per given area using SEM image analysis.	53
Figure 3.4 The SEM images of the side views of CNTFs for height measurement. a-f) shows the CNTs that are grown in N ₂ , and g-l) shows those in He.	55
Figure 3.5 Plot of the CNTF heights for different annealing times.	56
Figure 3.6 AFM images of the morphologies of annealed Fe NPs in both N ₂ (a-f) and He (g-l) environments.	57
Figure 3.7 Average Fe NP diameters for varying H ₂ annealing time in a) N ₂ and b) He environment.	59
Figure 3.8 Gaussian average of the NP diameters from N ₂ and He environment.	59
Figure 3.9 The average diameters calculated from the Gaussian curve in Figure 3.8.	60
Figure 3.10 Image of CNT sheets from CNT forests; one grown in He environment (top) and the other grow in N ₂ environment (bottom).	61

Figure 3.11 Raman spectroscopy of CNT sheet from a) N ₂ environment and b) He environment.	62
Figure 3.12 SEM images of two CNT forests synthesized in a CVD chamber using a) N ₂ environment, b) He environment, and c and d) Examples profile of a cross-section of the CNT forest.	63
Figure 3.13 Measured average bundle diameters of the SCNTFs from N ₂ (left) and He (right) environment.	64
Figure 3.14 TEM images of a) SCNT synthesized in N ₂ , b) non-SCNT synthesized in N ₂ , c) SCNT synthesized in He, and d) non-SCNT synthesized in He.	65
Figure 3.15 I-V curve of the layered CNT sheets. The resistances of each sample are shown in the inset image.	66
Figure 4.1 Diagram of the sensor fabrication process.	71
Figure 4.2 a) the diagram of the working mechanism of the strain sensor. b) the SEM images of CNTS (6 layers) at rest.	73
Figure 4.3 Plot of resistance vs the number of CNTS layers. Initial resistance (red) and the resistance after 50 cycles (black) are plotted. The inset image shows the actual devices assembled (2, 4, 6, 8 layers from left).....	74
Figure 4.4 Plots of a) resistive responses and the b) normalized sensitivities	75
Figure 4.5 Graphs of a) hysteresis test results and b) the sensitivities of 2, 4, 6, and 8 CNTS layers.	76
Figure A.1 Illustration of the vertical CVD chamber that was used for previous studies	83

LIST OF TABLES

Table 2.1. Experimental results for Fe thickness variation. The average diameter [§] and areal density [*] of the annealed NPs, the defect ratio of synthesized CNTs, and the CNTF grades are recorded.....	36
Table 2.2. Experimental results for H ₂ variation. The reported average diameter [§] and areal density [*] of the annealed NPs and the defect ratio of synthesized CNTs.	42
Table 3.1. Record of the CNTFs' vol%, height, and NPs average diameter [§] in both N ₂ and He environment	60

CHAPTER 1

INTRODUCTION

1.1 Introduction to Carbon Nanotube (CNT)

Since the discovery of carbon nanotube (CNT) by Suimo Iijima in 1991 [1], many studies were performed to explore the potential of the new material. This newly discovered material has the shape of a cylinder made from carbon atoms and soon was depicted as a “rolled up graphene.” One of the most famous materials that are formed with carbon is diamond, and in diamond structure, four carbon atoms surround one carbon atom in $2s^2$ and $2p^2$ orbitals. However, in graphene, graphite, and CNT, one *s-orbital* and two *p-orbitals* form 3 hybridized sp^2 -orbitals, allowing three carbons to bond to one center carbon that forms perfect 120° orbital angles. The remaining *p-orbital* is a relatively weak bond, π -bond, that does not contribute to the architecture of the graphene structure. This results in hexagonal formation on a 2-D plane that is usually illustrated as a honeycomb structure as shown in Figure 1.1. After investigations by scientists, it was found that CNTs have unique properties, such as high thermal [2] and electrical conductivity [3], high tensile strength [4], large surface area to volume ratio [5]–[7], and flexibility [8]; stronger, stiffer, and harder than steel and high electrical conductivity. The discovery of the CNT started a new flow of material studies, and new applications were studied including filter [9], battery [10]–[12], supercapacitor [13]–[17], resonator [18], hydrogen storage [19], bio/chemical sensor [20]–[24][25], and physical sensors [26]–[31]. Despite the countless investigations, the list of applications that CNTs could be utilized goes on.

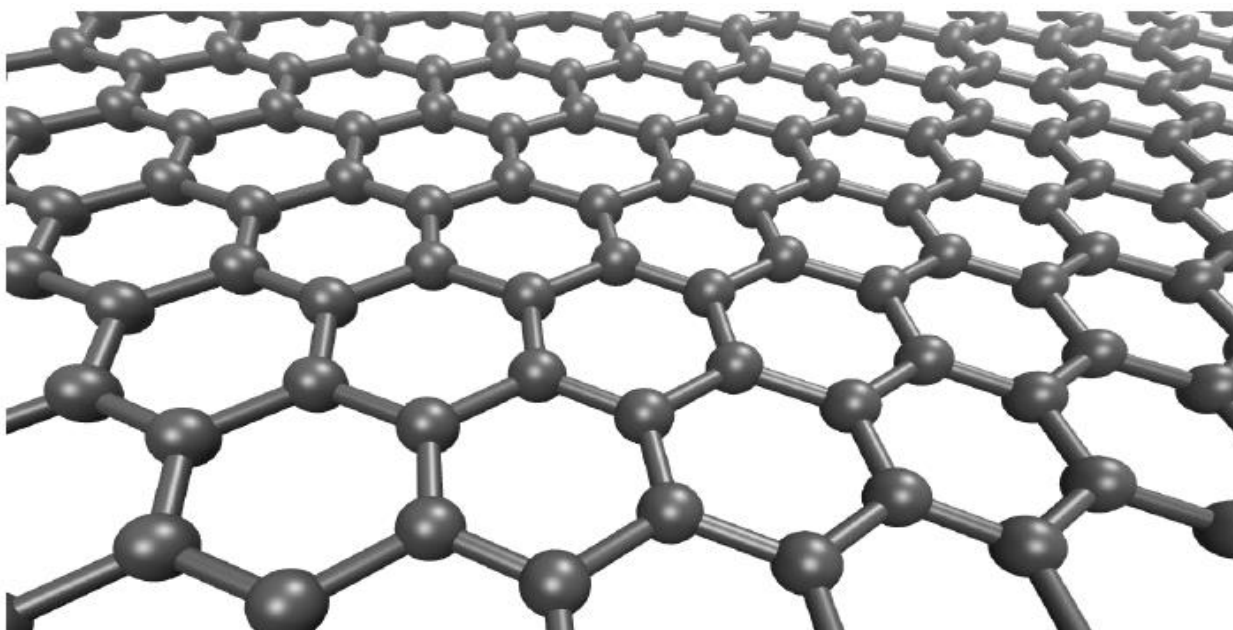


Figure 1.1. Illustration of hexagonal crystalline of ideal graphene by Armano et al.[32] permission from MDPI.

1.2 Structure of Single-wall CNT and Multi-wall CNT

There are different types of CNTs depending on the number of carbon layers that form the CNT. If one layer of carbon atoms forms a cylindrical shape, as shown in Figure 1.2 (left), it is referred to as a “single-wall” carbon nanotube (SWCNT). For two or more layers of carbon

atoms, as shown in Figure 1.2 (right), then it is called “double-wall” or “multi-wall” CNTs (DW or MWCNT), respectively [33].

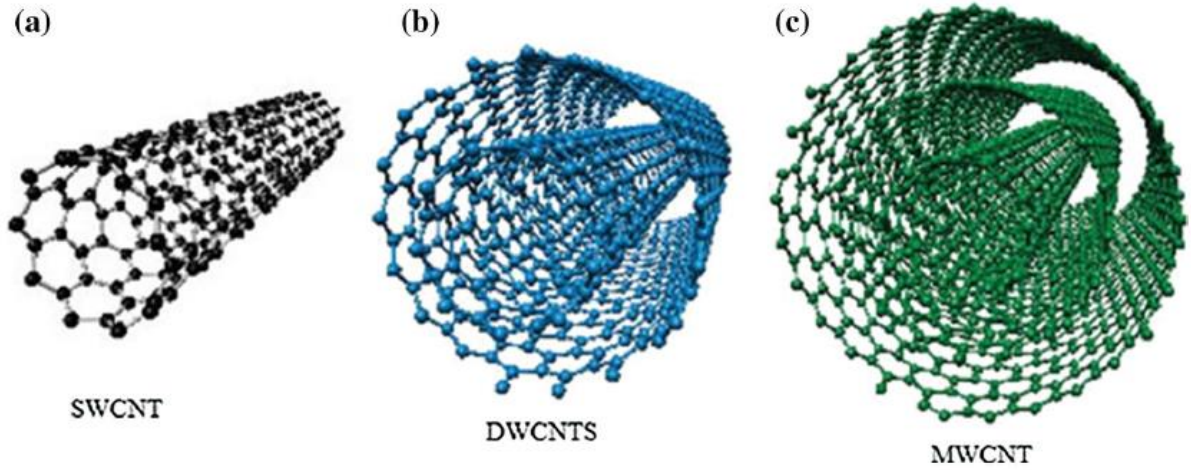


Figure 1.2. Illustration of a) SWCNT, b) DWCNT, and MWCNT from Labulo et al.[34] permission by Springer Nature.

More importantly, the SWCNT and MWCNT do not behave the same; the number of the walls changes the properties drastically. First, SWCNTs can be categorized into three different types depending on the chiral angle: zigzag ($\theta = 0^\circ$), chiral ($0 < \theta < 30^\circ$), and armchair ($\theta = 30^\circ$). In many cases, the armchair and zigzag show metallic properties, and chiral shows semiconducting properties [35]–[38]. As shown in Figure 1.3, the angle of the chirality is determined with the lattice vector, C , which is described as:

$$C = na_1 + ma_2$$

where n and m are coordinates/positions of the direction that CNT is rolled, and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors. Then the chirality angle is calculated by

$$\theta = \tan^{-1} \frac{\sqrt{3}m}{2n + m}$$

which can help to convert θ to (n,m) coordinate. For instance, CNT is a zigzag when $m = 0$, armchair when $m = n$, and chiral in other cases.

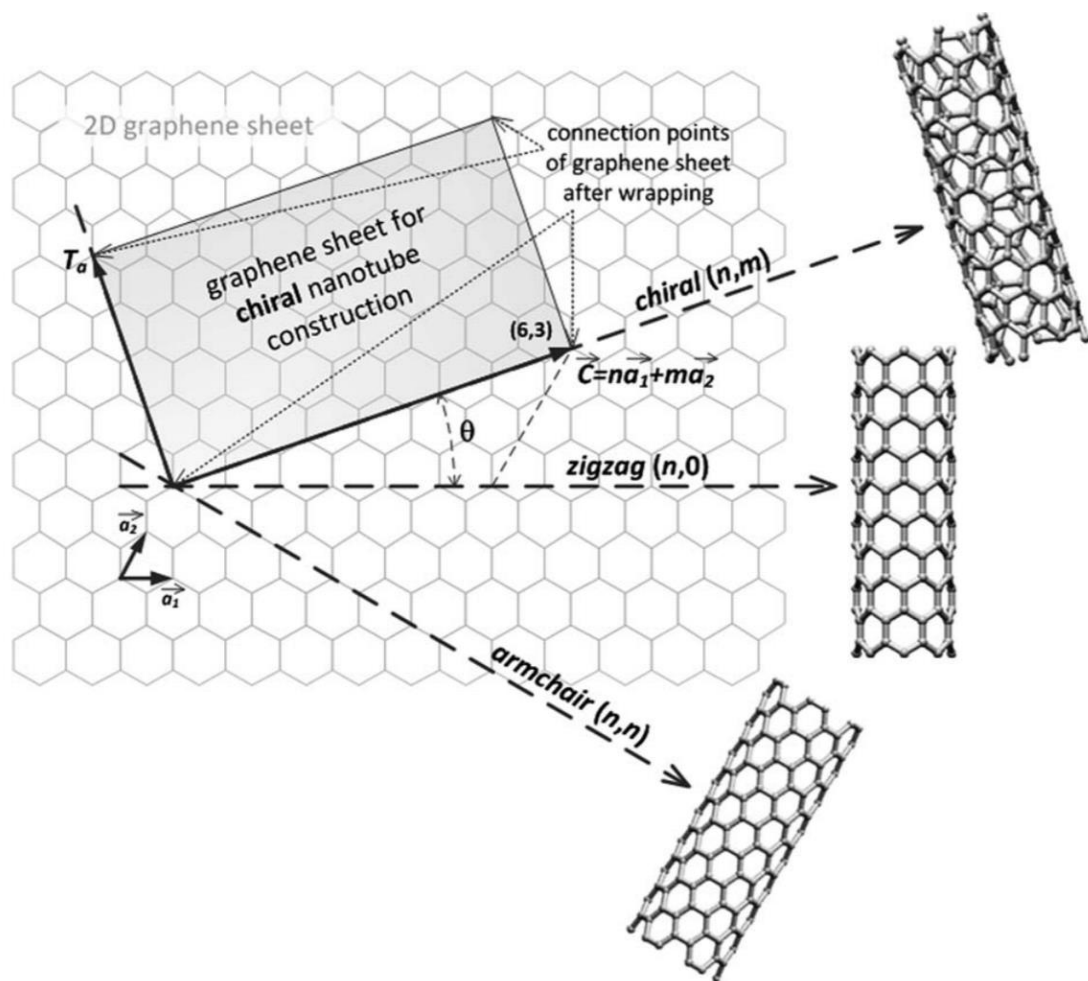


Figure 1.3. Illustration of the honeycomb structure carbon structure and the chirality of CNT by Prasek et al. [39] permission from the Royal Society of Chemistry.

When a CNT has more than one layer, it is considered a multi-wall CNT (MWCNT). Just like the SWCNT is illustrated as one graphene layer rolled in a cylindrical shape, the MWCNT can be explained as graphite in cylindrical form. However, unlike the SWCNT, MWCNTs always exhibit metallic behavior due to the graphitic structure. As shown in Figure 1.4, the graphite structure has multiple layers of the graphene stacked together, and the distance between each layer is around 0.34 nm [40]. At such a small distance, the electron orbitals from each layer

are affecting each other, and form patterned structures. It has multiple layers that are stacked in an alternating fashion with the π -bonding that was mentioned above. This π -orbital naturally positions itself to the middle of the other layer's hexagon where atomic hindrance is at the minimum, resulting in no space between the conduction band and the valence band allowing electrons to move freely between the lattices. This causes any CNTs with more than two walls, DWCNT and MWCNT, to become a conducting material. Shown in Figure 1.3, the stacked graphite crystal form ABABAB pattern.

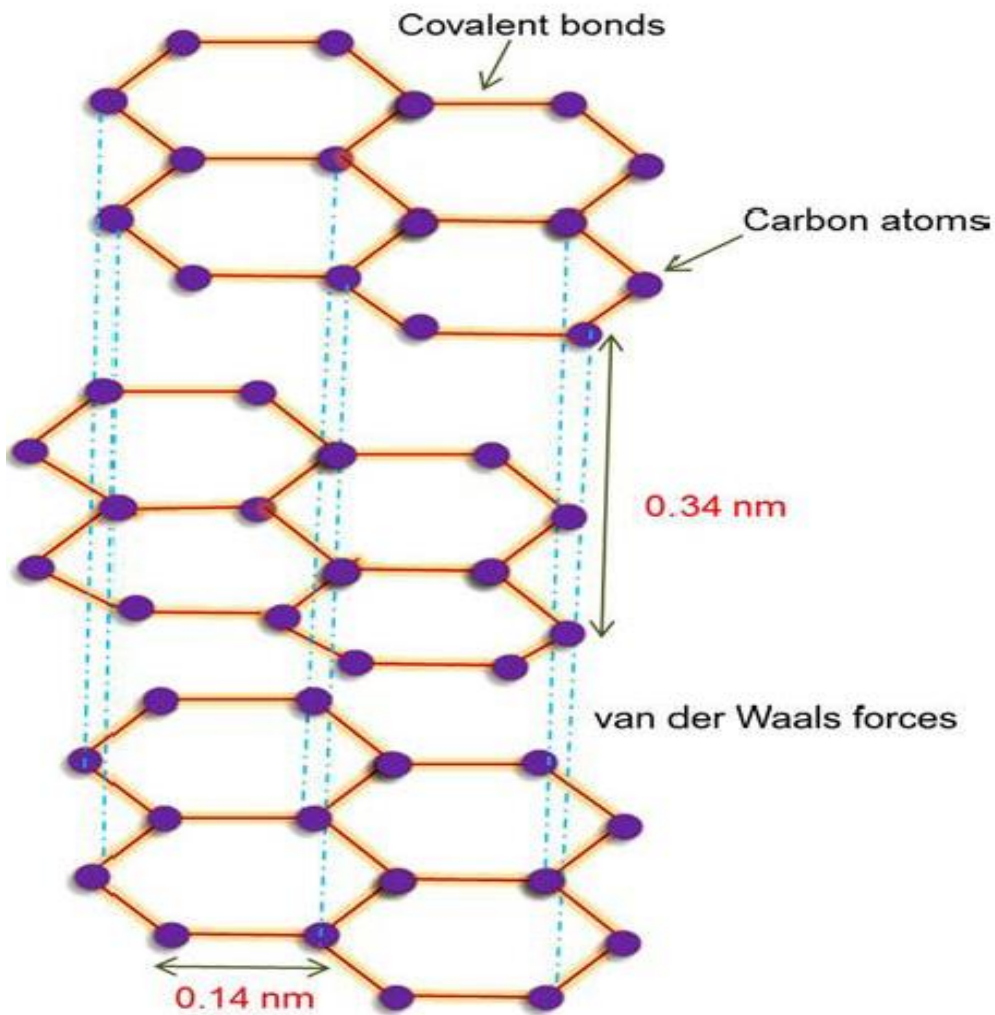


Figure 1.4. Graphite structure illustrated by Khan et al.[41] permission from Taylor & Francis.

1.3 Different Methods of CNT Synthesis

One of the easiest methods to obtain graphene is the exfoliation process with a commercial adhesive tape and a pencil, and as explained earlier, CNTs are illustrated as a “rolled graphene.” However, synthesizing CNT is not as simple as it is depicted. The synthesis is performed with many different methods, such as arc discharge (AD), laser ablation (LA), chemical vapor deposition (CVD), electrolytic, hydrothermal, and template, but the first three are

the most widely used to synthesize [42]. In this section, a brief explanation of the three methods, and their advantages and disadvantages will be discussed.

1.3.1 Arc discharge

The first method is the arc discharge (AD) method which utilized the gas plasma generated electrical breakdown. The AD is often used to synthesize different carbon materials such as fullerenes (buckyball) or nanotubes at low pressure (50 – 70 mbar) [43]. It was the method that Iijima used for the discovery of the CNT in 1991 [1]. Iijima found needle-like structures while synthesizing C60. A simple schematic of an arc discharge system is shown in Figure 1.5. The AD system consists of a power source to generate AC or DC voltage, precursor at the anode, and the target specimen at the cathode. The usual voltage range is near 20 V, and the arc current is around 100 A. The distance between the two electrodes is less than 2 mm for stable electric discharge. The precursor at the anode is usually powdered carbon, and the cathode is usually pure graphite. When enough voltage is built between two electrodes, the gas that is filling the entire chamber breaks down into electrons and ions which generates plasma between two electrodes. The ions fill the chamber and the electrons hit the anode with high velocity, breaking carbon bonds at the anode. The carbon atoms in vapor form slowly condense at the cathode where the relative temperature is lower [42]–[45]. The biggest advantage of this method is the easiness and the ability to select the type of CNTs (SWCNT or MWCNT) to synthesize at the cathode. With fine-tuning of the arc current, the pressure of the chamber, and types of gas and catalysts, both SWCNT and MWCNT can be synthesized by many studies [45]. However,

the disadvantages of the AD method are that the use of inert gas [46], low quality, short and random sizes of the CNTs [47].

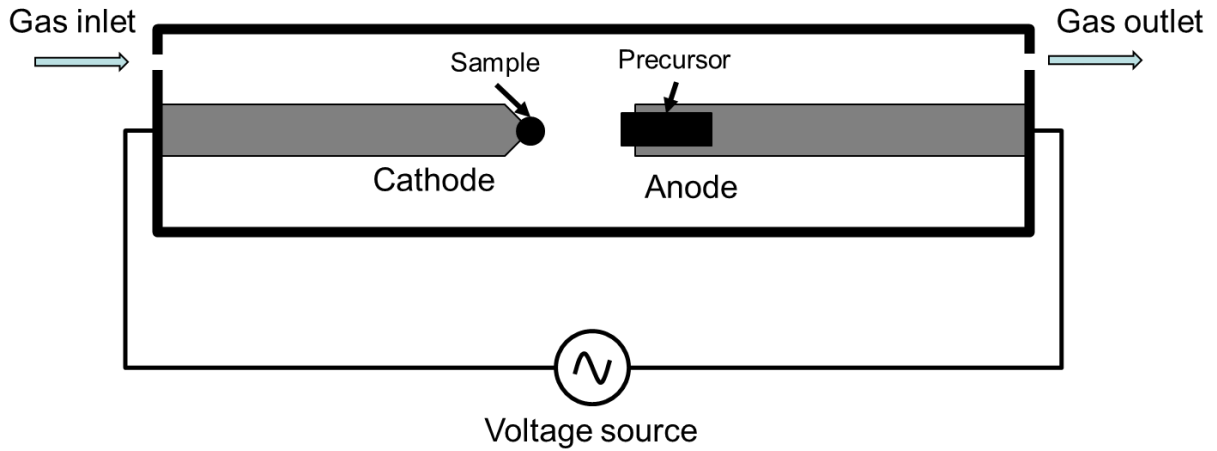


Figure 1.5. Simple Schematic of the arc discharge chamber.

1.3.2 Laser ablation

As mentioned above, the AD method is great for controlling the types of CNTs that one can produce. However, it contains too much amorphous carbon which results in low quality of the CNTs. On the other hand, the laser ablation (LA) method is used mainly to synthesize high-quality CNTs [48]. It also can control whether to synthesize SWCNT or MWCNT. Briefly, the LA contains four important parts: 1) furnace, 2) high-power laser, 3) carbon target, and 4) carbon collector. Figure 1.6 shows the simple schematic of the laser ablation chamber. First, the chamber must have a flow of gas that can deliver carbon atoms from the carbon source to the carbon collector. The laser (Nd:YAG) attacks and breaks the carbon source, which is usually pure graphite, and carbon atoms are dispersed into the chamber which is kept at high temperature

(~1200 °C). The flow of the gas, then, carries the carbon atoms to the end of the chamber where it is relatively cooler. The carbon collector is located at the end of the chamber to keep a cooler temperature (usually water-cooled). The carbon atoms then condense at the collector surface and form carbon nanotubes [49].

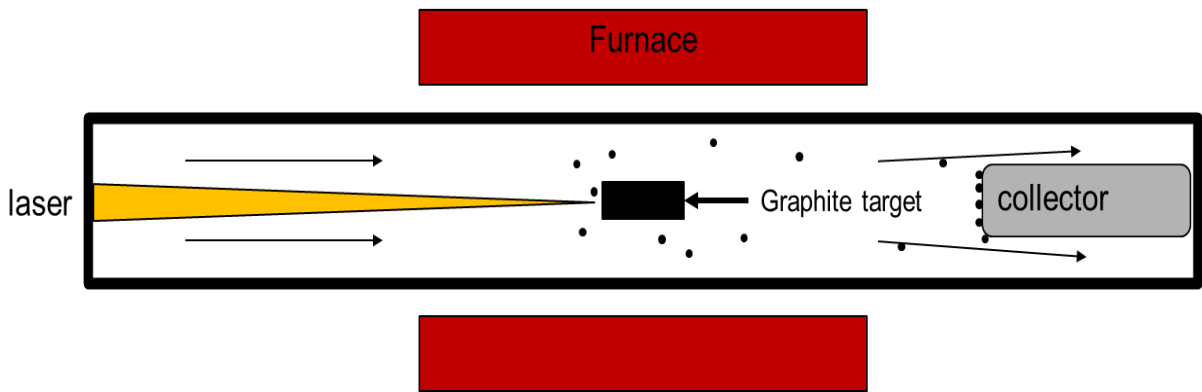


Figure 1.6. Schematic of the laser ablation chamber.

The advantages of the LA method are CNT diameter control, ability to select SWCNT or MWCNT to synthesize, high purity of the CNT, and long CNTs up to 20 μm [7], [39], [47]. However, it is an expensive process and very limited to the lab-scale processes only.

1.3.3 Chemical vapor deposition

The next method is the most popular method for large-scale production, and the author has used it for the experiments in this thesis. Figure 1.7 shows the conventional CVD system. The chemical vapor deposition (CVD) method also uses a furnace with a high-temperatures (500 ~1000 °C). While a sample with a metal catalyst is located at high temperature zone,

carbonaceous gases are introduced. At high temperatures, the carbonaceous gases on the surface of the catalyst break into carbon and hydrogen. The carbon atoms form bonds on the surface of the catalysts then the CNTs grow upward/downward. This method usually requires an inert environment and annealing gas or forming gas that helps reduce the oxide layer on the metal catalysts of the samples. Advantages of this method are easiness of the process, lower energy usage than other methods, and the production quantity per process. In addition to the quantity of the CNTs, it synthesizes much longer CNTs, from hundreds of μm to a few cm [50]. The disadvantages are that it is very challenging to make SWCNTs from the CVD system, and the defect ratio of the CNTs is relatively higher than the other two methods.

