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Aligned Carbon Nanotube Carpets on Carbon Substrates for High Power Electronic Applications

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Aligned Carbon Nanotube Carpets on Carbon Substrates for High Power Electronic Applications

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

By

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Abstract


One of the driving forces behind nanotechnology research is the miniaturization of electronic devices. Electrical and thermal transport properties of device materials at micrometer and nanometer scales become very important in such applications. Carbon materials, especially carbon nanotubes (CNTs), have exceptionally low density and superior electrical, thermal, and mechanical properties. Vertically aligned CNTs attached to lightweight carbon substrates may hold the key to fully use these outstanding properties. However, the majority of studies reported to date involve either loosely unattached CNTs or CNTs attached to traditional electronic grade silicon, which have limited use in lightweight electronic components. Studies of CNT arrays attached to carbon substrates are extremely scarce, but if successful, such a composition could lead to unprecedented lightweight electronic devices with superior electrical and thermal transport properties. This dissertation is aimed at performing detailed investigation of such structures.

This work investigates the synthesis-structure-property relationships of CNT arrays attached to carbon surfaces relevant to power electronic applications. Several detailed investigations were performed to achieve the goal of creating multiscale combination materials and to test their feasibility as high power electronic devices. Background
studies were piloted to determine the most practical growth technique and growth parameters in order to achieve dense CNT growth. Floating catalyst chemical vapor deposition was determined to be the most effective, scalable, and reliable growth method. In addition, an oxide buffer layer was deemed necessary for dense CNT growth on carbon substrate. Several oxides were compared in order to determine the most suitable for CNTs growth while providing superior thermal properties. Among the buffer oxides investigated in this study, the ALD Al₂O₃ buffer layer provided the fastest CNT nucleation and most uniform size distribution. However, Al₂O₃ buffer layer was plagued by adhesion issues, which may limit future applications. Plasma SiO₂ offers a slower initial nucleation rate, but yields the tallest carpet height in identical growth conditions, and also appears to be the most stable and repeatable.

Thermal properties investigations were conducted on the final products, which consisted of aligned CNTs arrays of different carpet heights on carbon substrates. Observations show that the thermal resistance of the CNT array varies linearly with CNT carpet height, as expected. This variation was used to estimate the thermal conductivity of multi-walled nanotube in the carpet, and found to be approximately 35W/m-K. This value shows promise that such lightweight structure can replace current commercially available products.

This dissertation will reveal key results and discuss the investigations from the following areas: comparing chemical vapor deposition growth techniques, the importance of oxide buffer layer on carbon substrates, the effect of buffer layer composition, structure and
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Dedication

This dissertation is dedicated to my lovely Mom

For the endless love, strength, support, and inspiration.
Section I: Introduction and Background

(Materials Information and Processing Techniques)
CHAPTER 1 Introduction

1.1 Introduction

As the technology trend shows, there is an extremely high demand for lightweight materials in wide ranges of industrial and consumer electronic devices. For example, in consumer industry, the ability to reduce weight can translate to lighter and more portable computing devices. In addition, lightweight components can also benefit industrial, and defense sector such as automotive and aerospace industries, because lightweight components translates into significant savings in fuel consumption and cost of operation.

However, as devices shrink in size, the amount of heat generated has less space to dissipate. Therefore, thermal conduction of nanometer material places a critical role in controlling the performance of nano/micro devices. Improper thermal management can affect performance, reliability and the life expectancy of the electronic component.

Exploring new material or materials combinations to address this issue is very important and can be beneficial. This research will attempt to address this issue by using materials that are both lightweight and have high thermal conductivity values.

Substituting bulk materials for lighter alternatives has evolved greatly over time. In order to properly select the optimal material for a specific task, balance among performance, reliability, cost, function, and manufacturability should be considered carefully. In the earlier days, natural materials were used such as wood, bulk metal, natural rubber, and simple alloys. As technology advanced, engineered materials such as complex alloys,
ceramics, and synthetic polymers became available. Breakthroughs in advanced engineered technology allowed for the creation of complex engineered materials such as thin films, patterned arrays, nanoparticles, foams, and fiber composites. Today, with the modern technology, specialized materials are engineered through precise technological processes that create customized configurations with specific dimensions and geometries that can range from nanoscale to bulk size. The advanced modern engineering processes enables engineers to combine different materials together to achieve the desired properties, performances and functionalities required for the next generation of products.