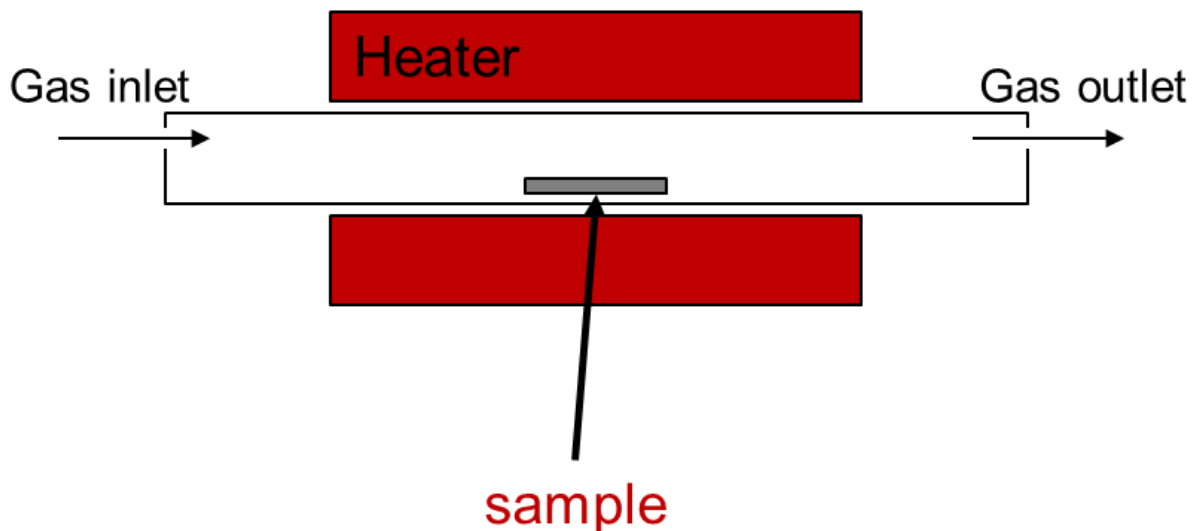


Figure 1.7. A simple schematic of conventional CVD system.

1.4 Introduction to CNT Forest and CNT Sheet

1.4.1 Carbon nanotube Forest

It is now well known that CNTs grow in one of the two fashions, tip growth or bottom growth. As shown in Figure 1.8 (a), the tip growth occurs when the carbon atoms in the atmosphere dissolve on the top surface of the catalysts and lifts the catalyst upward after surface diffusion and bulk diffusion. In the bottom growth fashion, Figure 1.8 (b), the carbon atoms are diffused on the surface of the catalyst and into the catalyst, but the catalyst and substrate adhesion are preventing catalysts to be lifted by the carbon chains, resulting in crystalline carbon structures to go upward. In both cases, the CNTs grow vertically to the surface of the substrate. This phenomenon allows hundreds of CNTs to grow vertically forming a beautiful alignment of CNTs. When millions of CNTs form vertically aligned and dense structures over a wide range, it appears to be a forest of CNTs. Hence, a group of vertically aligned CNTs (VACNT) is often referred to as CNT forests (CNTF). Figure 1.9 shows a CNTF that is grown on a silicon wafer, and the magnified image shows the alignment of the CNTs within the forest are dense and well-aligned.

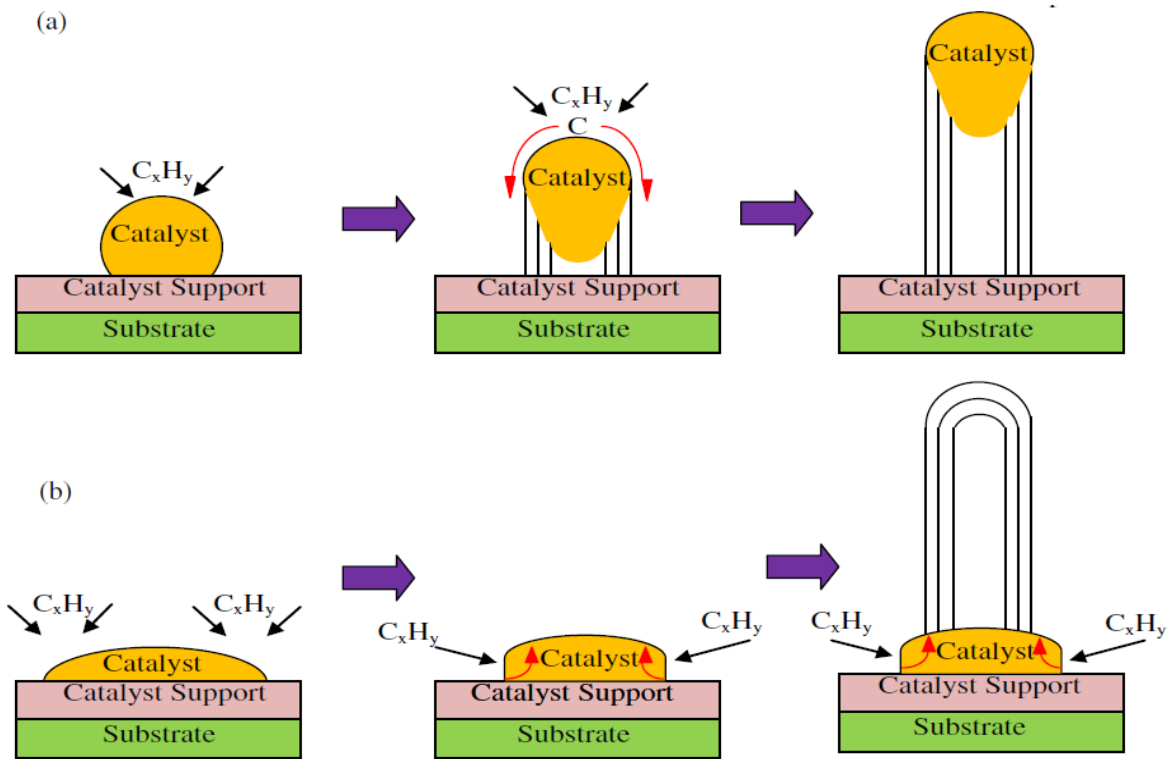


Figure 1.8. Illustration of CNT growth process by Azam et al. [51] permission from Springer Nature.

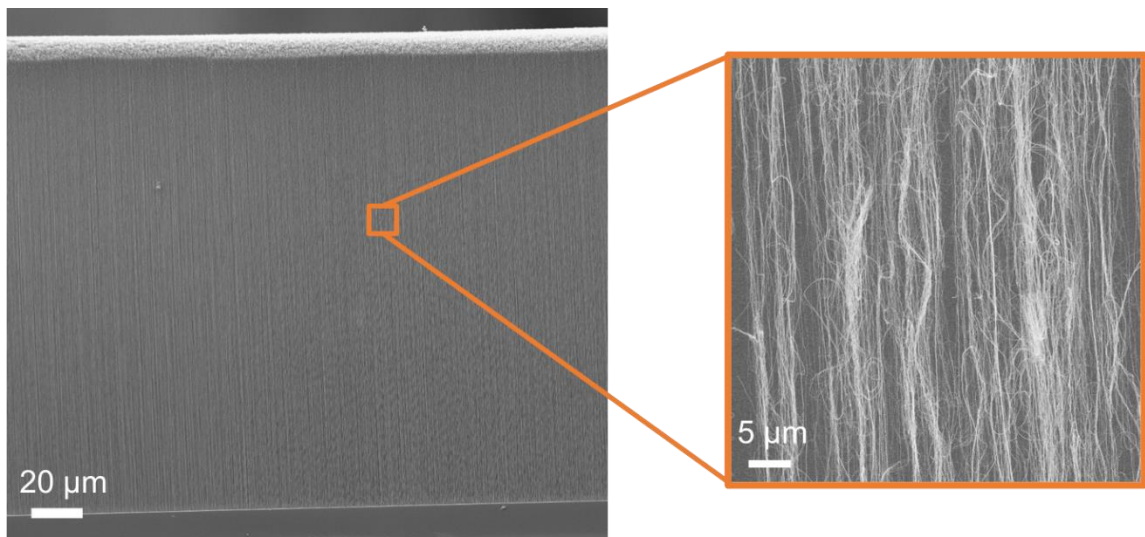


Figure 1.9. A SEM image of CNT forest and the alignment of the CNTs.

1.4.2 Carbon nanotube sheet and yarn

In addition to the discovery of the CNTF, another surprising discovery was made. In 2002, the spin-capable CNT (SCNT) is synthesized on silicon wafer via chemical vapor deposition CVD method by Jiang et al. [52]. The SCNTs produce hundreds of random surface connections of CNTs that consequently forms long chain of CNTs which forms a sheet like material, called “CNT sheet (CNTS).” The illustration of the CNTS production mechanism is shown in Figure 1.10. From a CNTF, a small portion of the CNTs is pulled, and it forms a long chain of connections that continues beyond the scope of nanomaterials. From the nanoscale range, the continuing links between individual CNTs form sheet-like material continued the connections to few meters. Due to the Van der Waals forces, the individual CNTs are attracted to each other and forms long chain of delicate connections [53]–[58]. Once CNTFs are grown on a silicon wafer, simply pulling them will generate CNTS that can extend to a large distance. From rough estimation, one CNT forest grown on $1 \times 1 \text{ cm}^2$ silicon wafer produced beyond 6 m long CNTS. This pseudo-2D material, which is only 5 – 30 nm thick, is made by MWCNT, therefore, conductive, very light, and flexible. The ability to continue achieving this feature from CNT forests is an undeniably attractive technology for multiple fields including electronics, mechanics, textile, fabrics, bio-chem, and storage applications.

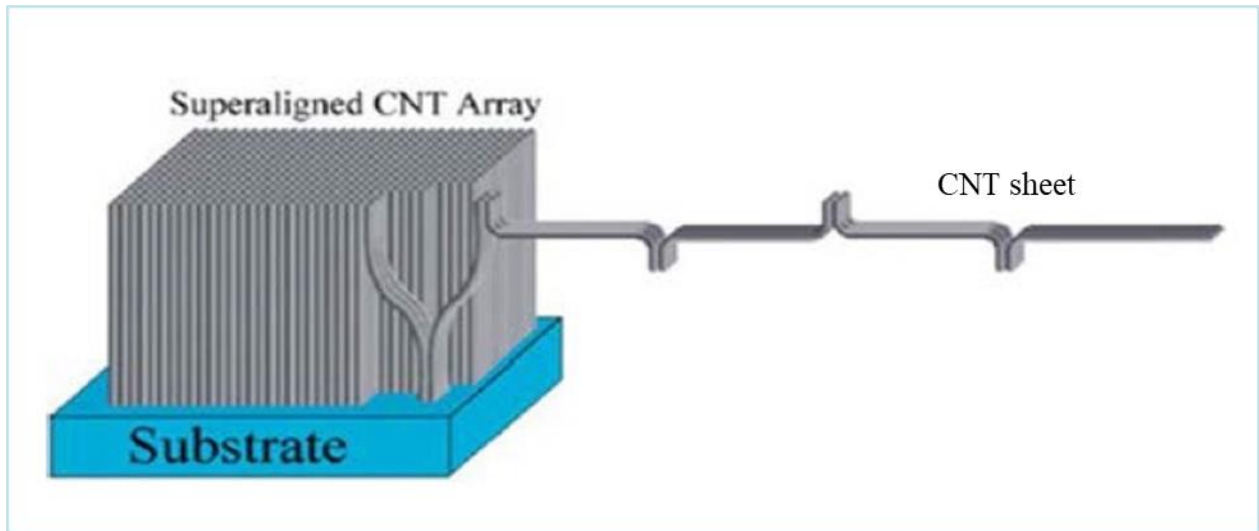


Figure 1.10. CNT growth mechanism explained by Zhang et al. [59] © John Wiley & Sons, Inc.

Figure 1.11 shows the CNTS produced from a CNTF simply by pulling and the SEM image from the top of the forest to see the boundary of the CNTS and CNTF. This discovery drew attention from many scientists and investors because it not only is an interesting material, but also a very cost-effective production of a thin film of CNTs. Many studies to this date are using random connections of the CNTs that are either dispersed in a liquid, then dried, or sprayed over the desired area. However, the aligned connections of the CNTs can be done at ease by simply pulling. As a derivative of the CNTS, a yarn of CNTs was formed.

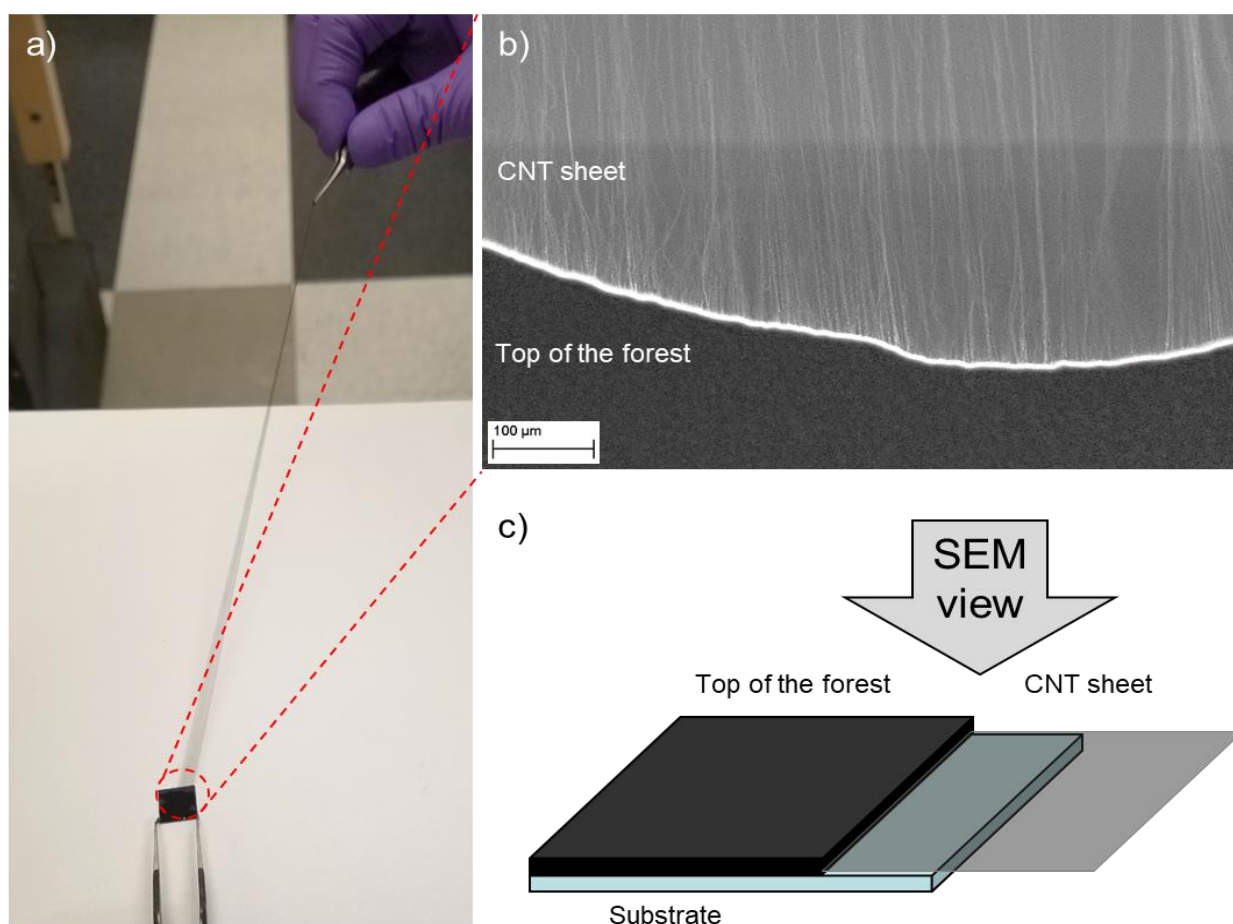


Figure 1.11. Images of a) CNTS produced from CNT forest, b) SEM images of CNTS pulled from CNT forest, and c) schematic of CNTS forming from CNTF.

Derivation of the CNTS, twisting the sheet created a yarn that exhibited stronger and more durable material [60], [61]. In Figure 1.12, the CNTS is pulled from the CNTF, and the CNTS is twisted to create a CNT yarn. The list of applications is endless. Any fields that required large surface area per given volume seek for materials like CNTS. Those that require strong, light, flexible conductors, such as the fabric and textile field, investigate the development of the CNT yarns.

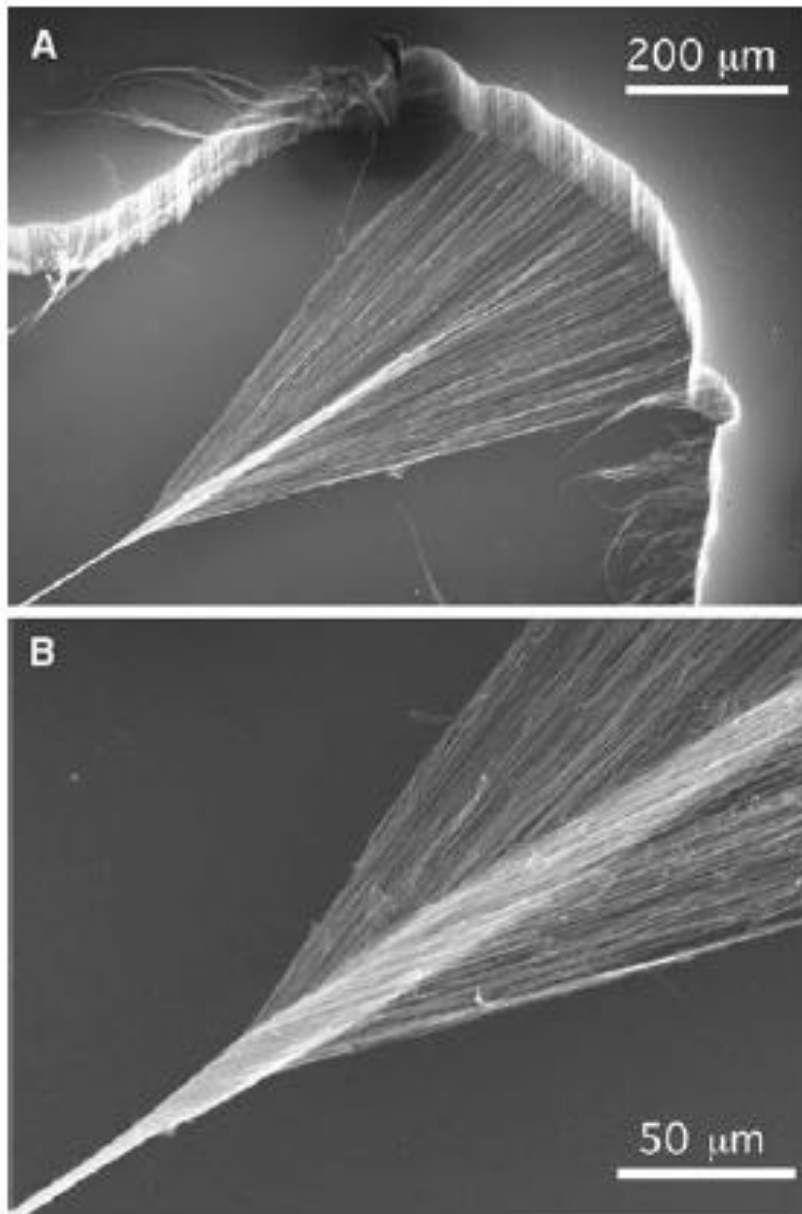


Figure 1.12. SEM image of CNT yarn produced by Zhang et al.[61] reprinted with permission from AAAS.

1.4.3 Conditions to synthesize CNTS.

Not all CNTF produces CNTS just by pulling a portion of them. CNTF is grown vertically from the catalysts to reach a certain shape and height. However, many CNTs that

forms CNTFs are not as straight as Figure 1.9 or Figure 1.10 presents. Depending on many factors, CNTs can grow in much curlier fashion as shown in Figure 1.13. The shape of the CNTs is one of the most critical factors of achieving the spin-capability of the CNTFs. When CNTs are too curly, the Van der Waals force cannot affect the CNTs to be attracted to each other. One of the controls that could also control the shape of the CNTs is to control the catalyst morphology. For CNTs to grow using the CVD method, a metal catalyst is required. On a silicon wafer with 100 nm of SiO₂ layer, a thin layer of Al₂O₃ is deposited as a buffer layer which can help metal particles to form nanoparticles on the surface [62]–[64]. Popular catalysts are Fe, Ni, Mo, and Co [39]; in this thesis, Fe is used. Typically, a thin layer of metal of selections is deposited on a silicon wafer, annealed to remove any oxide layers and formation of the catalysts at high temperature. Then hydrocarbon-gases (C₂H₂, C₆H₆, C₆H₁₄ [65]) are inserted as carbon sources; in this thesis, C₂H₂ is used. Jung et al. [57] have measured the sheet resistance of the metal catalyst layer and showed that the Fe catalyst morphology could influence the production of spinnable CNTF.

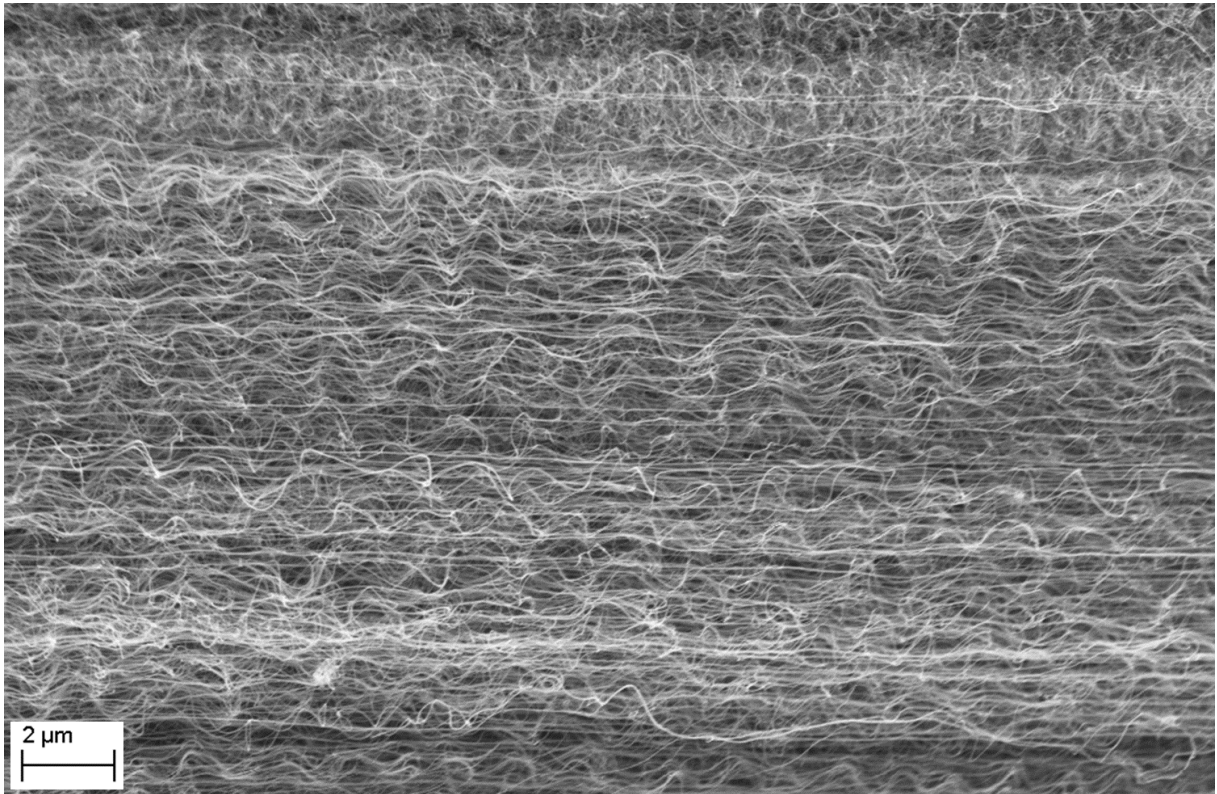


Figure 1.13. A SEM image of an example of CNTs grown in aligned but curly fashion.

The use of buffer layer, Al_2O_3 , was applied for the samples in this thesis. It is known that the interface of $\text{SiO}_2\text{-Fe}$ and $\text{Al}_2\text{O}_3\text{-Fe}$ react differently and the latter is much more beneficial for vertically aligned CNT arrays [62]–[64]. Zhang et al. also have reported that the Al_2O_3 thickness has a significant influence on the spinnability of the CNT arrays by changing 1) the Al_2O_3 morphology, 2) the chemical state of the Fe atoms, and 3) the diffusion of the Fe [63]. Kim et al. reported that having a buffer layer helps the growth of the CNT forests. They also have annealed the Al_2O_3 then deposited Fe catalysts, and it resulted in curlier and lower quality of CNT structures [64].

1.4.4 Spinning grades definition

Many of the studies show successful synthesis of CNTS/CNT yarn. However, the quality of the CNTS must be defined. Some CNT forests do show spinning properties, but they do not continue the long chain. This is not favorable for mass-production this thesis emphasizes. Therefore, it is notable to define the physical dimensions and grades that CNTF and CNTS exhibit after the synthesis process. First, the width of the CNTS is limited by the size of the substrate. CNTs are grown on the metal catalysts that are deposited on a substrate, therefore, the width of the CNTF simply cannot exceed the size of the substrate. Second, the maximum pulled length of the CNTS varied depending on the quality of the CNTF. Finally, the ranking or quality grades of the CNTF have been decided depending on the behavioral results of the CNTFs.

Synthesis process exhibited one of five different possibilities, which are:

1. a thin layer of carbon soot is deposited on the surface of the specimen,
2. CNTF is visibly tall for one to grab a portion of the CNTs but does not form any sheet or thread of CNT links,
3. CNTF produces visible threads or sheet of CNTs but the width of the CNTS decreases and eventually break the connection as the pulling distance increases,
4. CNTF produces CNTS and the width of the CNTS are kept even the pulled distance increased, and
5. CNTF produces CNTS that increase in its width and eventually consumes the whole forest without any waste.

Figure 1.14 shows an illustrated design of the five grades above. In order to produce the CNTS for mass-production purposes, the maintaining of the CNTS width was a required property.

Therefore, those that are with grades of 1, 2, and 3 are not considered as “spin-capable” for this thesis. For 4 and 5, which kept and increased its width, allowed to consume the whole CNTFs which is suitable for mass-production and commercialization.

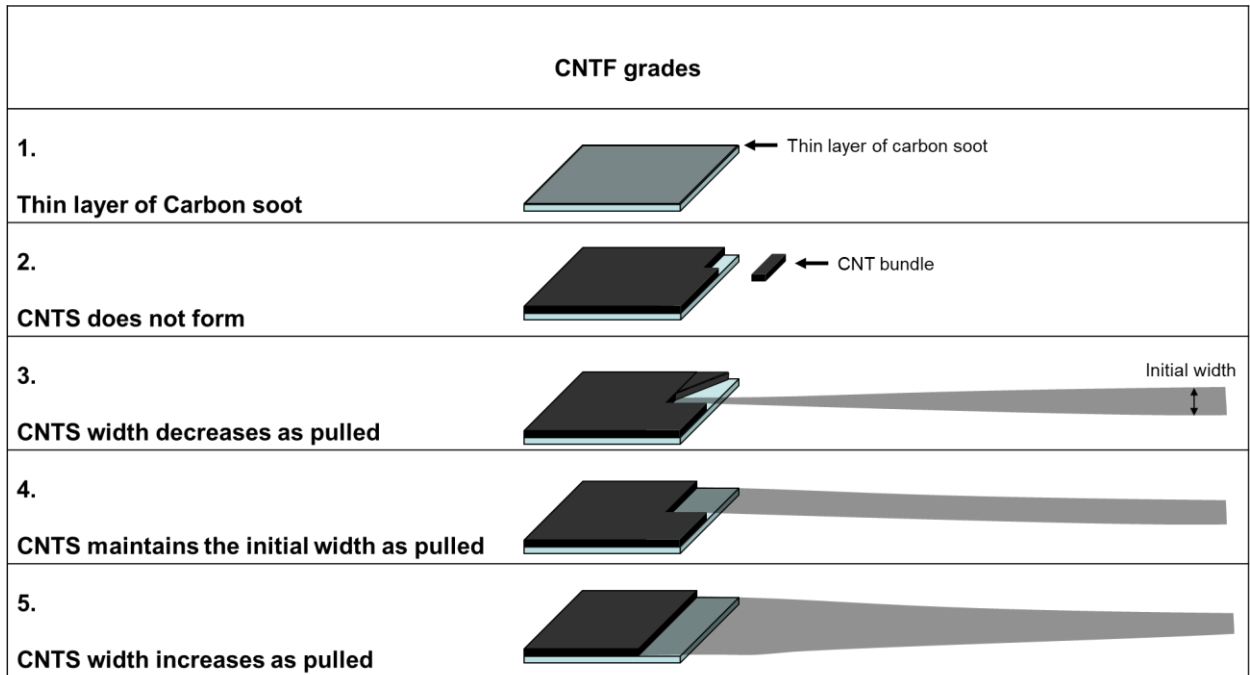


Figure 1.14. Schematic of CNT grades. The grades were labeled depending on the behavior that the CNTF exhibited.

It is true that there were mixtures of two different grades. For example, CNTS width increased at the beginning of the pulling process, but it then reduced in its width then broke. This was not considered “spinnable” since it broke. To clarify the ranking system, if the spinnability showed properties of both grades, then the forest is ranked with lower grade. Therefore, the example above was ranked as “3.”

1.5 Motivation and research goals

As explained above, the production of CNTF that can produce CNTS is an important task to be invested for many different applications that CNTs could help propel their development. However, there exists the main problem with the mass-production of the CNTS; the production cost is too high due to the increasing price of inert gases. Helium, the most popular inert gas that is commercialized at such an affordable price, now is being depleted from the earth. Even though helium is the second most abundant element in the universe, it is becoming rarer on the earth as time passes since it is the lightest element. The demand for helium is only increasing, and industries that use helium on daily basis are eager to replace the inert gases such as argon or xenon with much reliable and chemically stable gas. The replacement of helium in the CNT synthesis process is an urgent need for step forward in the mass-production of the CNTS.

In addition to the production of the CNTs using cheaper gas, the demonstration of a device that uses CNTS is an important task. One of the CNT's unique properties is conductivity and flexibility. Since the demand for wearable devices, health monitoring, and immersive gaming systems is increasing quickly, a flexible and semi-transparent strain sensor is demonstrated as an example device that uses CNTS synthesized in an N₂ environment.

Therefore, in this thesis, three main goals will be achieved:

- 1) investigate in controlling the catalyst morphology so that CNTF can produce CNTS in a repeatable fashion,
- 2) replace helium with nitrogen for possible commercialization of CNTS for more cost-effective production, and

- 3) demonstrate an application, a strain sensor, with the CNTS produced from the nitrogen environment as an example of the cheap and reliable application.

1.5.1 Controlling the catalyst morphology

CNTF that can produce CNTS requires certain conditions, such as CNT shapes and density. By controlling the catalysts' sizes and locations, one can potentially locate each CNT in the desired location. However, it is very challenging to change/modify the sizes and specific locations of the catalysts directly since the catalysts are too small to individually plant with current technology in a time/cost-efficient way. Therefore, in Chapter 2, efforts to control the morphology of the catalyst nanoparticles (NPs) are reported. The relationship between the initial catalytic layer thickness and the final NP morphology is studied. In addition, the annealing gas exposure time was varied to find the relationship between the total exposure time and the spin-capability of a CNT forest.

1.5.2 Replacing He with N₂

The next goal was to reduce the synthesis cost by replacing relatively expensive gas, helium (He). By simply replacing helium with nitrogen, we could achieve SCNT and CNTS from the same condition. However, it is necessary to compare their catalyst morphology and the general quality of the result. Therefore, the nano- and micro-structures of CNTs from the N₂ environment and the He environment will be compared with SEM and TEM. The general quality of the CNTs will be studied using the Raman spectroscopy by comparing their I_D/I_G ratio. The catalyst morphology of both conditions will be examined using AFM. In addition, their electrical

properties were tested by measuring current for given voltage (0 – 1 V) and calculating resistances.

1.5.3 Flexible strain sensor with CNTS synthesized in N₂ for motion detection

Finally, Chapter 4 will demonstrate that the CNTS from the N₂ environment can be adapted to an application, strain sensor. A flexible strain sensor using a silicon-based polymer and the CNTS from the N₂ environment was developed and tested for its performance. The Ecoflex 00-30 product, silicon-Pt polymer, is used to make a flexible substrate, then CNTS is applied on the top. Another layer of the polymer was applied on the top of the CNT layer to completely encapsulate the sensing material and protect it from environmental detects (dust and humidity). Tests including hysteresis, cycling, and resistance measurements are performed and reported.

CHAPTER 2

CATALYST CONTROL TO ACHIEVE SPIN CAPABLE CNT FOREST SYNTHESIS ¹

2.1 Introduction

The carbon nanotube (CNT) showed many exquisite properties to the scientific society. Their outstanding properties such as thermal and electrical conductivity, tensile strength, and flexibility are attractive characteristics for many different applications [53], [66]. In addition, the spin-capability of the CNT is the most intriguing property formed by the weak-atomic force named “Van der Waals” force [33], [35], [36], [38]. Since Van der Waals force is a weak force at the surface of a material, it is necessary for the CNTs to be straight and aligned to each other for the effect to dominate this phenomenon [68], [69]. In order to achieve such high alignment, the catalyst morphology needs to be adjusted within a certain range for the optimum result [56]. Kim et al. have tuned Fe catalysts to find what effect does it have on the spin-capable carbon nanotubes. Their results show that the Fe thicknesses of 4, 5, and 6 nm have resulted in CNTSs that were pulled beyond 3 m (limited by the physical laboratory space). They have reported that certain sheet resistance of the catalyst layer needs to be satisfied to produce the spin-capability. In agreement with the argument, we also perform the study of the catalytic layer. Since sheet resistances can change depending on the amount of the oxide layers that form naturally, there

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exists more chance of human-error occurrence. In addition, we have added a buffer layer, Al_2O_3 , that helps the formation of the NPs.

In this Chapter, two of the factors will be varied to study the effects of them on the catalyst morphology and the spin-capability of the CNT forests. First, the initial thickness of the catalyst layer (Fe) will be varied. Using electron beam deposition tool, 1.5, 2.0, 2.5, 3.0, and 3.5 nm of Fe layers are deposited on the silicon substrate with SiO_2 (100 nm) and Al_2O_3 layers (3 nm). The samples with different Fe thicknesses were annealed. Using AFM, the changes of surface morphologies of different thicknesses were analyzed. Then, the CNTs were grown on the samples. The synthesized CNTs from different Fe thicknesses were examined using TEM and SEM for their structural comparison. Second, the annealing duration will be varied to verify the morphology evolution for the different duration that the catalyst is exposed to H_2 gas. Similarly, the surface morphology was examined with AFM. Then CNTs were grown with different annealing duration, the SEM and TEM images were thoroughly studied and reported.

2.2 Experimental

2.2.1 Substrate

A p-type <100> silicon wafer was purchased from the University Wafer. Then the as-purchased Si wafers were put at 1050 °C, and 100 nm of SiO_2 layer was grown using a dry oxidation method. The wafer was thoroughly cleaned with methanol, ethanol, acetone, isopropanol, and distilled water. Then the sample is dried at 150 °C for 2 min. On top of the SiO_2 layer, a 3 nm Al_2O_3 layer was applied with an atomic layer deposition (ALD) tool at a rate of 2 Å/min. A thin layer of the catalyst, iron (Fe), was deposited using e-beam deposition at a rate of

3 Å/s or slower. Then the e-beam equipment was cooled down to room temperature (22 °C) at vacuum. When the sample was taken out from the e-beam tool, it was shortly exposed to the air then put into a vacuum to prevent further contamination. However, the formation of a naturally built oxide layer on the top of the Fe film from the oxygen in the air is inevitable.

2.2.2 Chemical vapor deposition

The chemical vapor deposition (CVD) process was performed in a conventional horizontal quartz CVD system at atmospheric pressure. In addition to a conventional CVD system, a small adaptation was added to reduce the total experiment time. As shown in Figure 2.1, a magnetic arm is added to push the sample quickly into the growth zone. Then the furnace was modified so that when the growth process was finished, the furnace was slid to the end of the quartz tube to expose the substrate to cool down to room temperature within 13.5 ± 1.5 min. Figure 2.2 shows the CVD process in terms of the gas flows and temperature. After N₂ is purged for 5 min, He was purged for the rest of the process. While the specimen is at room temperature, the furnace was heated up to 780 °C. Then the specimen was pushed in with a magnetic arm, then the magnetic arm was retrieved. The annealing process was performed by turning on the H₂ gas (70 sccm), and the growth process continued as 20 sccm of acetylene (C₂H₂) entered the CVD chamber for 3 min. After the growth process, both H₂ and C₂H₂ were turned off, then the furnace was slid to the other end of the quartz tube to expose the sample at RT instantly. When the temperature of the specimen was cooled down to RT, the sample was taken out and exposed to the air. Spin-capability was checked with ease by simply pulling a small portion from the corner of the CNT forest.

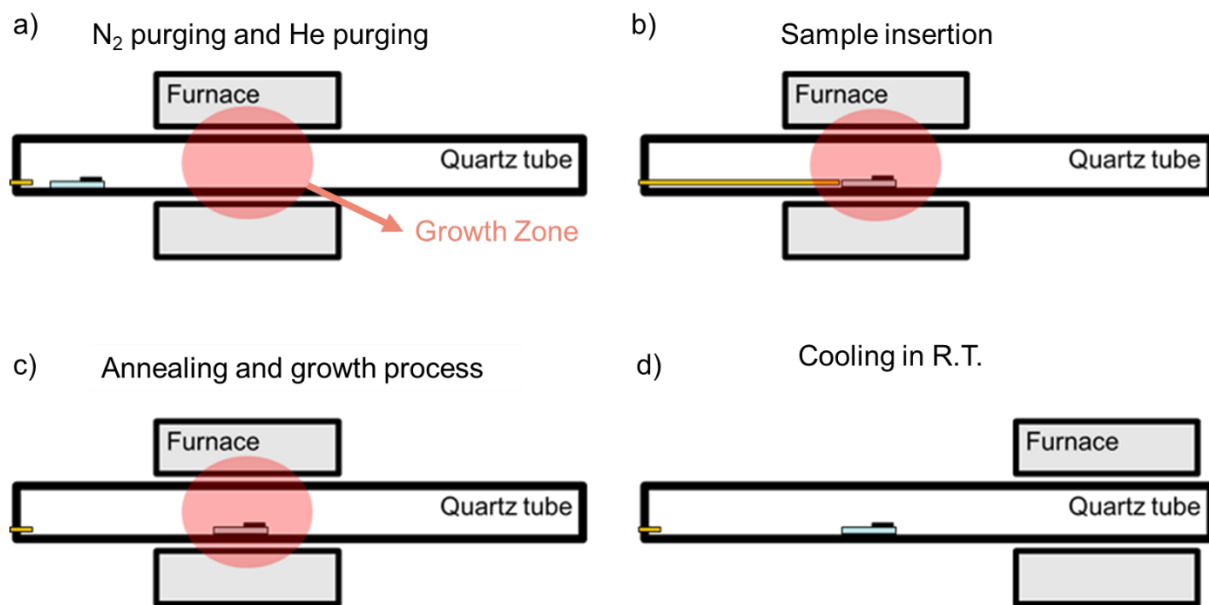


Figure 2.1. Diagram of CVD process with the mobile furnace.

2.2.3 Fe film thickness variation

For the first set of the experiment, the thickness of the Fe film on the specimen was varied. Using e-beam deposition, 1.5, 2.0, 2.5, 3.0, and 3.5 nm of Fe film was deposited at a rate less than $3\text{\AA}/\text{s}$. The thicknesses were monitored by the quartz crystal thickness monitor. For each condition, the samples were examined after the annealing process (Figure 2.2b) and after the growth process (Figure 2.2a). The former was to study the Fe NP morphologies, and the latter was to examine the difference of the CNT structures for each case. The flow rates of the gases are 2000, 70, and 20 sccm for He, H_2 , and C_2H_2 , respectively. The sample insertion was done in 3 seconds, the annealing time was 30 sec, and the growth time was 5 minutes.

2.2.4 Annealing time variation

To test the effect of the annealing duration, Fe film thickness was kept at 2.5 nm while the annealing duration varied. Hydrogen gas was inserted for 20, 40, and 60 s with a flow rate of 70 sccm. Other gases kept the same flow rate (He:2000 sccm and C₂H₂:20 sccm). The insertion time and the growth time remained the same.

2.2.5 Equipment

Catalyst morphologies were examined using atomic force microscopy (AFM), and the actual CNTs' structural studies were done with scanning electron microscopy (SEM). With help of image analyzing tools, such as ImageJ and WSxM, the average diameter and the thickness of the Fe NPs and the CNTs were measured. Additionally, to test the defect ratio and the overall quality of the CNTs grown, Raman spectroscopy (wavelength = 532 nm) was used. By calculating I_D/I_G of the Raman results, defect ratios were calculated, which is a popular method for quality checking of the carbon materials [70], [71].

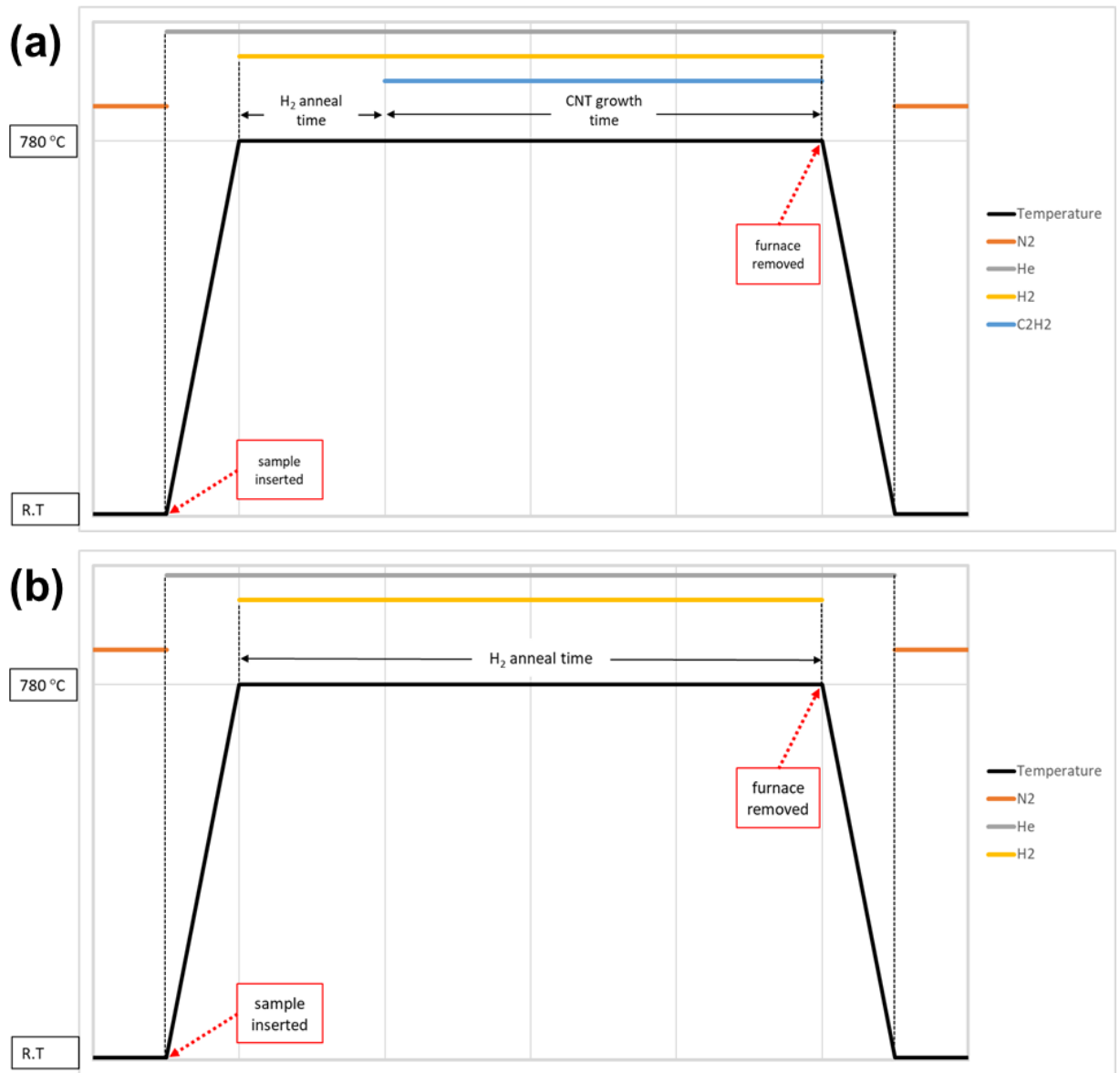


Figure 2.2. CVD process for a) regular CNT growth process and b) annealing process without the growth of CNTs.

2.3 Result and Discussion

2.3.1 Effects of Fe Film Thicknesses

CNTs were synthesized to observe the effect of different Fe thicknesses on the shape of CNTs and the spin-capability. Figure 2.3 a-e) shows the CNT forest grown from 1.5, 2.0, 2.5, 3.0, and 3.5 nm of Fe films, respectively. For the spin-capable CNTs (CNTs from 1.5, 2.0, and 2.5 nm), the shape of the individual CNT is straight and the CNTs are well-aligned. However, for the CNTs from 3.0 and 3.5 nm of Fe film, the CNTs were curly, unaligned, and not spin-capable. Based on Figure 1.14, the CNTFs were ranked 5, 5, 4, 3, and 2 for Fe film of 1.5, 2.0, 2.5, 3.0, and 3.5 nm, respectively. Then, each CNTF was taken under the Raman spectroscopy to calculate the defect ratios, which are reported in Figure 2.3. The measured defect ratios for 1.5, 2.0, 2.5, 3.0, and 3.5 nm of Fe films were 0.82, 0.85, 0.86, 0.9 and 1.04, respectively. This shows that curlier

To investigate further, the morphologies of the annealed Fe films were examined. Figure 2.3 (f-j) are the AFM images of the Fe NPs. The average particle diameters were measured, and areal densities were calculated. The measured diameters are 16.91 ± 1.88 , 19.79 ± 1.18 , 23.28 ± 5.42 , 24.47 ± 4.54 , and 26.78 ± 2.27 nm for the Fe films of 1.5, 2.0, 2.5, 3.0, and 3.5 nm, respectively. The areal densities were 4450.3, 3250.8, 2350.3, 2127.0, and $1175.3 \mu\text{m}^{-2}$. Both average NP diameter and the areal densities are plotted in Figure 2.5, the CNTF grades were also labeled as CNTF:n, where n is the grade from Figure 1.14.

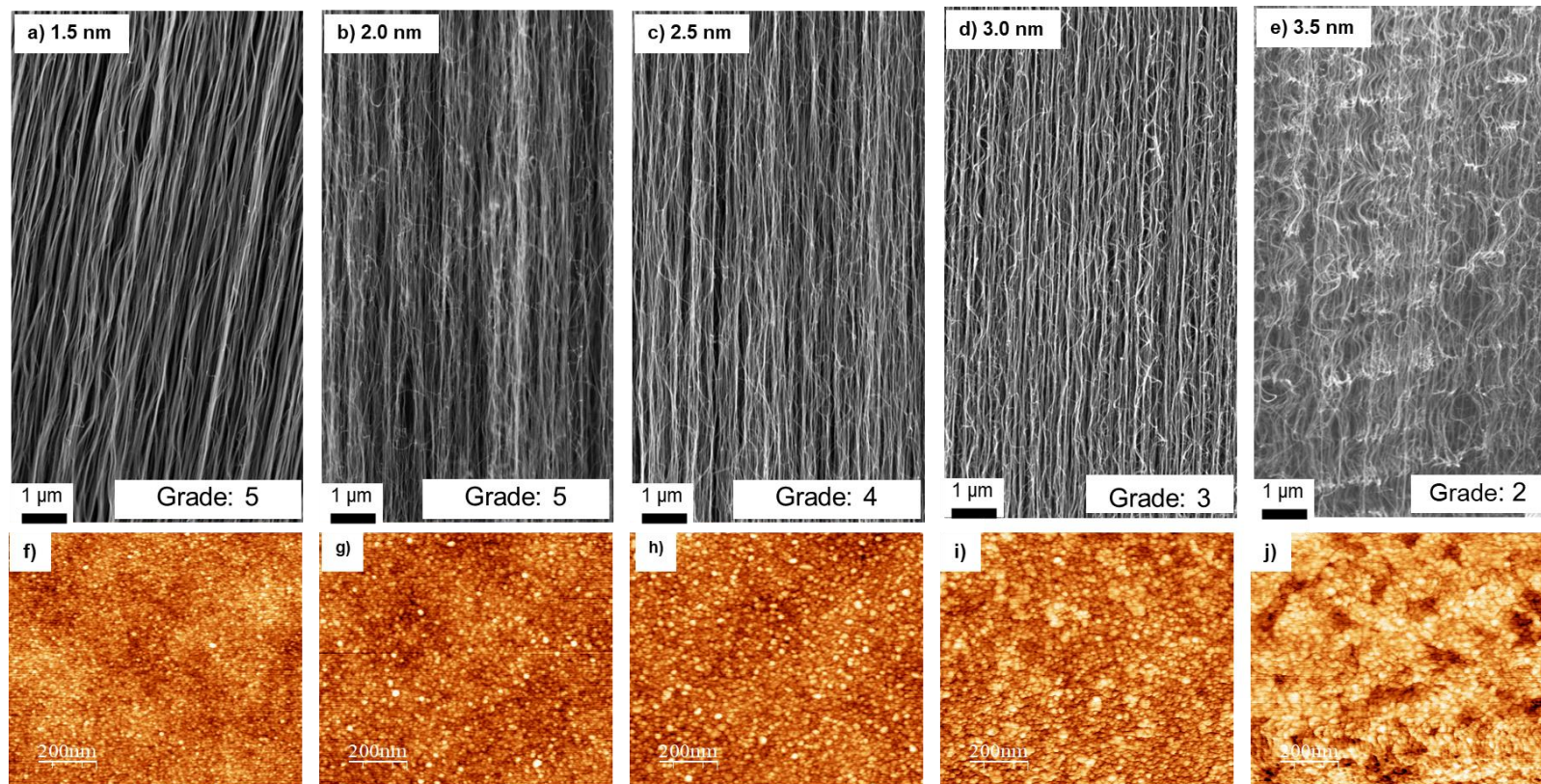


Figure 2.3. The SEM (a-e) and AFM (f-j) images of CNT forests grown from a,f) 1.5, b,g) 2.0, c,h) 2.5, d,i) 3.0, and e,j) 3.5 nm of Fe films. The SEM images show side wall of the CNTF, and the AFM images show top morphologies.

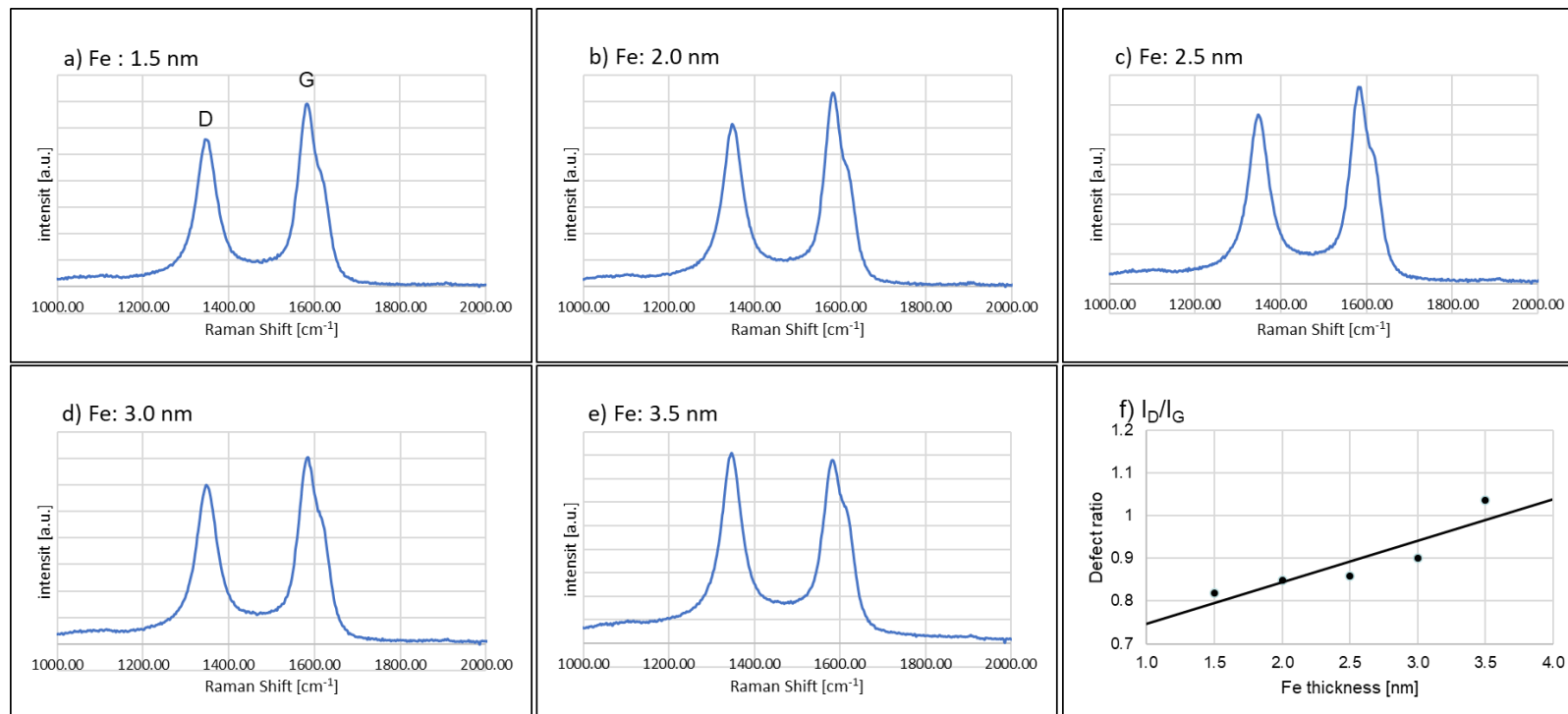


Figure 2.4. Raman spectroscopy results for each Fe film thicknesses (a-e) and f) the plot of I_D/I_G ratio.

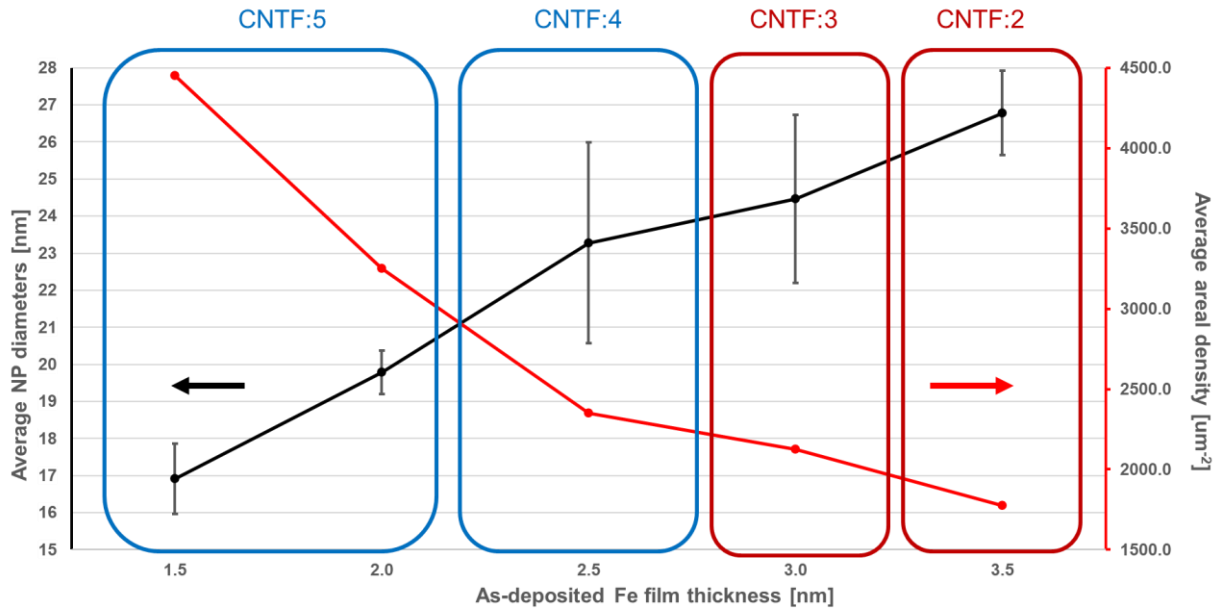


Figure 2.5. Plot of Average NPs diameters (black) and the average areal density (red) calculated from the diameters. The qualities of the CNTFs are also shown in the boxes: blue for spin-capable and red for not spin-capable.

From Figure 2.5. it is evident that as the initial thickness increases, the diameter increases which results in less areal density per given area. The Ostwald ripening phenomenon explains the process of increasing particle sizes. The Ostwald ripening is a well-known phenomenon observed in molecular studies, and it states that smaller particles will decrease its size until they disappear and larger particles will consume the smaller particles to grow its size [16], [56], [57], [72], [73]. The particle coarsening is a complicated process that involves many factors such as diffusion, pressure, molecular weight, interfacial tension, and temperature [74], [75]. By changing the Fe thickness, the molecular weight is controlled.

During the annealing process, H_2 reacts with Fe-oxides on the surface, reduces the Fe oxide to Fe NPs, and the Fe starts growing in size due to the Ostwald ripening phenomenon [56]

at such high temperature. From the result, we can conclude that thicker of Fe film produced larger NPs given the same amount of annealing period. While the NPs are forming, thicker Fe film provided a larger volume of NPs which allowed the NPs to overlap much more rapidly and resulted in larger particles than those of thinner Fe films.

Starting from less areal density, the CNTs grown from those will be less dense as well, which are shown in Figure 2.3 a-f). Less dense implies that there is a larger distance between individual CNTs. This provides more room for the CNTs to tilt while its root is pushing up the whole structure. As seen from the Raman results, curlier CNTs have a much higher defect ratio than those that are straight. While the SCNTs have defect ratios of 0.81, 0.85, and 0.86, the non-SCNTs have 0.9 and 1.04. The Raman data shows that there is an increasing number of defects compared to the graphitic links. However, it is difficult to draw a clear line to say that the spin-capability can be determined only by using the defect ratios due to the sampling method of Raman can have a considerable range for human-errors to sneak in. The summarized results are recorded in Table 2.1.

Table 2.1. Experimental results for Fe thickness variation. The average diameter[§] and areal density^{*} of the annealed NPs, the defect ratio, and the CNTF grades are recorded.

Fe thickness [nm]	NP		CNT	CNTF Grade
	[§] ϕ [nm]	[*] ρ [μm^{-2}]	I_D/I_G	n
1.5	16.91 $\pm$ 1.88	4450.3	0.82	5
2.0	19.79 $\pm$ 1.18	3250.8	0.85	5
2.5	23.28 $\pm$ 5.42	2350.3	0.86	4
3.0	24.47 $\pm$ 4.54	2127	0.9	3
3.5	26.78 $\pm$ 2.27	1175.3	1.04	2

Additional to the catalyst diameter measurement, the average CNT diameters were also measured using transmission electron microscopy (TEM) in Figure 2.6. The average diameters of the CNTs are increasing as the initial Fe film increases. The average diameters were measured using ImageJ. The measured diameters are 11.60 $\pm$ 1.39, 13.40 $\pm$ 1.53, 14.51 $\pm$ 2.00, 15.27 $\pm$ 1.36, and 16.10 $\pm$ 1.77 nm for 1.5, 2.0, 2.5, 3.0, and 2.5 nm of Fe film, respectively. The increasing behavior can be explained due to the growth process of the CNTS. Larger NPs can adsorb and absorb more carbon atoms at the nucleation sites. This leads to larger and more CNT walls before the growth happens. Whether this is tip growth or bottom growth, in either case, a larger NP diameter will allow larger CNT diameters.

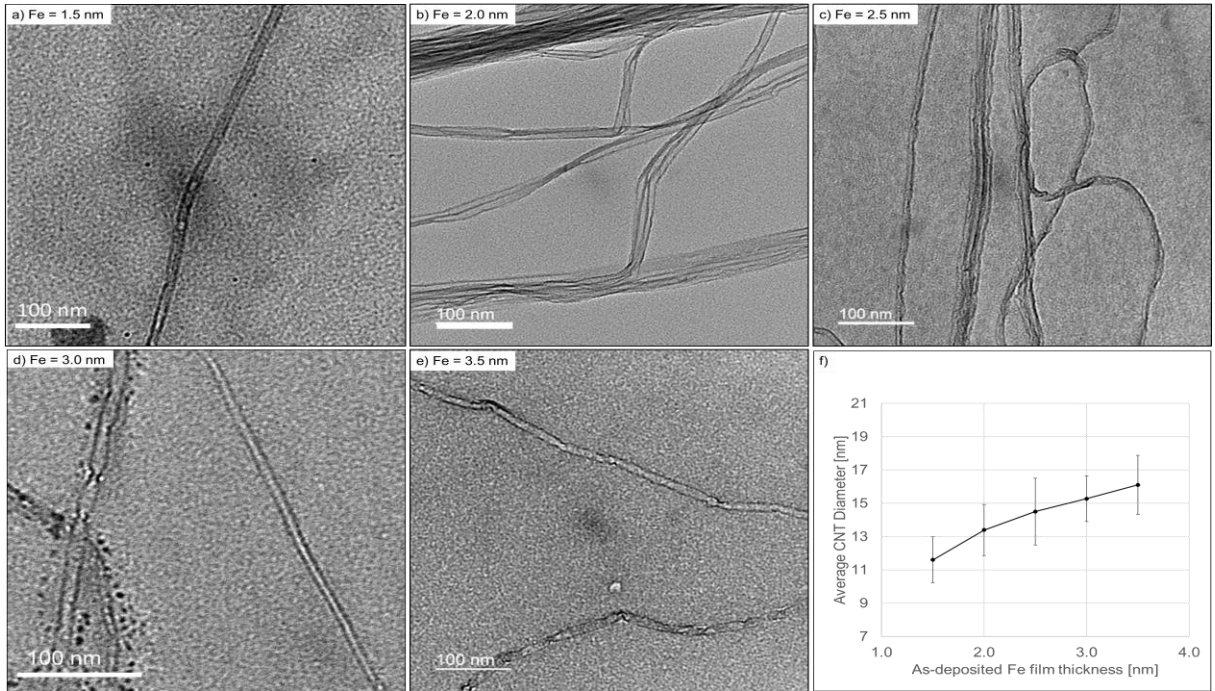


Figure 2.6. TEM images of the CNTs that are grown from Fe film thicknesses of a) 1.5, b) 2.0, c) 2.5, d) 3.0, e) 3.5 nm, and f) plot of average diameter with respect to the film thickness.

2.3.2 Effects of Different H₂ Annealing Duration

Similar studies have been performed for the second set of the experiment. This time, the thickness of the Fe layer was set as 2.5 nm and kept as constant. This thickness was chosen for it has resulted spinnability of 3 which could be controlled to produce better quality of CNTF by controlling the annealing time. The annealing duration, where the Fe film is exposed to the H₂ gas, was varied to see the effect. After annealing 20, 40, and 60 seconds, CNTs were grown and put under SEM to study its structure. As shown in Figure 2.6, shapes of the CNTs changed as the exposure duration changed. CNTs under H₂ exposure for 20 and 40 s were SCNTs. However, CNTs that experienced 60 s of H₂ exposure time were non-SCNT. The CNTFs that produced CNTSs are those from 20 and 40 s. This result shows that CNTFs from different conditions not

only change the structural format, but also the total density of the CNTs. To study in detail SEM images were analyzed with ImageJ.

Raman spectroscopy was performed again to see if there are any relationships between the H₂ exposure duration and the defect ratio of the CNTs. As shown in Figure 2.7 are the Raman spectroscopy results of the CNTs that were grown in different conditions. As shown, the defect ratio increases as the H₂ annealing time increases. The CNTs that were grown after 20, 40, and 60 s H₂ exposure time, their defect ratios were 0.66, 0.67, and 0.76, respectively. The trend is clear when the catalysts are exposed to H₂ longer, there exist more defects on the surface of the grown CNTs. This relationship is not as direct as the plot in Figure 2.7d shows. For a more direct explanation, the catalyst layer after annealing was examined.

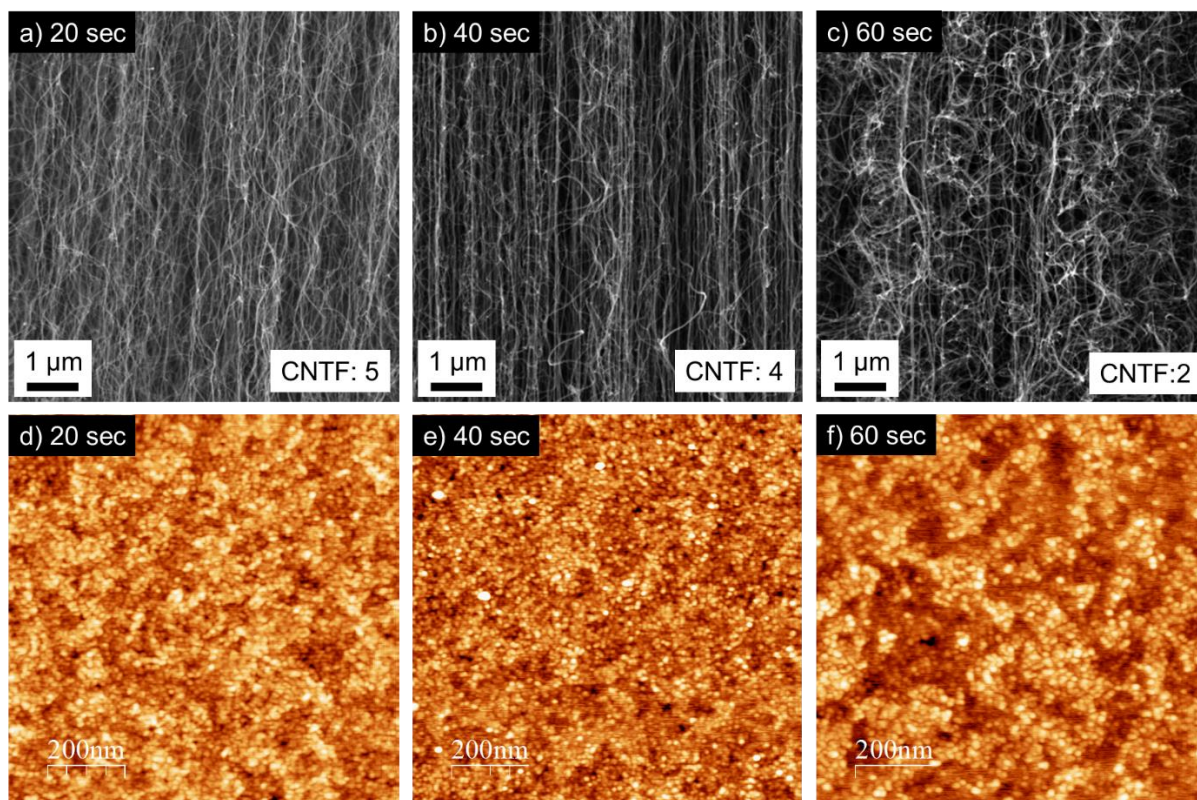


Figure 2.7. The SEM (a-c) and AFM (d-f) images of the CNT forest and the catalysts annealed for a,d) 20, b,e) 40, and c,f) 60 s.

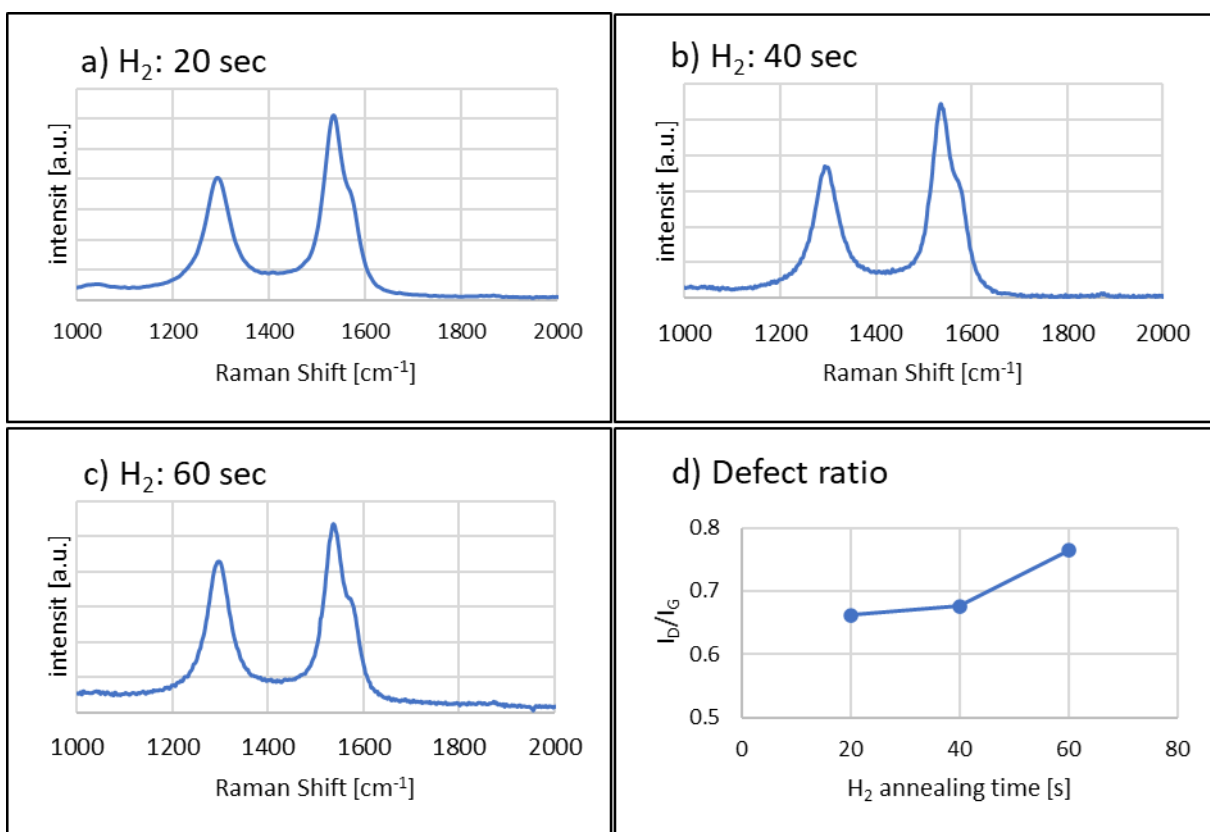


Figure 2.8. Raman spectra of CNTs that were annealed for a) 20 sec, b) 40 sec, c) 60 sec and d) plot of the defect ratio.

As mentioned earlier, the state of the catalyst morphology governs the structure of the CNTs and consequently, the spin-capability. The Fe NPs right after the annealing process were examined using the AFM, shown in Figure 2.6 d-f). The measured average diameters are 16.45 ± 2.2 , 16.88 ± 3.99 , 34.41 ± 5.79 nm for 20, 40, and 60 s exposure time, respectively. Calculated areal densities are 4702.44, 4469.19, and $1075.55 \mu\text{m}^{-2}$, respectively. The plot of the NP diameter and area for different annealing times is illustrated in Figure 2.8. The NPs have increased as they were longer exposed to the H_2 which can be explained via Ostwald ripening again. As mentioned in the previous section, the Ostwald ripening phenomenon states that the

neighboring nanoparticles or liquid droplets will merge and be absorbed by larger particles for less surface energy [56], [72], [74], [75]. The time of coarsening process is also participating in the particle growing. In other words, when the NPs are both at high temperature and dense enough, the particles will coarsen to form larger and larger particles as time allows, producing the CNT forests with less density that results in less spin-capability. In summary, the catalysts will change and coarsen when exposed to H_2 at high temperatures. That will lead to larger diameters of the NPs and fewer densities per given area. Consequently, the CNTs that are rooted on each NPs will have less density when they grow and have larger gaps between each other. Since the van der Waals force requires a much more compact environment, the spin-capability of the CNTF decreases quickly. Summarized results are recorded in Table 2.2.

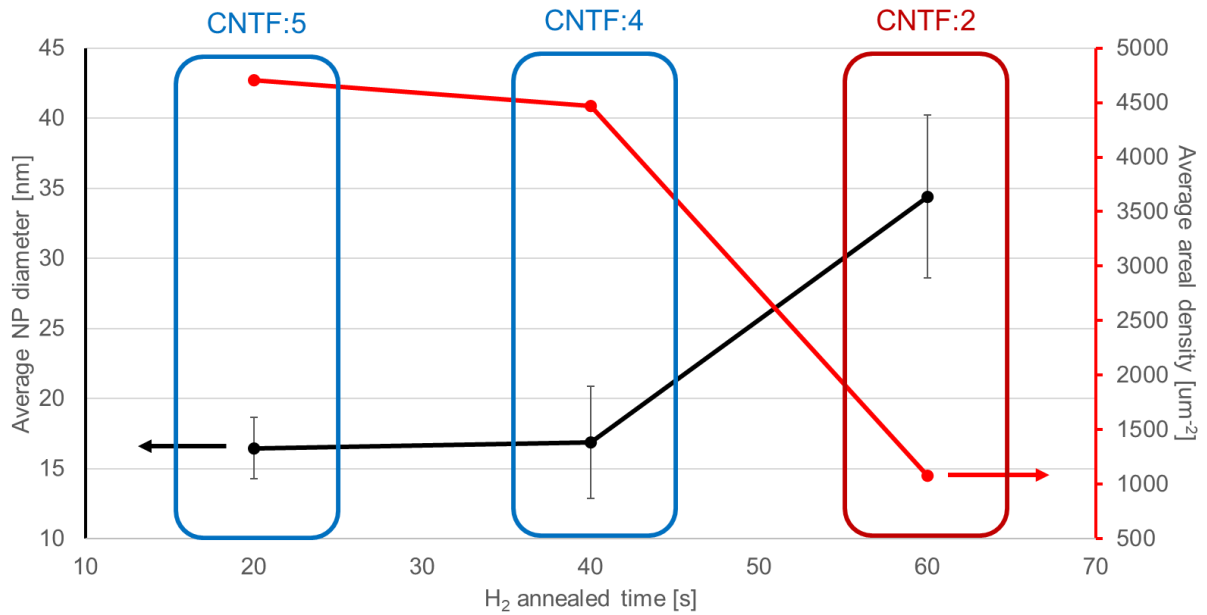


Figure 2.9. Plot of average NP diameter (black) and the average areal density (red) in respect to the H_2 annealing time.

Table 2.2. Experimental results for H₂ variation. The reported average diameter[§] and areal density^{*} of the annealed NPs and the defect ratio of synthesized CNTs

H ₂ annealing time [s]	NP		CNT	
	[§] ϕ [nm]	[*] ρ [μm^{-2}]	I _D /I _G	n
20	16.45±2.2	4702.44	0.66	5
40	16.88±3.99	4469.19	0.67	4
60	34.41±5.79	1075.55	0.76	2

The CNTs from different H₂ annealing durations were put under the TEM to measure average diameters of the CNTs. Figure 2.10 shows the TEM images and the average diameters measured by ImageJ. For 20, 40, and 60 s of H₂ annealing time, the CNT diameters were 15.96±0.70, 17.83±2.10, and 19.69±1.65 nm, respectively. It must be noted that there was not a large change in the catalyst diameter for 20 and 40 s, but the CNT diameters increased about 2 nm. The average diameter has not increased as much, but the standard deviation has doubled. This shows that the smaller particles became smaller, and the larger particles grew larger at a similar rate. In contrast, for the Fe NPs from the 60 s, general particle sizes have increased quickly, which implies that the smaller particles have disappeared, and the only larger particles grew.

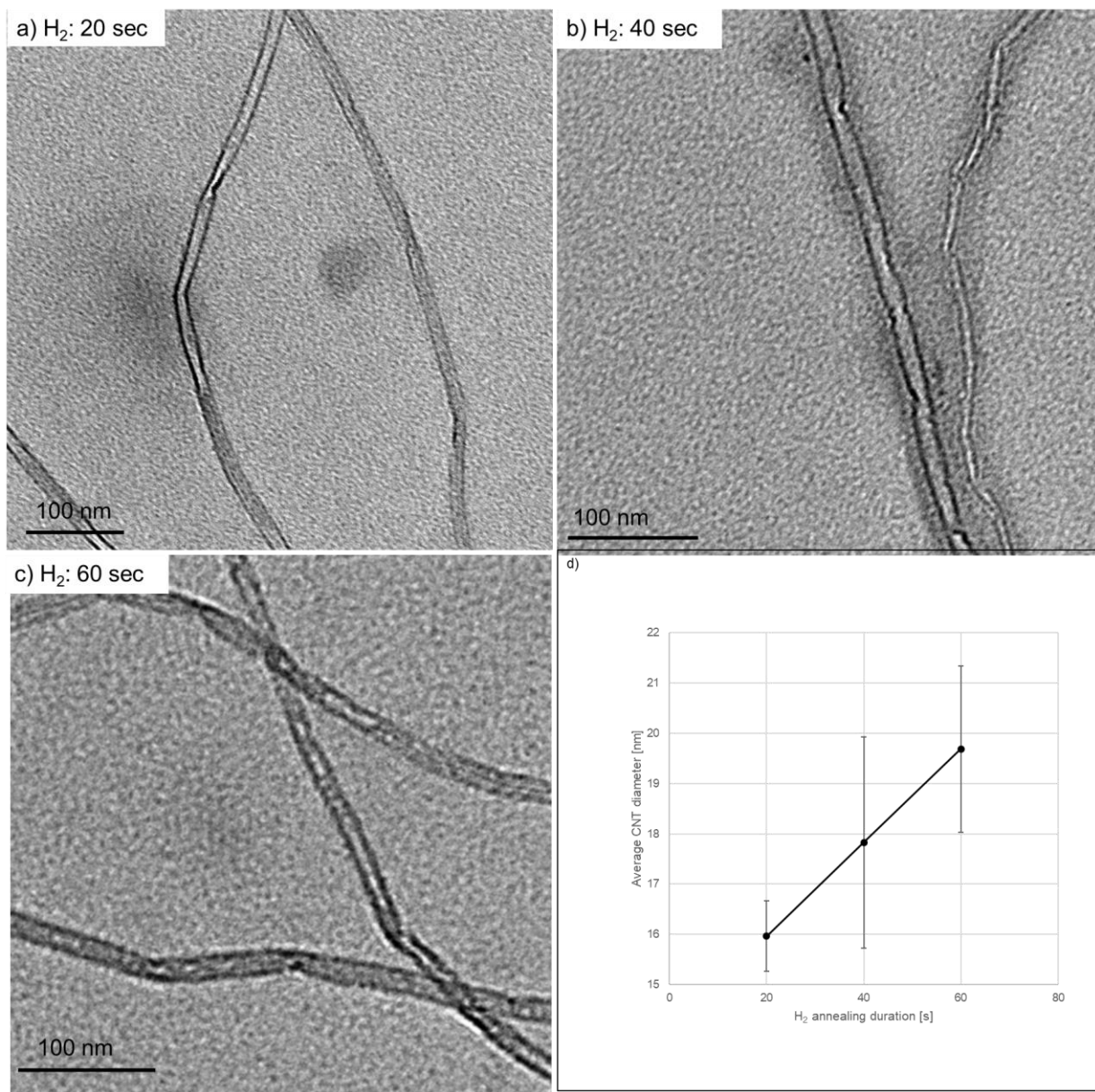


Figure 2.10. TEM images of the CNTs from annealing duration of a) 20, b) 40, c) 60 seconds, and d) the plot with respect to the average CNT diameters.

2.4 Conclusion

Spin-capable CNT shows great potentials as a material to be utilized in a broad range of fields due to its unique chemical, mechanical and electrical properties. However, for repetitive

and consistent results, it is important to understand different aspects of the CNT synthesis processes such as the structure of the CNTs and states of catalysts. In terms of the film thicknesses, the thicker Fe films resulted in the larger NP diameters since they have higher chances of overlapping and growing faster. For Fe thickness of 1.5, 2.0, and 2.5 nm, the spin-capable CNT forests were synthesized from the catalysts with diameters of 16.91 ± 1.88 , 19.79 ± 1.18 , 23.28 ± 5.42 nm, respectively. The H₂ annealing duration also affected the spin-capability of the CNTs. For the annealing times of 20, 40, and 60 s, the NP diameters were 16.45 ± 2.2 , 16.88 ± 3.99 , 34.41 ± 5.79 nm, respectively, and this process is well-understood via Ostwald ripening phenomenon. For longer the Fe NP was exposed to the annealing condition at high temperature, the smaller catalysts were consumed by the larger catalysts to reduce the total surface energy. We concluded that the spin-capability of CNT forests can be produced by carefully controlling the as-deposited Fe film thickness and the H₂ annealing duration.

CHAPTER 3

SPINNABLE CARBON NANOTUBE FOREST SYNTHESIS IN A NITROGEN ENVIRONMENT ²

3.1 Introduction

Spinnable carbon nanotubes (SCNTs) have been studied and synthesized by many researchers for its unique structure and characteristics [52], [55], [56], [60], [76]–[79]. From a group of vertically grown and highly aligned CNT forests (CNTFs), CNT sheets or yarns are produced by simply pulling one side of the forest with adhesive tape or with a fine tweezer. This is allowed by the van der Waals force. The CNTs attract neighboring CNTs and form random networks of CNTs which results in a sheet/yarn form [57], [80], [81]. These SCNTs promise a wide range of applications, such as energy storage [82]–[85], sensors [26], [86]–[90], and supercapacitors [91], because of their unique structures and properties. There exist many CNT synthesis methods including laser ablation, arc discharge, and chemical vapor deposition (CVD), but the CVD method is advantageous to study the specific conditions of CNT production due to their wide range of flexibility which enables different testing conditions, such as precursor, pressure, temperature, and location of samples [92], [93]. Many studies have reported that consistent SCNTs were synthesized with the conventional CVD method [94]–[98].

However, like other sensitive systems, the CVD method requires an inert environment, and the majority of scholastic studies have used popular noble gases, helium (He) or argon (Ar)

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[4–6,8,12,13,19,27,28,30–33], to achieve the inert environment. Despite the chemical advantages of the noble gases, neither gases are considered as cost-effective. Helium price is increasing rapidly due to its shortage from natural sources [103], and argon requires the fractional distillation of liquid air to be extracted [104]. Finding a replacement for noble gas is the inevitable step for allowing mass-production of SCNTs and their commercialization. One of the cheapest and most abundant gases that can be extracted from the atmosphere is nitrogen (N_2); about 78 % of the air is N_2 . Also, the triple bond structure of N_2 results in great chemical stability which provides the pseudo-inert environment required for SCNT synthesis [105]. Therefore, N_2 has a high potential to serve as the replacement of noble gases for the SCNT synthesis process.

In this Chapter, a successful SCNT synthesis process using the conventional CVD method with N_2 as a carrier gas is reported. There are studies that successfully grew CNTs in N_2 environments via CVD chamber or fluidized-bed reactor, but few reported the spin-capability of the CNTF [106]–[111]. Zhang et al. [37] showed that N_2 can be used to grow vertically aligned CNTFs with ethylenediamine as a carbon source, but they have not reported information regarding spin-capability. Our lab has reported a spin-capable CNT forest (SCNTF) made with N_2 in 2014 [73], Jung et al. reported that SCNTs from He had much better quality than those from N_2 . However, the previous study used a homemade vertical CVD system which is not suitable for the mass-production of CNT that this report emphasizes, and their Fe catalyst layer did not have an Al_2O_3 layer as a buffer layer which has been used for a higher quality of CNTF synthesis [62], [64]. For this paper, we used the conventional horizontal CVD chamber and catalyst layer on the Al_2O_3 buffer layer. We explored the influence of the carrier gases on the spinnabilities of CNTs and showed that N_2 can also be used as a carrier gas for the SCNT

synthesis process. To prove that the qualities of the SCNTs are compatible, SEM was used to measure the average thicknesses of the CNT bundles and to calculate the average areal densities. TEM was used to measure the accurate diameters of CNTs and to determine the number of the wall numbers. Additionally, since the spinnability of CNTs heavily depends on the catalyst morphology, we studied the Fe catalysts at the root of the CNTs to prove further that the SCNTs can be synthesized in N₂ as well. The catalyst morphologies and the particle densities were measured by atomic force microscopy (AFM).

3.2 Experimental

3.2.1 Substrate preparation

On a p-type (100) silicon wafer, a 100 nm layer of SiO₂ was grown by dry oxidation at 1050 °C. On the top of the SiO₂ layer, a 3.0 nm layer of Al₂O₃ was deposited as a buffer layer by atomic layer deposition (ALD) with a deposition temperature of 250 °C. Then using the electron-beam evaporation method, a 2.5 nm layer of iron (Fe) was deposited at a deposition rate of 0.1 – 0.3 Å/s for the catalytic layer. The thickness of the catalytic layer was measured by the quartz-crystal sensor mounted on the e-beam evaporator.

3.2.2 Catalyst annealing process and SCNT synthesis in N₂ environment

The catalyst annealing process was performed in a horizontal CVD chamber. The CVD chamber consisted of a cylindrical quartz tube with a furnace to heat up the center of the quartz tube, and a magnetic arm was installed to push the sample in and pulling it out from the hot zone while the sample was in an inert environment. To observe the effect of different types of carrier

gases, 2000 sccm of N_2 gas (99.999%) was used to purge for 20 minutes to set an inert environment. The gas flow rates were measured by the mass flow controllers (MFCs). After purging for 15 min, the furnace temperature was raised to 780 °C from 22 °C at a rate of 10 °C/min, and the sample was pushed to the middle of the hot zone as the annealing gas (H_2) was simultaneously introduced. To study the influence of the annealing time on the catalyst morphology, the duration of the annealing process was varied for 20, 40, and 60 s. After the annealing process, the H_2 was turned off, and the sample was pulled back to room temperature (22 °C) in the inert environment. After the annealing process with the variation of the annealing duration, the surface morphologies of substrates were studied via AFM. Then, the catalyst particle diameters and densities were measured using ImageJ and WSxM.

The CNT synthesis process requires one extra step to the annealing process described above. After inserting H_2 for the annealing duration, 20 sccm of C_2H_2 was introduced as the carbon source for 3 min. Then both H_2 and C_2H_2 were turned off and the sample was exposed to room temperature by relocating the sample in the N_2 environment. Figure 3.1 shows the diagrams of the furnace and the sample movement, and the synthesis process with temperature and gases used. Once the CNTF was grown, we determined whether the forest is spinnable or not by simply pulling the sidewall of CNTF with adhesive tape or forceps.

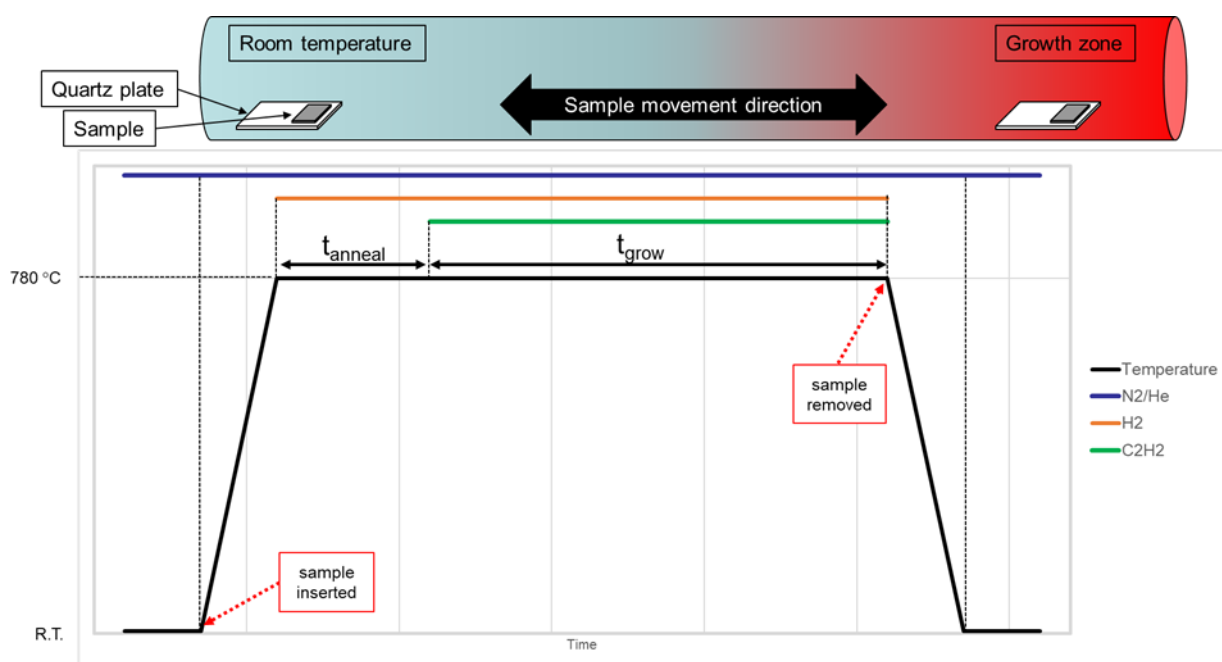


Figure 3.1. Diagram of CVD chamber and CNT synthesis process for the new furnace.

3.2.3 Comparison of the SCNTs synthesized in N_2 and He

To compare the quality of the CNTs from both environments, all the other factors of the synthesis process were kept the same other than the carrier gas type. The same amount of He (99.999%) was inserted (2000 sccm) as a carrier gas to keep the gas ratio of percent volume constant, and the rest of the synthesis conditions remained as well as reported above in section 3.2.2. First, we measured the average CNT bundle diameters and areal density by measuring the greyscale of SEM images using an image analysis software, ImageJ. This method is suitable for micro-scale measurement, but not for nanoscale. Therefore, we have added TEM images for the nanostructures of the CNTs synthesized. Second, using Raman spectroscopy (wavelength = 532 nm), the defect densities were measured for both sets of samples by measuring the intensity of D-

peak and G-peak of the Raman spectrum. Finally, electrical current flow for a range of voltage (0 – 1 V) was measured using Keithley 2400 Source meter to test whether the SCNT from the N₂ environment is compatible in other popular applications such as sensors, electrodes, and capacitors where the electrical resistance can play an important role. We applied 1, 2, and 3 layers of CNT sheets on glass substrates and used conductive tape for the electrodes. The width of the CNT sheet and the distance between the two electrodes were 1 cm.

3.3 Result and Discussion

3.3.1 Effect of H₂ annealing duration on the CNT areal density

To study the effect of annealing gas, H₂, under the N₂ environment, we first measured the areal density of the CNTs in the forest. According to many studies, there is a close relationship between the CNTs' areal density and the spinnability of the CNT forest [73], [112]. Since van der Waals's force between the tubes is the key mechanism of the spinnability, the gaps between CNTs need to be narrow, resulting in a compact structure of the forest. Under the assumption that the sample is uniform, the profile of the cross-section of the CNT forest from SEM images was used to calculate the density of the CNT bundles. In order to achieve the optimal condition for the SCNT, the H₂ annealing duration was varied to study its influence. The annealing time, t_{anneal} , had been varied for 20, 40, 60, 80, 100, and 120 s, then C₂H₂ was inserted to grow CNTs. As H₂ exposure time increases, we observe that CNTs per unit area decreased. The shapes of the CNTs became curlier and less aligned as the annealing duration increased. Shown in Figure 3.2 are the SEM images of CNT forests that are from different t_{anneal} in H₂. From Figure 3.2., it is evident that the sample from shorter t_{anneal} produces forests with better alignment. It is important

to note that the spinnable samples were from t_{anneal} of 20, 40, and 60 s (Figure 3.2 a-c, g-i). The CNTF grades are also labeled as in Chapter 2, following the same criteria shown in Figure 1.14. Similarly, it will be noted in form of CNTF:n, where n is the grade of the synthesized forests after a trial of creating CNTS from the forest. The grades of the CNTFs synthesized from N_2 resulted in 5, 5, 4, 3, 2, and 2, and those from He resulted 5, 5, 4, 3, 3, and 2 for H_2 annealing time of 20, 40, 60, 80, 100, and 120 s.

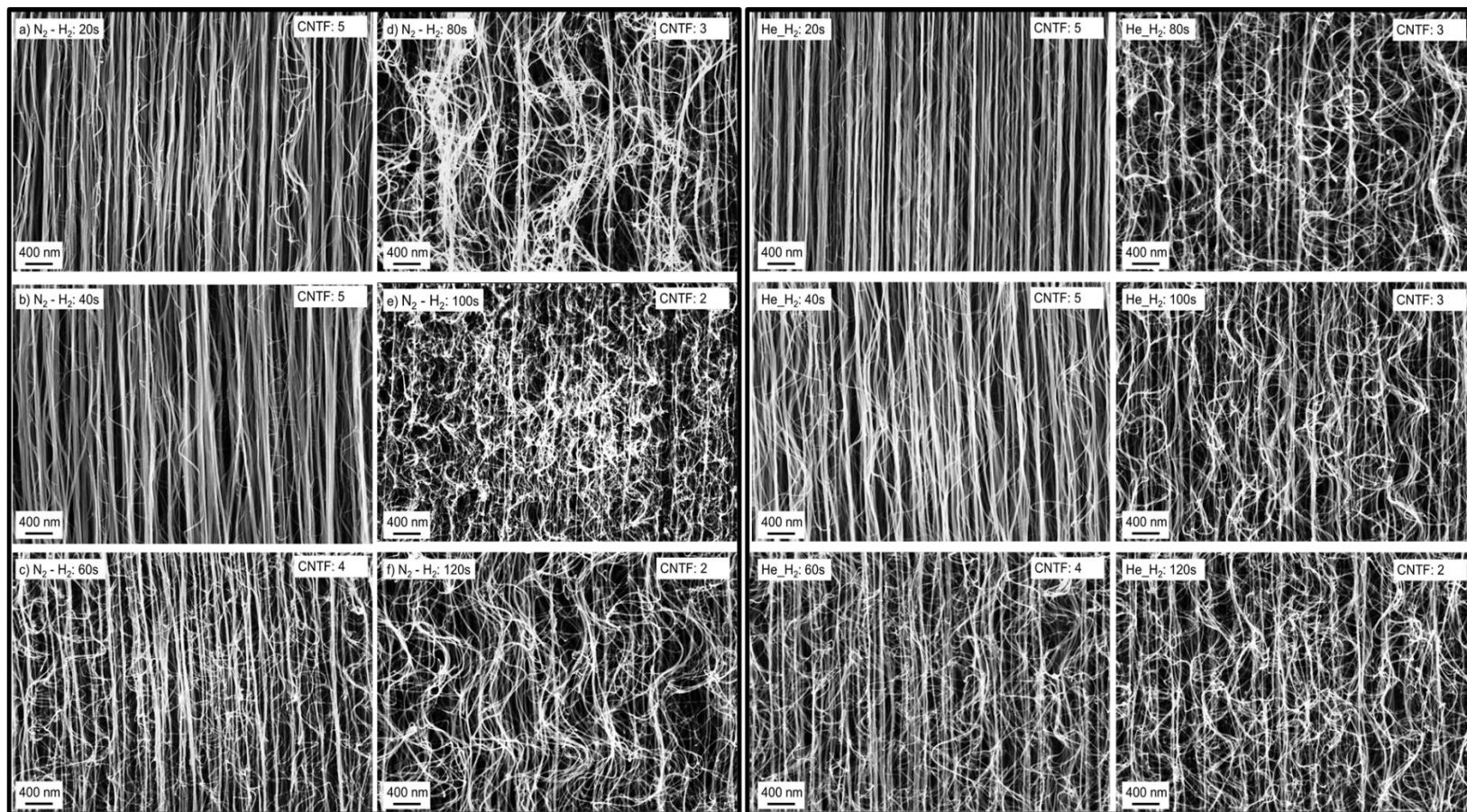


Figure 3.2. SEM images of CNT forests that were synthesized in N₂ (a-f) and He (g-l) environment with different H₂ annealing time; a,g) 20 s, b,h) 40 s, c,i) 60 s, d,j) 80 s, e,k) 100 s, f,l) 120 s.

Five different measurements were taken from each SEM image to find the average volume density of the CNTs. Since the images only show one side of the forests, the ratios were squared to find the vol% under the assumption that the CNTs are uniformly distributed through the sample. The volume densities of the CNTs (vol%) from samples that were annealed for 20, 40, 60, 80, 100, and 120 seconds in N₂ and H₂ environment were 77.83 ± 3.63 , 75.19 ± 2.90 , 72.50 ± 2.94 , 64.16 ± 5.57 , 60.09 ± 7.52 , and 56.67 ± 6.00 %, respectively. Also, the volume densities of the CNTs from He environments were 78.51 ± 2.36 , 84.58 ± 0.99 , 77.13 ± 2.56 , 72.15 ± 3.24 , 65.07 ± 3.54 , 63.93 ± 2.81 % for the annealing time of 20, 40, 60, 80, 100, and 120 s, respectively. Figure 3.3 shows the plot of the volume ratio results above.

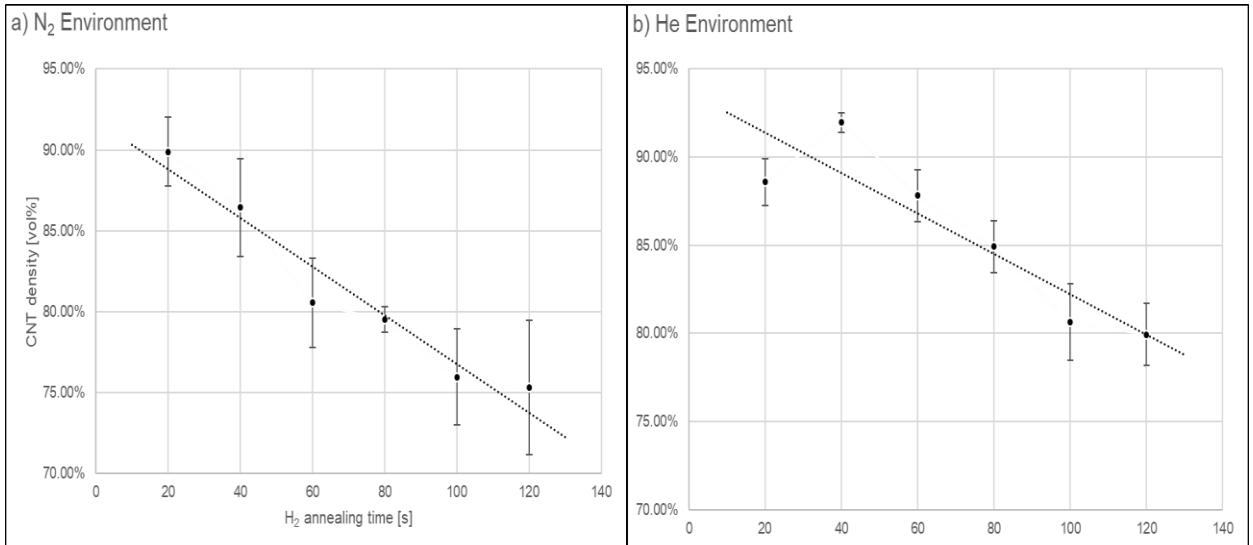


Figure 3.3. CNT volume density per given area using SEM image analysis.

As shown in Figure 3.3, as the H₂ annealing time increases, the CNT volume density decreases in both cases; indicating that the number of CNTs is decreasing and the gap between each CNTs is

larger. This leads to a weaker attraction force between each CNTs. However, it is not clear why the CNTs become less dense as the annealing time increases. The more direct relationship lies in the catalyst structure change due to the longer exposure to H₂ gas.

Another characteristic that needs to be studied is the heights of the forests. The heights of each forest have been measured to see if the annealing time influences the result differently in two environments (N₂ and He). For the CNTFs grown in N₂ for annealing time of 20, 40, 60, 80, 100, and 120 s, the heights were 205.48, 171.61, 162.58, 146.13, 98.71, 77.10 μm , respectively. Those from the He environment were 203.87, 150.65, 126.13, 127.10, 105.48, 100.32 μm . As shown in Figure 3.4, the CNT heights decrease as the H₂ annealing duration increased in both N₂ (a-f) and He (g-l), and Figure 3.5 shows the plot of measured heights for each case. This can be explained by the curliness of the CNTs.

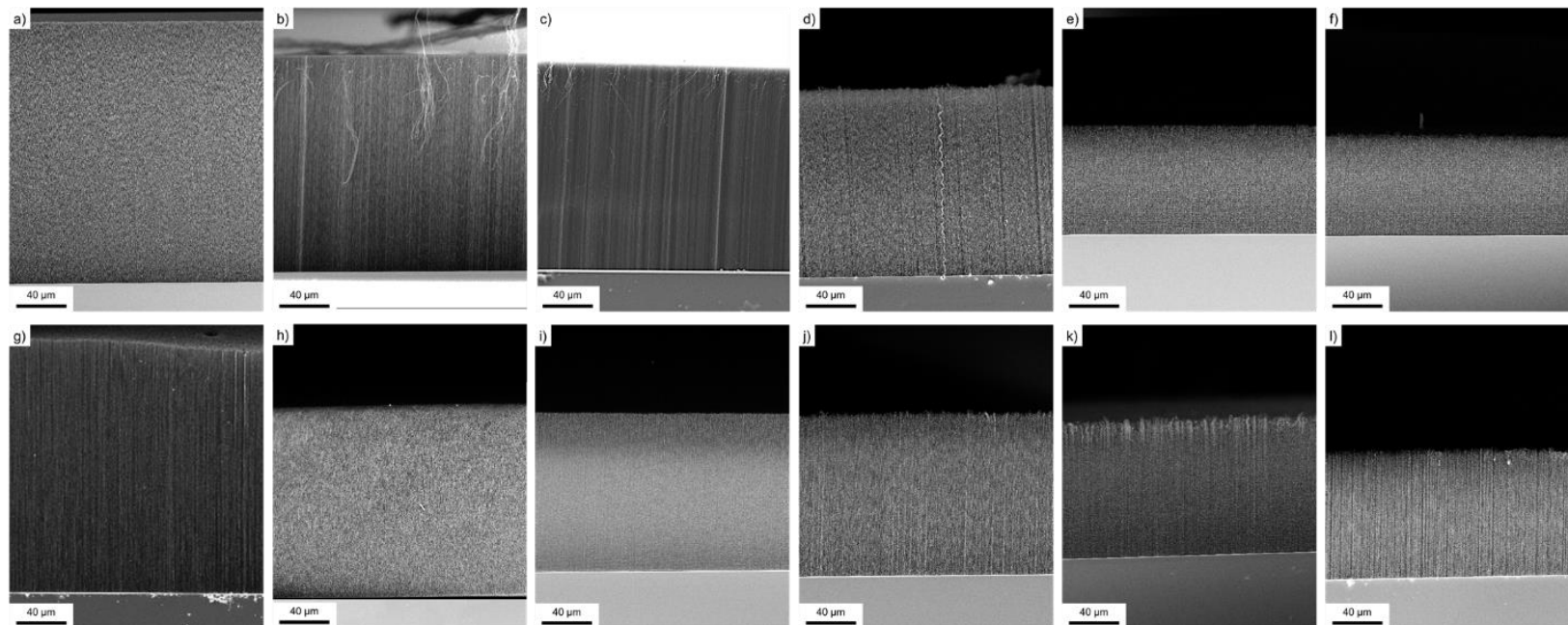


Figure 3.4. The SEM images of the side views of CNTFs for height measurements. a-f) shows the CNTs that are grown in N_2 with annealing time of 20, 40, 60, 80, 100, and 120 s, respectively. g-l) shows those in He with annealing time of 20, 40, 60, 80, 100, and 120 s, respectively.

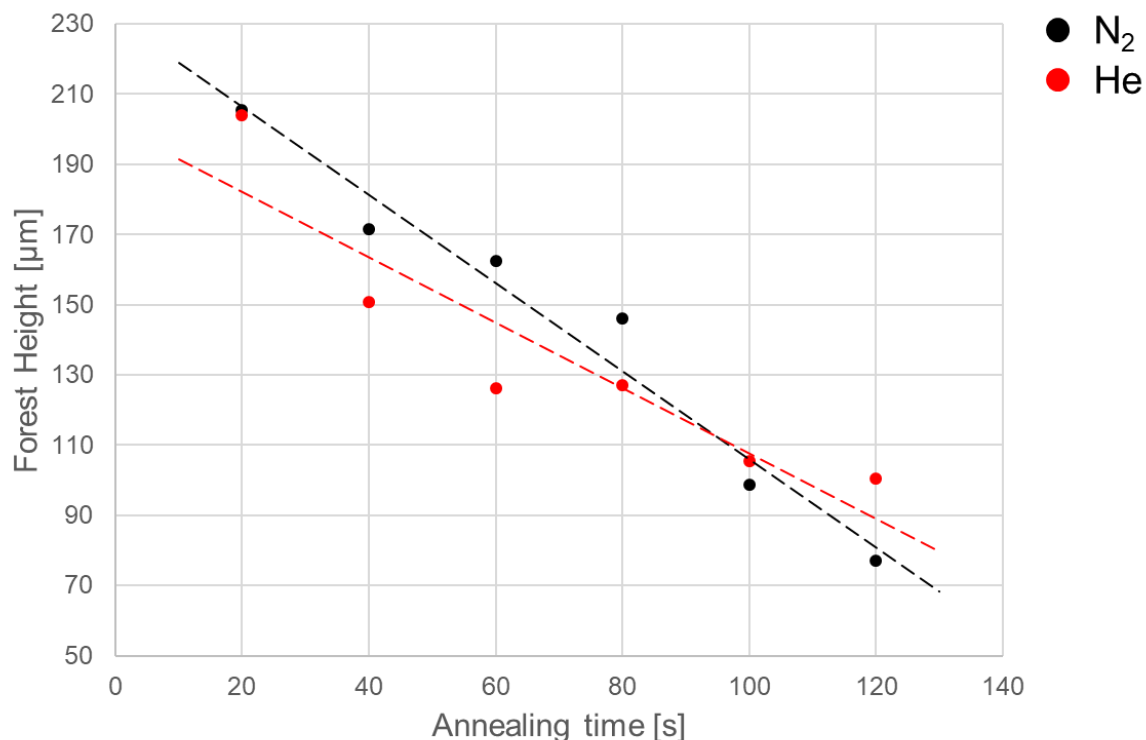


Figure 3.5. Plot of the CNTF heights for different annealing times.

From Figure 3.5, the height of the CNTFs does not show a notable difference between the two growing environments. However, in both cases, there is a clear relationship between the annealing duration and the height of the CNTFs. As the annealing time increases, the height of the CNTFs decreases. However, it would be too quick to judge that the total amount of the CNTs decreased along with the height since the CNT structures become curlier as the annealing time increases which has been shown in Figure 3.4. To understand why the CNTFs become shorter as the annealing time increases, we need to understand the morphologies of the catalysts that become the seed of the CNTs.

3.3.2 Effect of H₂ annealing duration on the catalyst areal density

As mentioned above, the catalyst layer we deposited is Fe. This not only allows H₂ gas to remove the Fe_xO_y layer on the surface of the film by reduction process but also changes the Fe film to Fe nanoparticles (NPs) via Ostwald ripening [113], [114]. To study a more direct relationship between the H₂ annealing time and the morphology of Fe catalyst, the catalyst layer had been exposed to N₂ and H₂ (2000 and 70 sccm) for 20, 40, 60, 80, 100, and 120 s. Then the catalyst morphology was studied via AFM for analysis and reported in Figure 3.6. As mentioned above, Fe NPs from H₂ annealing time of 20, 40, and 60 s resulted in SCNTFs and non-SCNT at 80, 100, and 120 s.

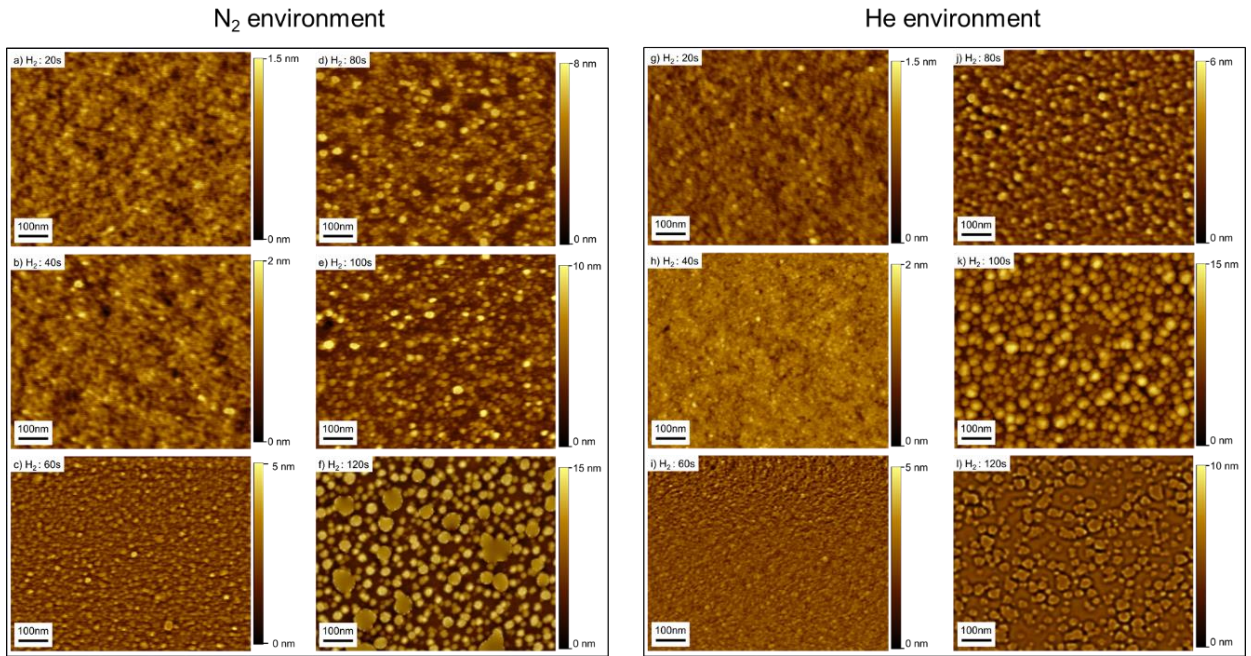
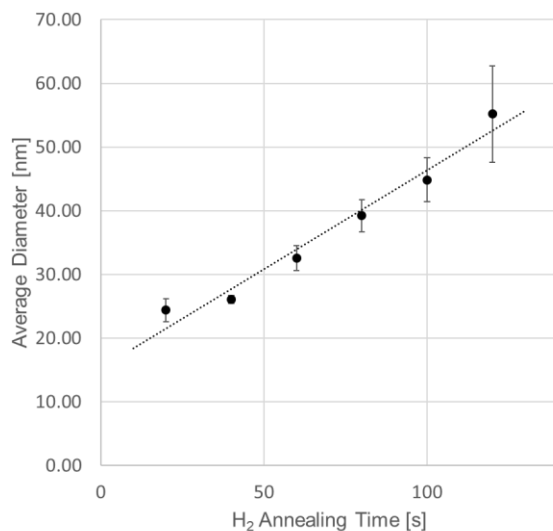


Figure 3.6. AFM images of the morphologies of annealed Fe NPs in both N₂ (a-f) and He (g-l) environments.

We measured the average particle diameter and the areal density with an image analysis software, ImageJ, to analyze further the morphologies of the NPs. For the N₂ environment, the average diameters of the Fe NPs from exposure of H₂ for 20, 40, 60, 80, 100, and 120 seconds are 24.38±1.82, 26.05±0.59, 32.56±1.98, 39.22±2.52, 44.85±3.45, and 55.20±7.56 nm, respectively. For He environment, they are 21.57±0.79, 22.89±2.21, 23.37±2.53, 33.39±1.58, 46.98±9.97, and 72.62±10.44 nm for the same range of the H₂. Figure 3.7 is the plot of average Fe NPs diameters for different H₂ annealing times. As expected, the particle size increases as the H₂ annealing time increases. The histograms of the Fe NPs are shown in Figure 3.8 for the Gaussian average, and Figure 3.9 is the plot of the average diameters calculated from the Gaussian curve. The result shows a slight shift in the measurement, but the trend is the same. Revisiting the density of the CNTs from Figure 3.2 and 3.3, as the average diameter increases, the number of the catalysts that act as a seed of individual CNTs decreases in a given area, and therefore, the number of the CNTs also decreases per unit area. The summarized table of the CNTFs' vol%, height, and the NPs' average diameters are recorded in Table 3.1.

a) Average Fe NP diameter from N₂



b) Average Fe NP diameter from He

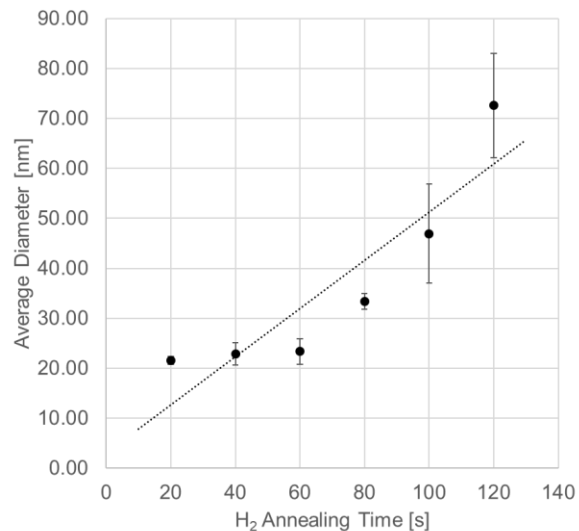


Figure 3.7. Average Fe NP diameters for varying H₂ annealing time in a) N₂ and b) He environment.

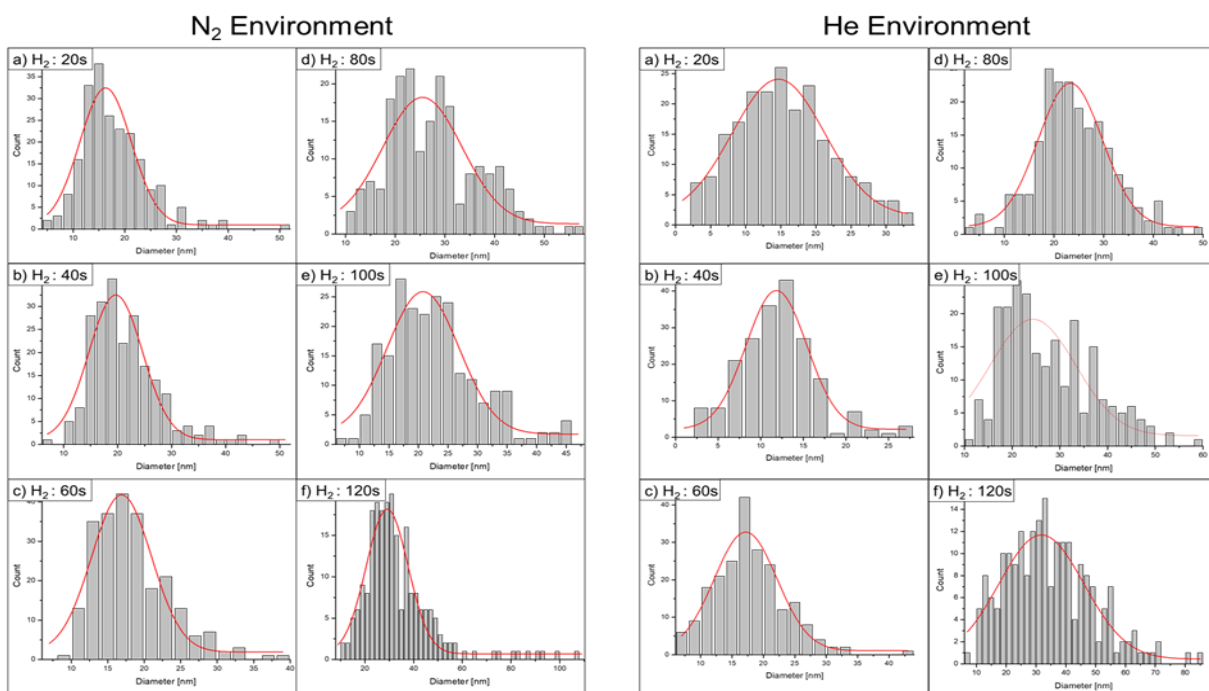


Figure 3.8. Gaussian average of the NP diameters from N₂ and He environment.

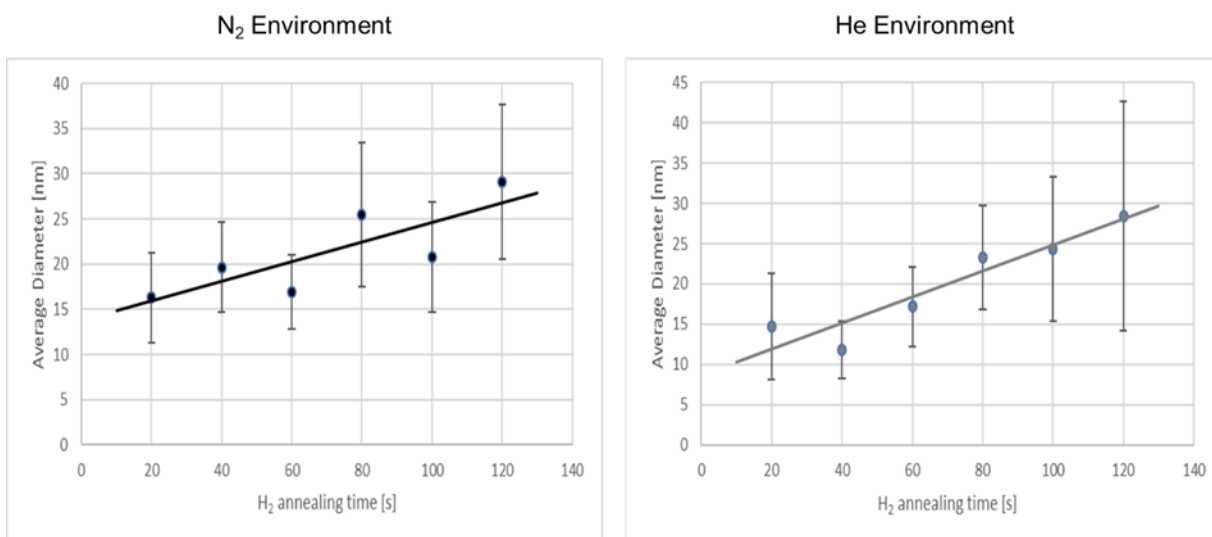


Figure 3.9. The average diameters calculated from the Gaussian curve in Figure 3.8.

Table 3.1. Record of the CNTFs' vol%, height, and NPs average diameter^s in both N₂ and He environment

H ₂ time [s]	N ₂			He		
	CNT		NP	CNT		NP
	vol%	height [μm]	^s φ [nm]	vol%	height [μm]	^s φ [nm]
20	77.83±3.63	205.48	24.38±1.82	78.51±2.36	203.87	21.57±0.79
40	75.19±2.90	171.61	26.05±0.59	84.58±0.99	150.65	22.89±2.21
60	72.50±2.94	162.58	32.56±1.98	77.13±2.56	126.13	23.372±2.53
80	64.16±5.57	146.13	39.22±2.52	72.15±3.24	127.10	33.39±1.58
100	60.09±7.52	98.71	44.85±3.45	65.07±3.54	105.48	46.98±9.97
120	56.67±6.00	77.10	55.20±7.56	63.93±2.81	100.32	72.62±10.44

3.3.3 Characteristics of CNT forests synthesized in N₂ or He

One set of CNTFs was grown in He, and another set was grown in N₂. The flow rates were the same for all the gases (He: 2000, N₂: 2000, H₂: 70, C₂H₂: 20 sccm). Also, the annealing time was set to 40 sec. The samples were tested under the same condition for their spinnability; when the sample was cooled to room temperature in the CVD chamber, we simply pulled a corner of the CNTF and observed its behavior as the pulling distance increased. As result, CNTs from both He and N₂ environments were able to produce highly aligned CNTF and provide a high quality of spinnable CNTs. As shown in Figure 3.10, the CNTs from N₂ and those from He environment do not show any significant visible difference in macro-scale. Both samples were pulled by forceps with ease and showed the widening behavior mentioned above.

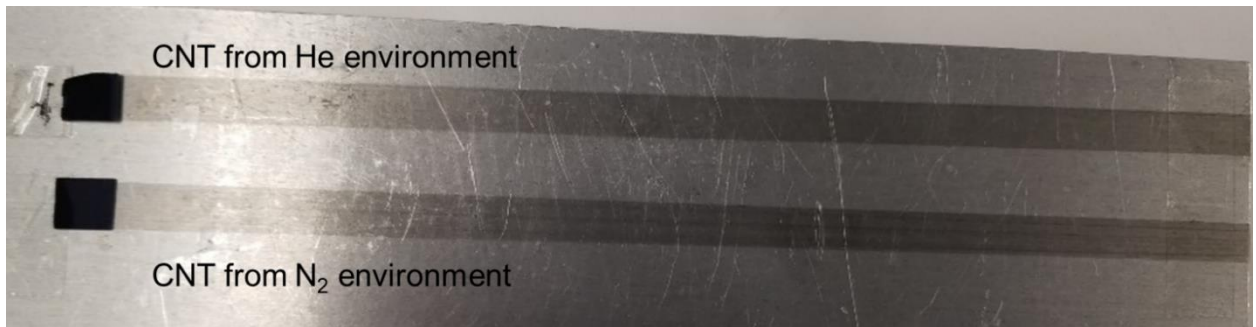


Figure 3.10. Image of CNT sheets from CNT forests; one grown in He environment (top) and the other grow in N₂ environment (bottom).

One critical method commonly used to determine the quality of CNTs is Raman spectroscopy. For a graphitic material, including the CNTs, by finding the ratio of intensities of two peaks, D-peak at 1350 cm⁻¹ and G-peak at 1590 cm⁻¹, the defect ratio of the sample can be measured [97], [115], [116]. Shown in Figure 3.11 is the Raman spectrum of the CNT sheet from a) N₂ environment and b) He environment. The measured defect ratios, I_D/I_G, are 0.5165 and

0.6399 from N₂ and He environment, respectively. This indicates that the replacement of the carrier gas from He to N₂ did not affect the crystalline structure of the CNTs or create amorphous carbon soot on the wall of the CNTs.

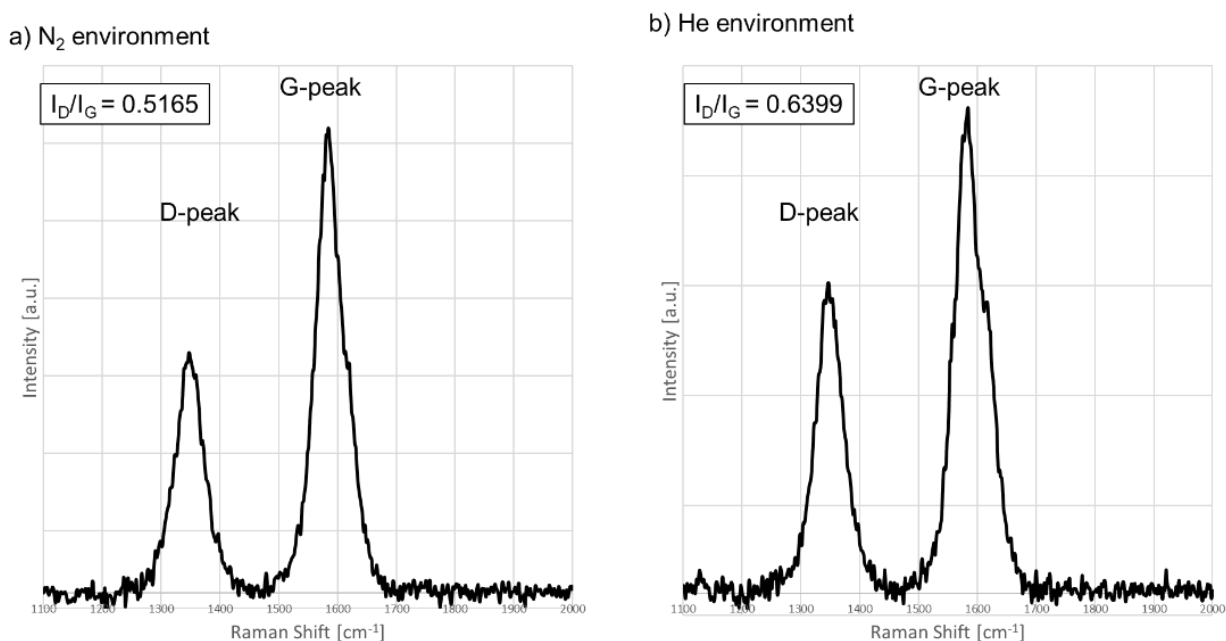


Figure 3.11. Raman spectroscopy of CNT sheet from a) N₂ environment and b) He environment.

Next, we measured the areal density of the CNTs from the SEM images in Figure 3.12 to confirm that the spinnability of the samples was still reserved under different synthesis environments. The measured areal densities were 75.78 ± 5.79 and 78.96 ± 6.78 nm for N₂ and He environment, respectively. In comparison to the differences of the CNT bundle diameters resulted from different H₂ annealing duration, the result indicates that the difference between the CNT bundle diameters of the CNTs from N₂ and He environment is negligible. Figure 3.12

shows the average CNT bundle diameters of the SCNTFs synthesized in N_2 and He. As shown, the average diameters of the CNT bundles are very similar in both cases.

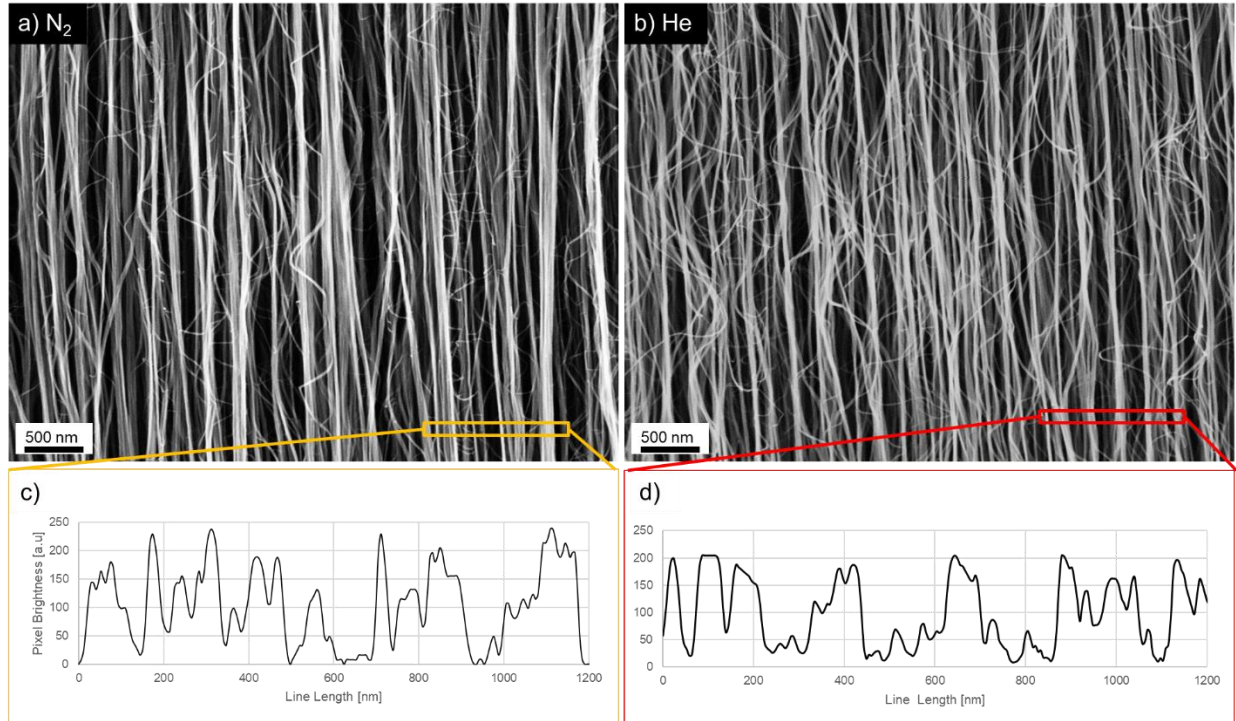


Figure 3.12. SEM images of two CNT forests synthesized in a CVD chamber using a) N_2 environment, b) He environment, and c and d) Examples profile of a cross-section of the CNT forest.

From five different measurements, Figure 3.13 has been plotted for comparison. The average diameters of the CNT bundles from the SEM images are 75.78 and 78.96 nm from the N_2 and He. Dividing them by the measured diameters from the TEM images, we can calculate a rough number of the CNTs per bundle. The results are 8.8 and 9.5 CNTs per bundle.

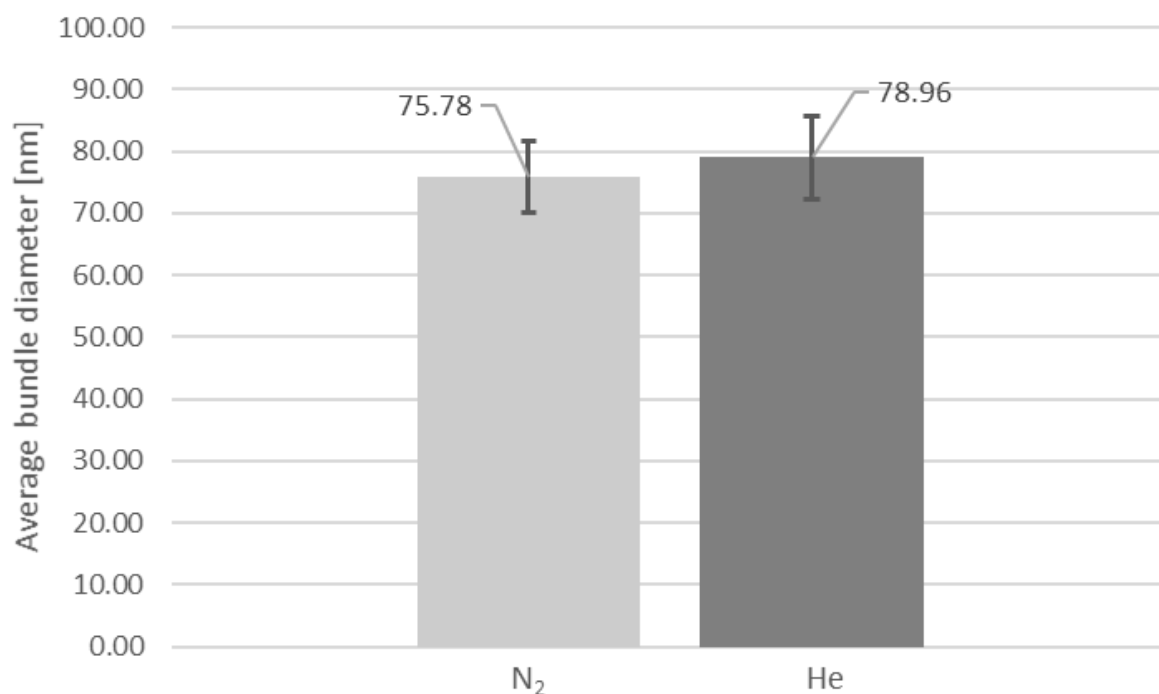


Figure 3.13. Measured average bundle diameters of the SCNTFs from N₂ (left) and He (right) environment.

Although the SEM images above show detailed features of CNT bundles in micro-scale, it is difficult to conclude that the nanostructure of the CNTs is similar in N₂ and He. Therefore, TEM images of the CNTs from both environments were taken for comparison. As shown in Figure 3.14, the TEM images indicate that all the CNTs grown from either environment are multi-walled CNTs which are known to show metallic properties and very common in conventional CVD systems. Also, the diameters of SCNTs are 8.6 ± 0.1 nm and 8.3 ± 0.2 nm from N₂ and He, respectively. For non-SCNTs, the diameters were 16.5 ± 0.7 nm and 16.2 ± 0.5 nm from N₂ and He, respectively. The CNTs synthesized from N₂ and He did not show a noticeable difference from the TEM images. Both exhibited multi-walled CNTs with a similar number of

the wall and diameters.

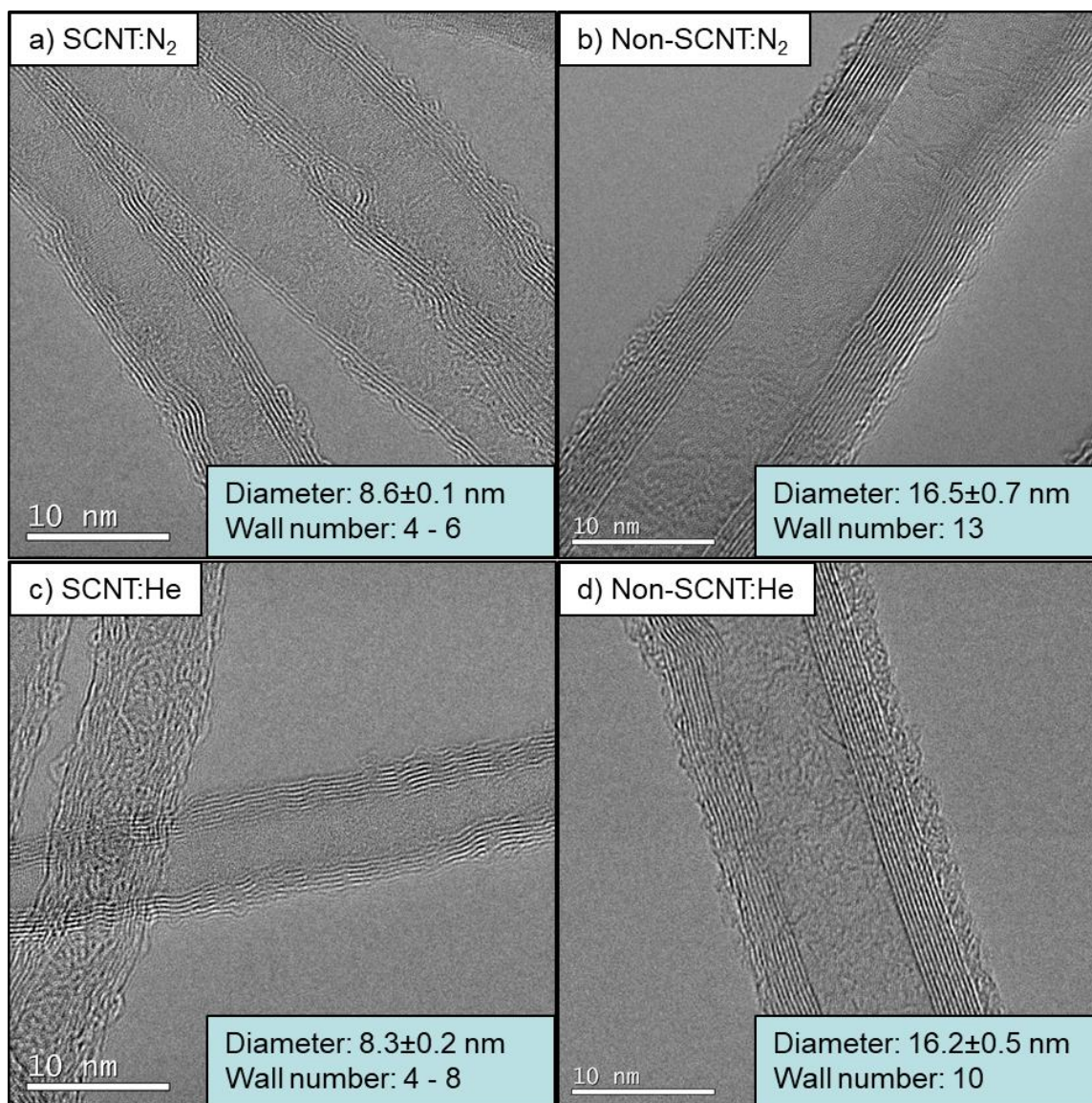


Figure 3.14. TEM images of a) SCNT synthesized in N₂, b) non-SCNT synthesized in N₂, c) SCNT synthesized in He, and d) non-SCNT synthesized in He.

As for the electrical resistance, the CNT sheets from the N_2 environment showed that they are compatible with those from the He environment. As shown in Figure 3.15, all the measurements have a linear relationship and show a clear distinction between 1, 2, and 3 layers. In the inset image of Figure 2.13 is the resistance of the samples that were measured by simply finding the inverse of the slopes of each plot. It is important to note that the resistance of the 1-layered samples might show a significant difference, however as the number of the layers increased, the difference of the resistances decreased. For the 3 layered samples, the resistances were very close to each other; 989 Ω and 1029 Ω for He and N_2 , respectively.

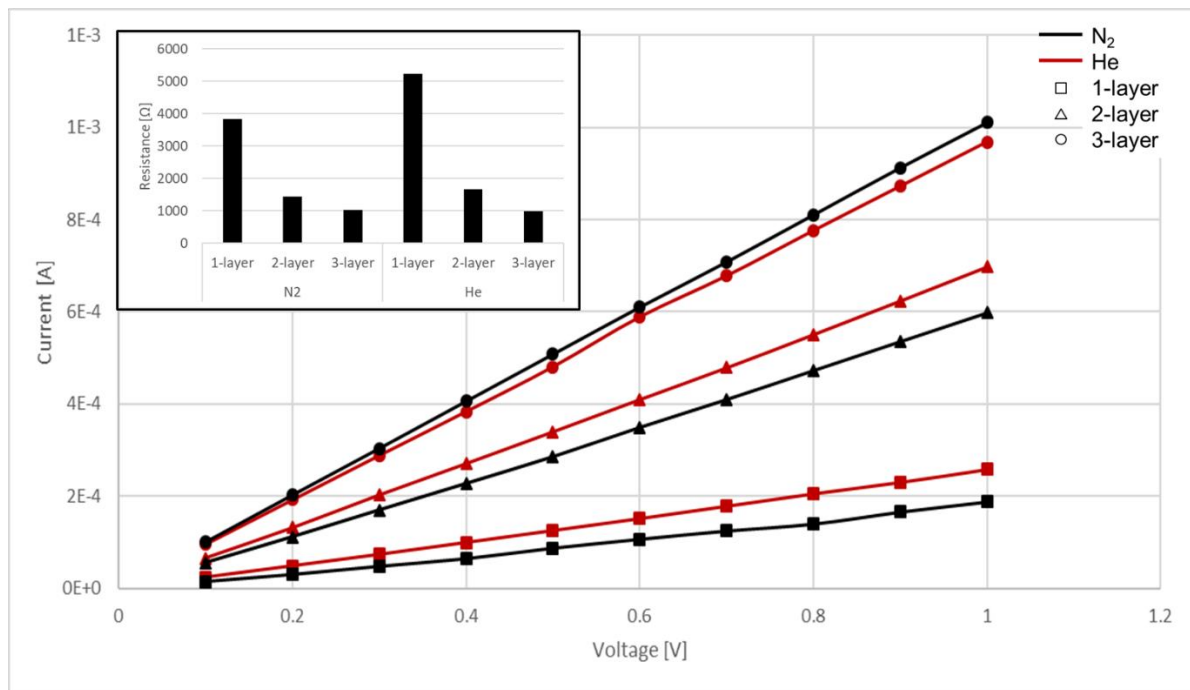


Figure 3.15. I-V curve of the layered CNT sheets. The resistances of each sample are shown in the inset image.

3.4 Conclusion

CNTs have been studied for decades by researchers and industries, but their commercialization was challenging due to various reasons including the synthesis cost. One of the most expensive gases that are used in the conventional CNT synthesis process is the noble gas, He. We replaced the noble gas with N₂, the most abundant gas in the atmosphere, to grow CNTs. We not only synthesized CNTs in N₂ successfully but also synthesized the CNTs that were spinnable, which is another attractive factor for the mass-production of the CNT-based devices. In terms of the catalyst and the CNT areal densities, fine-tuning of H₂ annealing duration resulted in high-quality CNT sheets. Additionally, by comparing the areal densities, defect ratio, and the resistance of the CNT sheets from N₂ and those from He environments, we conclude that the CNT sheets from the N₂ environment have compatible structure and properties with those from the He environment. In conclusion, the CNT sheets from N₂ environment resulted in high-quality CNT sheets as those from the He environment, and N₂ gas can replace the He gas for the spinnable CNT sheet fabrication process.

CHAPTER 4

CHARACTERISTICS OF FLEXIBLE STRAIN SENSOR USING CARBON NANOTUBE SHEET SYNTHESIZED IN N₂

4.1 Introduction

Recently, human-machine interaction technology has developed rapidly due to the increasing interest in health monitoring, motion detection, and immersive gaming. One of the popular methods for suitable performances is wearable devices that are flexible and stretchable. Several studies have developed devices to detect human motion using popular flexible polymeric matrixes such as PDMS and kinds of conductors to read electrical property changes such as capacitance and resistance [117]–[124]. These devices are usually structured with liquid-based polymer matrixes and conductive material as the sensing layer. In terms of polymers, PDMS is the most popular material for their convenience, price, and bio-compatibleness [125]. Silicone-Pt composites are also popular for its softness and flexibility [126], [127]. For the sensing layers, popular materials are nanowires [128]–[130], nanolayers [124] and carbon-based materials including graphene and carbon nanotubes[8], [87], [117], [120]–[122], [126], [131]–[135].

Carbon nanotubes (CNTs) are favorable for these fields as a great sensing material for their unique characteristics such as high electrical conductivity [3], tensile strength [4], and flexibility [8]. Many studies have shown that the random connection of the CNT layer can be used as a sensing layer for different purposes. Lee et al. showed that the random connection of the CNTs on a PDMS polymeric substrate resulted in a high response device depending on the number of the spraying of the CNT layers [136]. As expected, the randomized connection of CNTs created random electron paths, which has a higher potential of losing energy over time

than those of aligned structures. On the other hand, Santos et al. made aligned structure of CNT sensors by growing vertically aligned CNTS and, by a transferring method named “knockdown”, they successfully created an aligned pattern with CNTs [137]. It is important to uniformly distribute the CNTs on a surface and aligning them would be efficient for energy-saving applications.

Our previous work demonstrated the spin-capable CNTs or CNT sheets (CNTSs) can be synthesized in N_2 environment in a chemical vapor deposition (CVD) system which conventionally uses, relatively expensive, He/Ar for its inert environment [138]. By using the CNTS from the N_2 environment, we can not only achieve the aligned CNT structures for increased performances but also decreased fabrication price by completely cutting the usage of He or other inert gases for the synthesis process.

In this paper, strain sensors using flexible polymer, Ecoflex 0030 from Smooth-On, and CNTS from the N_2 environment are assembled. We tested the effect of the numbers of the CNTS layers on the resistance of the sensors which is important in terms of power consumption. Also, we demonstrate that by controlling the number of the CNTS layers, the resistance of the device and the sensitivity also can be controlled with ease. In addition, the sensor responses were very consistent after few cycles of applying strain (20%) and remained its peak-to-peak response range up to 50 cycles.

4.2 Experiment

4.2.1 CNTS synthesis

The CNTS are grown in a CVD system, the same method was used in the previous Chapter. Briefly, dry oxidation was performed on a Si wafer to grow 100 nm of SiO₂ layer. Then, using atomic layer deposition (ALD), 3 nm of Al₂O₃ layer was deposited with a rate of 1Å/min. Using e-beam deposition, 2.5 nm of Fe layer was deposited at a rate less than 3Å/s. The prepared wafer was diced into 1 x 1 cm² samples which are inserted in the CVD furnace, purged with N₂ gas. While purging the system with N₂ gas for more than 20 min, the sample was left at room temperature (25 °C). Once the furnace reached the growth temperature, 780 °C, the sample was pushed from room-temperature to the growth zone in 3 seconds. As soon as the sample was inserted, H₂ gas was inserted for 30 s, then C₂H₂ was introduced to the chamber as the carbon source for 3 min. After CNTs are vertically grown, one side of the CNTs are stuck to a slice of adhesive tape and pulled to form a sheet via van der Waals interaction [4], [26], [52], [55], [56], [139].

4.2.2 Sensor fabrication

Figure 4.1 shows the diagram of the sensor fabrication process. For the polymeric substrate for flexible material, we have chosen Ecoflex 0030 for its large elongation of 900% [140]. First, The Ecoflex composition was mixed thoroughly for 1 min and was put under a vacuum to remove any air bubbles. The mixture was poured into a 20 × 40 × 1 mm³ mold printed by a 3D printer (Qidi). Second, the Ecoflex was removed from the mold (Figure 4.1a), and 2, 4, 6, 8 layers of CNTS were applied on the top of the cured Ecoflex (Figure 4.1b). Few

drops of ethanol were dropped to ensure the adhesion of the CNTs to the substrate (Figure 4.1c), electrodes, 30 mm apart from each other, were created by a wire and silver paste (Figure 4.1d). Finally, another layer of Ecoflex was poured on the top of the device and cured (Figure 4.1e).

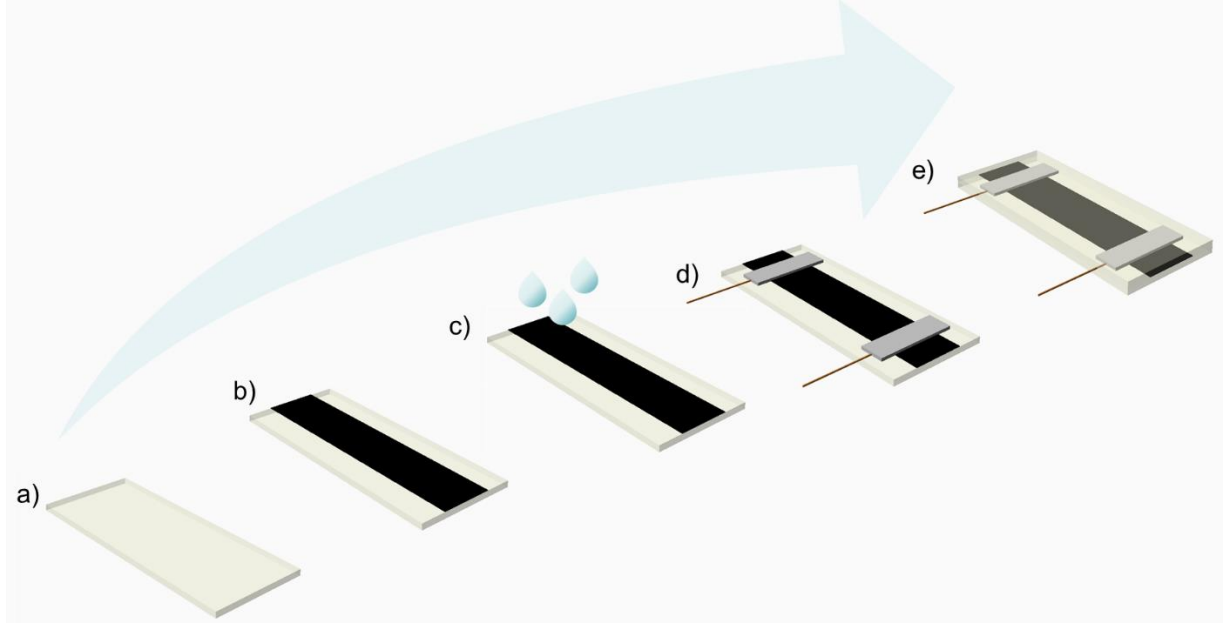


Figure 4.1. Diagram of the sensor fabrication process.

4.2.3 Strain test

The strain is calculated by the equation,

$$\varepsilon = \frac{\Delta L}{L_0},$$

where ΔL is the change in the total length of the device and L_0 is the initial length. Similarly, the equation for the sensitivity is

$$S = \frac{\Delta R}{R_0},$$

where ΔR is the change in the resistance and R_0 is the initial resistance. In this paper, both strain and sensitivity will be shown in %.

We have used a homemade strain sensor device to apply strain and measure resistances. A 3D-printer vice was used as the strain stage. Using Arduino Uno and a stepper motor, the vice was controlled to apply strain to the devices. Resistances were measured using Labview with Keithley digital multi-meter.

Before applying any strain to the devices, as-fabricated resistances were measured to record the relationship between resistance and the number of the CNTS layers. Over fifty cycles of strain of 20% was applied to test the durability of the sensors. After 50 cycles, resistance without any applied strain was measured to record the discrepancy in resistances before and after applying strain. All the tests were done with a constant strain speed of 0.35mm/s, which converts to 1.17%/s in terms of strain, ϵ .

4.3 Result and Discussion

4.3.1 Number of CNTS layers and resistance

The working mechanism is illustrated in Figure 4.2a. At rest, the CNTs will create compact current path with physical connections. At this stage, the total resistance would be consisting the majority of the contact resistance and minority tunneling resistance. As the applied strain increases, the gaps between individual CNTs will increase, creating more tunneling resistance, and for the last stage, the CNTS are distanced enough to make open circuits where there is no

connection, hence increasing the resistance. As expected, electron paths become longer as the number of randomly connected CNTs are decreasing. Shown in Figure 4.2b is the SEM image of the CNTS at rest.

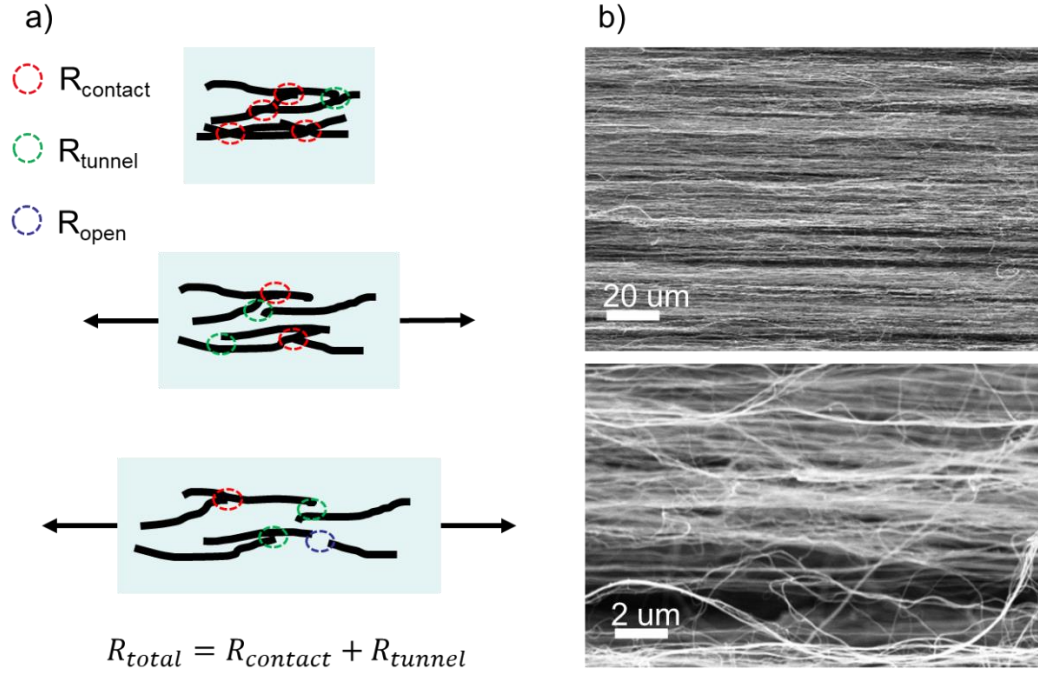


Figure 4.2. a) the diagram of the working mechanism of the strain sensor. b) the SEM images of CNTS (6 layers) at rest.

We have laid 2, 4, 6, 8 layers of CNTS on the Ecoflex slabs, created the electrodes, then measured resistances. The inset image of Figure 4.3 shows the completed sensors. The resistance measurement results are plotted in Fig. 4 (red); the measured resistances were 6.17, 1.96, 1.14, and 0.54 $\text{k}\Omega$ for 2, 4, 6, and 8 layers of CNTS, respectively. This indicates what was expected; a larger number of the CNTs on the substrate would create more random connections and bring the total resistance down. In addition, resistances after 50 cycles of 20% strain were measured to compare the stabilized resistances that are plotted in black in Figure 4.3. The measured

resistances after 50 cycles were 2.96, 1.79, 0.78, and 0.49 k Ω for 2, 4, 6, and 8 layers, respectively. While the resistance of the 2-layer device decreased more than 52% (6.17 to 2.96), the 8-layer device only dropped about 9% (0.54 to 0.49) of the initial resistance. This result shows that more layers not only have lower resistances but also have less change before and after numbers of stresses. However, the exponential decrease trend shows that there is a difficulty of lowering resistance even further just by adding more layers of CNTs.

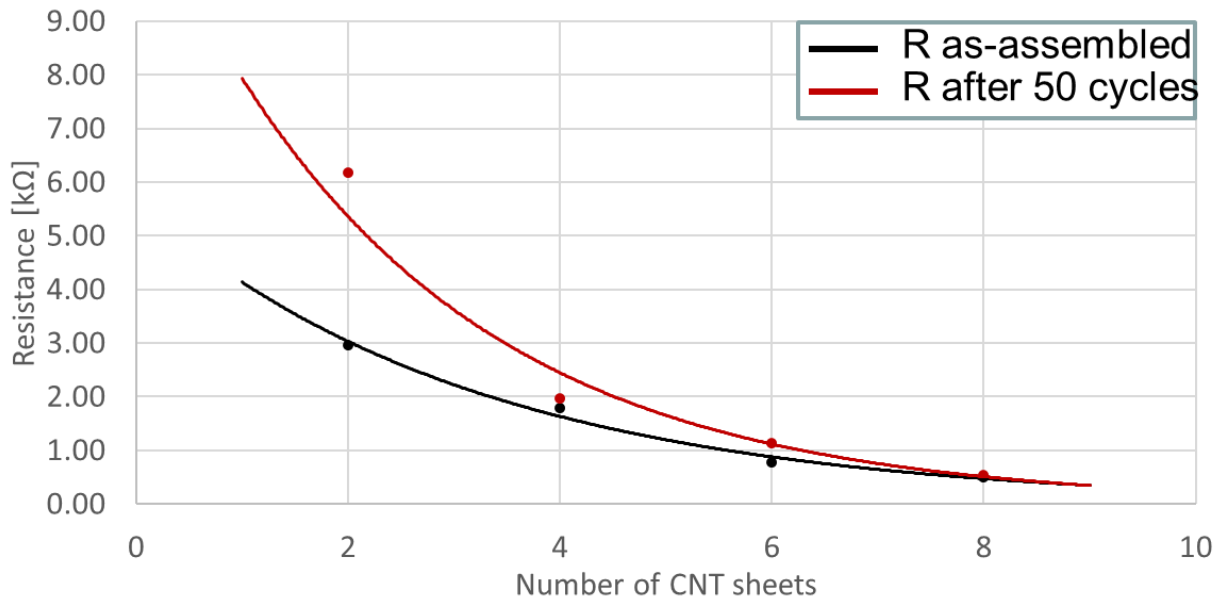


Figure 4.3. Plot of resistance vs the number of CNTS layers. Initial resistance (red) and the resistance after 50 cycles (black) are plotted. The inset image shows the actual devices assembled (2, 4, 6, 8 layers from left).

4.3.2 Cycle tests and hysteresis test

In the previous section, resistances of the sensors are analyzed; as-assembled and after applying 50 cycles of strain and relaxation. In this section, the 50 cycles will be analyzed. As shown in Fig. 5a, all the devices resulted in uniform responses after first few cycles. As

mentioned in the previous section, the initial resistances show large differences. However, it is difficult to detect the peak-to-peak differences for the different numbers of the layers in Figure 4.4a. The normalized sensitivities for each are calculated and plotted in Figure 4.4b. It is evident that the sensitivities for different layers of CNTSs show distinctive results, showing visible differences. The measured sensitivities are 4.00, 8.44, 11.14, and 15.40 % for 2, 4, 6, and 8 layers of CNTSs respectively.

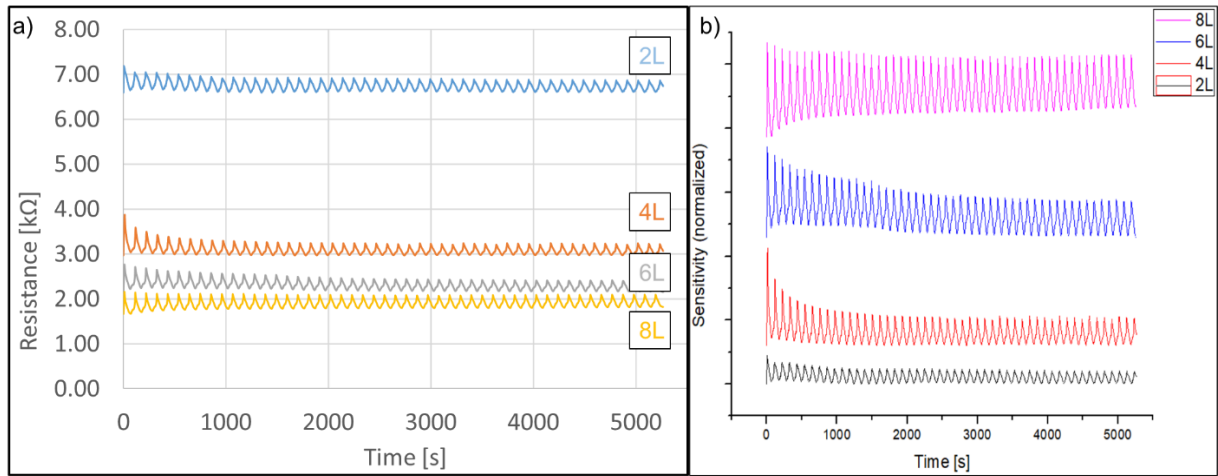


Figure 4.4. Plots of a) resistive responses and the b) normalized sensitivities

Continued from the cycling test, hysteresis data were also collected and plotted in Figure 4.5a. The data were collected after the first 20 cycles and minima and maxima of individual peaks are taken every 0.5s and averaged. For Figure 4.5b, the maximum sensitivities are plotted for 20% strain. The relationship between the result implies that the maximum strain can be changed and controlled by the total number of the CNTSs that are on the actual device. However, it is important to note that the resistance will stop decreasing as shown in Figure 4.3. Therefore,

putting more layers of CNTS to decrease resistance and increase the efficiency of energy consumption would be not as efficient once it reaches a certain point (around 1 k Ω in this study). On the other hand, in terms of sensitivity, the number of the CNTS layers has a direct relationship. More CNTS layers will create more resistance changing sites (contact, tunneling, or open) and provide more available pathways for the currents to flow.

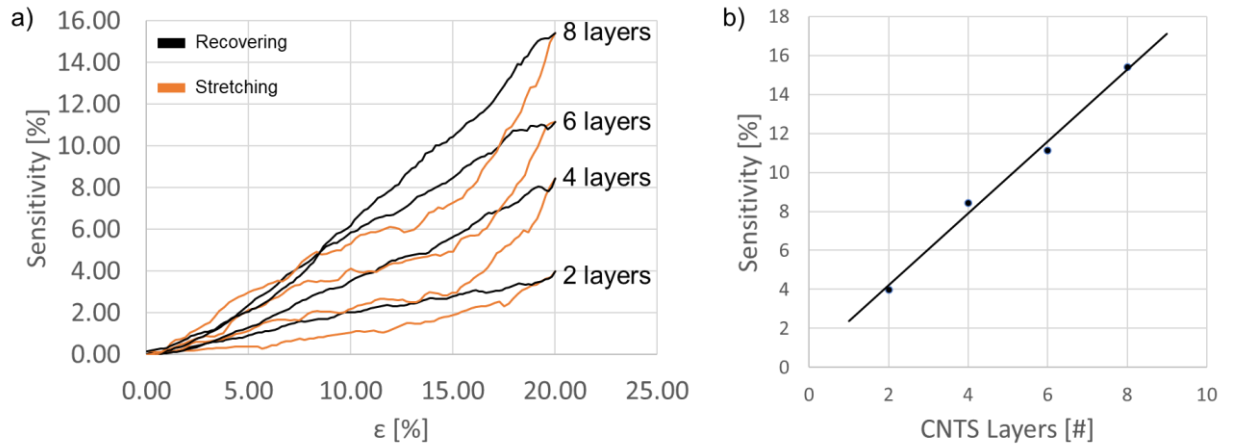


Figure 4.5. Graphs of a) hysteresis test results and b) the sensitivities of 2, 4, 6, and 8 CNTS layers.

4.4 Conclusion

The development of strain sensors at a cheaper price and easier fabrication steps are critical for wearable devices for the purpose of motion detection and health monitoring. The aligned CNTs or CNT sheets (CNTSs) are very suitable for this application for their unique strengths, such as chemical and thermal stability, physical durability, high conductivity, and flexibility. The synthesis process usually consists of a CVD system with relatively expensive inert gas, but we have successfully shown that CNTSs can be repeatably produced in the N₂ environment without use of He or Ar. We have applied 2, 4, 6, and 8 layers of CNTSs on a flexible polymer substrate

(Ecoflex) to develop a strain sensor that not only showed uniform responses over 50 cycles and notable sensitivity (12% resistance change) for 20% strain. The initial resistances of the devices were lower for more CNTS layers, but the trend does not show any efficiency of increasing layers to decrease resistance further. However, the sensitivity has shown a linearly increasing trend as the number of the CNTS layers increased, which gives wider application windows for other applications.

CHAPTER 5

SUMMARY AND POTENTIAL FUTURE WORK

5.1 Summary and Conclusion

As mentioned earlier, CNTs exhibit unique characteristics that are favorable for many different applications. With such a large potential, synthesizing CNTs for different purposes and applications have been studied for decades. However, the biggest obstacle for it to shine was the production cost. Continuous flow of helium, argon, or xenon gas was the most important conditions for many researchers to remove oxygen in the system and to keep an inert environment. Also, the carrier gases actually deliver an annealing agent and a carbon source to the substrate. The importance of the carrier gas cannot be emphasized more. However, again, the gases are not cost-effective. Helium will be depleted from the earth soon, xenon and argon require complicated filtration processes. Meanwhile, N_2 are cheap and abundant. The effort to replace helium with nitrogen must be done for the commercialization of CNTs for cheaper price. Therefore, this dissertation puts efforts to step toward mass-production of the spin-capable CNTs are reported, and a flexible strain sensor is fabricated to demonstrate that CNTs from N_2 can be utilized in many fields.

First, two of the factors that affect the quality of the CNTs are studied. We found that the catalyst morphology was very important for the spin-capability of the CNTs. However, it is very challenging to pattern and implements the catalysts one by one with current technology because the catalysts are within nanometer range. In order to control the catalyst morphology, the initial thickness of the catalytic layer was controlled by e-beam deposition. The deposited Fe thicknesses were 1.5, 2.0, 2.5, 3.0, and 3.5 nm, monitored by the quartz crystal sensor. In Chapter

2, we report that the thicker layer resulted in much larger nanoparticles after the annealing process. Also, the larger NPs resulted in less dense CNTs, therefore not spin capable. In addition, the annealing time was varied by flowing H_2 for 20, 40, and 60 s. In result, the shorter exposure duration produced smaller NP diameters, which resulted in denser morphology. This helped the CNTs to grow much straight and aligned fashion. Both effects, the initial thickness and the annealing time, on the spin-capability of CNTFs are explained by the Ostwald ripening phenomenon. For the former, a thicker catalyst layer will provide more materials to the NPs to coarsen at a given time. For the latter, more exposure time provides more time for the NPs to move around and consume or be consumed. By thorough control of both, it is possible to produce CNTSs in a repeatable fashion.

Helium is not only one of the most expensive gases, but also being depleted as time passes. The price is expected only to increase. As for a potential replacement, nitrogen (N_2) was inserted instead of He gas in the CVD system. Even though it was well known that the N_2 acts as an inert gas at room temperature and potentially could replace He, none successfully demonstrated to grow spin-capable CNTs. In Chapter 3, we have reported different catalyst morphologies for different annealing times in both He and N_2 . AFM was used to calculate the average particle diameter and density. They exhibited insignificant differences. Once the CNTs were grown from different environment, SEM images were used to calculate average density and thickness, TEM was used to compare the nanostructures of CNTS, and the Raman spectroscopy was used to compare the general quality of the CNTs. From all of the measurements, we concluded that N_2 can definitely replace the He, and other inert gases such as argon or xenon, for the synthesis process of SCNT in CVD system.

Finally, in Chapter 4, we have demonstrated that the CNTs grown in the N_2 environment show a great potential to be used as the critical material in an application, strain sensor. Using a flexible polymeric matrix, Ecoflex 0030 (Smooth-On inc.), a flexible substrate was prepared. Then, on the substrate, 2, 4, 6, and 8 layers of CNTS synthesized in N_2 were stacked as the sensor material. The initial resistance, which is related to the power consumption of the device, showed exponentially decaying behavior as the number of the sheet increased. However, the sensitivity of devices showed linearly increasing behavior with the number of layers. Through the cycling test, it exhibited consistent responses after first few cycles. From this test, we have demonstrated that the CNTs from the N_2 environment can be utilized as a strain sensor.

In conclusion, the catalytic layer and annealing process can be controlled to obtain the indirect control of spin-capability of the CNT forests. By replacing He with N_2 , the CNTS can be fabricated at a much lower cost. Finally, the CNTS from N_2 is compatible as a great sensing material.

5.2 Potential Future Research

5.2.1 What has already been done

Countless applications using CNTs have already been studied. There are battery electrodes, chemical and physical sensors, air/liquid filters, supercapacitors, actuators, FET, energy harvesting materials, and textile industries. It is not difficult to find an application where CNTs can be used. As our group member, Behnoush Dousti, already has shown, wrapping/covering a large surface with CNTs will be done simply by pulling and rolling them. Unlike non-SCNT, CNTS will not require any complicated processes such as sonification and

spraying. Even further, the sheet of CNTs has large surface coverage for a given amount of the material. This is very advantageous in terms of the mass-production of any applications that adopt CNTSs. So far, they were grown in He, Ar, or Xe environments. However, CNTS can now be produced in N₂.

5.2.2 Future Works

First, the definition of what is considered “spin-capable” is different from everyone. Throughout this thesis, the CNTF grading was mentioned and labeled on the results based on Figure 1.14 that is ranked by the author’s experiments and personal standard of “suitable for mass-production”. However, this standard was done by physical exhibited results that were detected by human eyes. Even though this thesis reports the catalyst morphology, areal densities of CNTs, and the CNTF gradings, this measurement sets up a blur boundary between each condition of the CNTFs. More investigation is needed for clearly divided and tangible boundaries that could be agreed upon by other researchers and have a common definition throughout the field.

APPENDIX

VARIATIONS OF CVD SYSTEMS

Vertical Chemical Vapor Deposition System

From this lab, a vertical chemical vapor deposition system was used for years. Shown in Figure A.1, the vertical CVD system had a copper heater that supported the sample near the gas showerhead. This system provided quickly heating up and cooling down very quickly. However, there were few problems that we had to fix. First, the gas showerhead had patterned holes, which resulted in the carbon nanotubes growing in a pattern that portrayed the showerhead pattern. Also, the copper heater was located below the sample. This was a problem because there was not a simple method to measure the surface temperature of the specimen when the room temperature gases are poured on the top of the sample while the bottom of the sample was at 780 °C. Previous studies reported that the growth temperature was at 780 °C under assumption that the surface of the sample will be at the same temperature as the copper block. However, the assumption did not have enough evidence or studies to simply bypass. Second, the sample was heated up from RT to 780 °C with the copper block. There was not enough study done on the catalyst change or effect of the rising temperature on the catalyst layer when the sample is heated up slowly. Instead of raising the temperature slowly, we had to modify so that we can insert the sample to high temperature instantly.

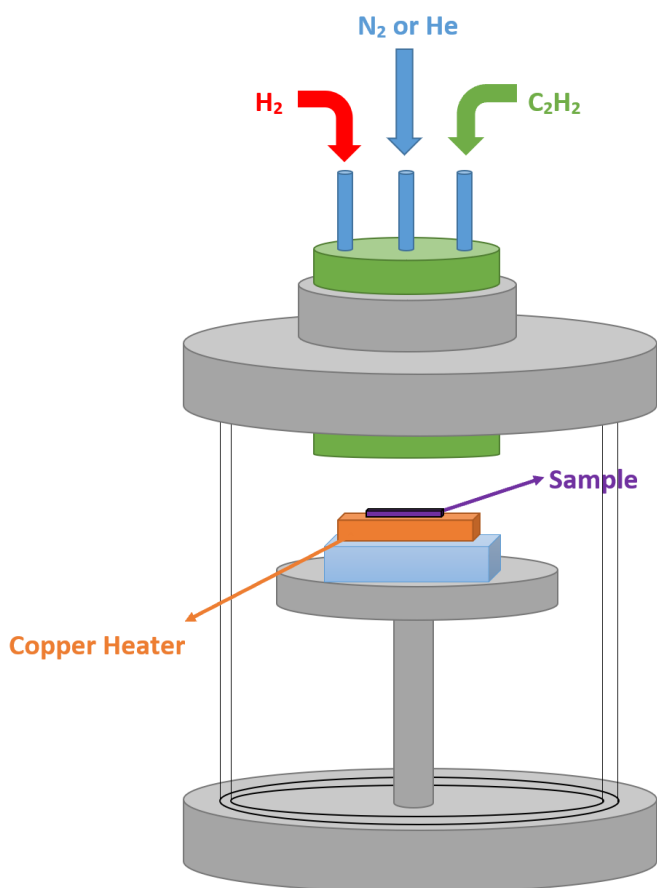


Figure A.1 illustration of the vertical CVD chamber that was used for previous studies.

Horizontal CVD system with slidable Furnace

The second furnace was closer to the conventional systems that were used by many other studies. As shown in Figure 2.1, there were two modifications to the CVD system. First, a magnetic arm was installed to push the sample from room temperature to the growth temperature instantly. This prevented the questions of the catalyst morphology changes due to the high-temperature exposure during the temperature increase. Second, the furnace was modified it so that it could

slide to another side of the tube. When the growth process was over, the furnace is simply slid to the other side of the chamber so that the part of the chamber where the sample is located could be exposed to room temperature instantly. This modification cut the total cooling time by 90%. However, this system also had a major problem to be solved for the mass-producible approach. The cooled-down portion of the chamber had to be re-heated for the experiments after experiments. Even though we could cut down the cooling time, the heating time still existed for repeated experiments.

Horizontal CVD system with retractable magnetic arm

As shown in Chapter 3, relocation of the sample was an important feature to be achieved. The magnetic arm was modified so that it could push and pull the sample and relocate the samples at any position desired. With this modification, the sample was pushed from room temperature to the growth temperature within 3 seconds, then pulled out from the hot zone after the experiment was over. As implied, the furnace was kept on, and the temperature at the growth zone was consistently maintained. The following experiments were done almost instantly once the purging of the chamber was done. This cutdown both the heating time and cooling time of the experiments. With few modifications on the furnace, a CVD system that is suitable for mass-production was designed and performed.

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BIOGRAPHICAL SKETCH

Ye Il Choi was born on July 1, 1990, in Daejeon, South Korea. He received his BS. degree in Electrical Engineering at The University of Texas at Dallas in 2015. He joined Dr. Gil S. Lee's research lab as a graduate student while pursuing a MS degree, then he decided to join the UT Dallas PhD program. His main research topic was the development of the carbon nanotube (CNT) synthesis process to help mass-production of the CNTs and finally commercializing them. This dissertation is for his PhD degree, and was filed May 2021.

CURRICULUM VITAE

Michael Yeil Choi

Address: 800 W. Campbell Road, Richardson, Texas 75080

Email: yxc091720@utdallas.edu

EDUCATION

2021 The University of Texas at Dallas. PhD in Electrical Engineering
2014 The University of Texas at Dallas. BS in Electrical Engineering

PROFESSIONAL EXPERIENCE

2014 - 2021 Graduate student researcher. Synthesis of carbon nanotubes and its applications (Advisor: Prof. Gil S. Lee).
2014 - 2021 Cleanroom user. Used various cleaning, deposition, and analysis equipment.
2014 - 2021 Teaching/Research assistant. Helped professors grading and planning for courses. Helped students on course materials.

RESEARCH INTERESTS

- Synthesis of carbon nanotubes using chemical vapor deposition system
- Development of chemical vapor deposition system for faster production
- Synthesis carbon nanotubes in nitrogen environment for cheaper production
- Gas, pressure, strain sensors using carbon nanotubes
- Surface morphology and nanostructures

TECHNICAL SKILLS

- Chemical vapor deposition, atomic layer deposition, e-beam deposition, sputtering, SEM, AFM, Raman spectroscopy, XPS.
- Use of basic characterization equipment; DMM, oscilloscope, function generator
- PSpice, OrCad, Matlab, OpenSCAD, LabView, Origin
- Microsoft Word, Excel, PowerPoint

TEACHING/RESEARCH ASSISTANT EXPERIENCE

- 2014 – 2021 Teaching Assistant Courses:
Introduction to Electrical Engineering II (EE 1202)
Electronic Devices Laboratory (EE 3110)
Electric Circuits (EE 3311)
Electronic Circuits Laboratory (EE 3111)
Electrical Network Analysis (EE 3301)
Electrical Network Analysis Laboratory (EE 3101)
Computer Architecture (EE 4304)
- Sum 2020 Research Assistant (Gil S. Lee's lab)

PUBLICATIONS

1. Maeum Han, Jae-Keon Kim, Ye I. Choi, Daewoong Jung, "Carbon nanotube-based strain sensor for structural health monitoring," JJAP 58(SD), SDDJ07, 2019.
2. Vahid Qaradaghi, Behnoush Dousti, Ye I. Choi, Gil S. Lee, Wenchuang Hu, Siavash Pourkamali, "Surface Area Enhancement of Nanomechanical Disk Resonators Using MWCNT for Mass Sensing Applications," IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control vol. 66, NO. 3, p. 609-615, 2019.
3. Ye I. Choi, Cho Chen, Jin W. Park, G. S. Lee, "Spin Capable Carbon Nanotube Synthesis in Nitrogen Environment," Diamond & Related Materials 110, 108155, 2020,
4. Behnoush Dousti, Ye I. Choi, Stuart F. Cogan, Gil S. Lee, "A High Energy Density 2D Microsupercapacitor Based on an Interconnected Network of a Horizontally Aligned Carbon Nanotube Sheet," ACS Appl. Mat. & int 12(44), 2020.
5. Ye I. Choi, Behnoush Dousti, Daewoong Jung, Gil S. Lee, "The Effect of Fe Film Thickness and the H₂ Annealing Time on the Spin-capability of Carbon Nanotube Forest with CVD Method," JNN 21, 1-6, 2021.
6. Behnoush Dousti, Sachin Babu, Ye I. Choi, Jeong B. Lee, Gil S. Lee, Stuart F. Cogan, "Highly flexible all-solid-state on-chip microsupercapacitors for portable electronics: a self-powered integrated system," Carbon, (to be submitted) 2021.
7. Ye I. Choi, S. Babu, J. B. Lee, Gil S. Lee, "Characteristics of Flexible Strain Sensor Using Carbon Nanotube Sheets Synthesized in N₂," (to be submitted to IEEE sensors) 2021.

CONFERENCE PRESENTATIONS

1. Y. I. Choi, Behnoush Dousti, Dae W. Kwon, Kevin J. Choi, J.H. Choi, Daewoong Jung, and Gil S. Lee, "Optimizing Spinnable Carbon Nanotube Growth in N₂ Environment by Chemical Vapor Deposition Method, 14th Nano Korea Symposium, Seoul, Korea, July 2016

2. Y. I. Choi, Jung H. Choi, Gil S. Lee, “Effect of Acetylene to Hydrogen ratio for Synthesis of Spinnable Carbon Nanotube Forest Using Chemical Vapor Deposition Method in Nitrogen Environment,” AVS Texas Chapter Conference at Dallas, Texas, August 3-4, 2016.
3. M. Han, Y. Hwang, Y. Choi, Gil S. Lee, D. Jung, “Flexible, transparent, conductive films using spin-capable carbon nanotubes,” United State – Korea Conference, Dallas, Texas, August 2016.
4. B. Dousti, Y. I. Choi, G.S. Lee, “A High Performance Micro-Supercapacitor Based on on Carbon Nanotube Sheets,” TECHCON, Austin, Texas, September 16-18, 2018.
5. V. Qaradaghi, B. Dousti, Y. I. Choi, G. S. Lee, S. Pourkamali, “Effective Surface Enhancement of Nanomechanical Disk Resonators Using CNT for Mass Sensing Applications,” IEEE International Frequency Control Symposium, Olympic Valley, CA, May 21 – 24, 2018.
6. Y. I. Choi, B. Dousti, and G. S. Lee, “The Effect of Catalyst Thickness and the Hydrogen Annealing Time on Spin Capability of Carbon Nanotube Forest with a Fast Temperature Ramping Rate CVD System,” 235th ECS Meeting, Dallas, TX, May 26-30, 2019.
7. B. Dousti, Y. I. Choi, Gil S. Lee, “Miniaturized Electrochemical Supercapacitor with Patterned Horizontally Aligned Carbon Nanotube Sheets,” 235th ECS Meeting, Dallas, TX, May 26th – 30th, 2019.

AWARDS & HONORS

2018, 2019	Certificates of achievement Recognition for instructional excellence, Teaching Assistant
2013	UTD & Agilent Technologies test and measurement equipment training

LANGUAGES

English & Korean