In recent years, technology has advanced in ways that allow electronic devices to become more robust, compact, and portable. However, to continue the trend of miniaturization certain issues involving thermal management need to be addressed. As electronic devices shrink in size, components are designed closer together. The amount of heat generated by these components has increased with less area to dissipate. Excess heat, if not rapidly dissipated away from the nanoscale electronic components, can lead to signal instabilities and rapid device degradation over time. To keep these components operating effectively and avoid overheating damage, there is a significant need for efficient thermal management. In addition, one common issue is the failure at the device/substrate interfaces due to thermal expansion mismatch between different compositions. Therefore, optimizing the thermal transport through the interface is necessary to ensure stable performance. This calls for new strategies of integrating emerging materials and/or material combinations for future thermal management devices. One of the ways of
addressing the above issue is to investigate fabrication methods involving advanced materials, structures, and surface modifications for the next generation of thermal management materials suitable for high power electronic devices.

1.2 Motivation

This research is motivated by the need to create lightweight components that are efficient at addressing thermal transport properties. To accomplish this, the focus of the research will be on the investigation of carbon-based architectures that can simultaneously address the demands of lightweight materials as well as and their critical thermal management advantages. The goal is to provide insight for the design and manufacturing of sophisticated multifunctional thermal interface materials in the nanoscale range. This research seeks to incorporate nanomaterials with bulk materials, so that innovative structures with superior performance can be fabricated with specific design metrics.

Carbon is lightweight material that has very strong potential for use in future thermal management devices. Carbon comes in a variety of allotropic forms, and offers high thermal conductivity along specific planes. Combining different forms of carbon can improve thermal throughput while minimizing thermal expansion mismatches and improve device compliance. One configuration of particular interest is a carbon substrate with vertically aligned carbon nanotubes (CNTs) attached perpendicular to the surface. It is believed that carbon materials paired in this configuration would enable higher thermal conductivity interfaces while offering interfacial mechanical flexibility.
Due to its fascinating inherent material properties, CNTs have achieved an iconic status in recent scientific and engineering research communities. These properties include high aspect ratios, lightweight, high thermal conductivity, superior mechanical properties, and attractive electrical characteristics\[1\]–[5]. These properties enhance the attractiveness of CNTs in a wide variety of advanced applications such as biological sensors\[6\], biological applications [7]–[9], antennae [10], purification filters [12],[13], composites\[13]–[17], catalyst supports [9], [12], [18], thermal management [3], [19]–[21] and thermal interface materials [1], [21]. However, current lab-scale devices made with CNTs still struggle to demonstrate properties that are close to theoretically predicted values. Often, the discrepancies are related to the qualities of the CNTs, their arrangements, and the interfaces involved.

Previous model studies have validated that by incorporating CNTs on silicon substrates, the interfacial thermal conductivity of the composite was improved [22]. Currently, many of the CNT-based thermal device studies reported use CNTs in a dispersed manner that is loosely supported on a surface or on electronic silicon substrates. However, thermal transport properties may be improved if CNTs are attached vertically on the necessary substrate. Therefore incorporating CNTs on unconventional lightweight substrates, such as carbon-based solids, should be investigated.

Growing CNTs on carbon substrates has several advantages. Not only are they the same chemically, but they also satisfy the lightweight, chemically inert, and high conductivity requirements needed for robust devices. However growing CNTs on carbon substrate has
known to be challenging, and only a few investigations were conducted in the recent years [23], [24]. In Pulikollu’s dissertation work it was observed that through surface modification, the surface of carbon can change between an inert or reactive surface [23].

It was also found that a reactive surface can promote other carbon structures, such as CNTs, to grow on the surface thereby increasing the surface area by several order of magnitude [7], [12], [23], [24]. Investigations that utilize this new combination of CNT on carbon includes biological applications [7]–[9], water filtration [12], and phase change heat storage [24]. It is also believed that components in this configuration, CNT attached on graphite, benefits thermal applications. CNTs used as a thermal interface material is beneficial because it can make the thermal interface more mechanically compliant, which reduces interface delamination. Additionally, CNTs do not suffer from drying, which is a common problem that thermal greases have, therefore CNT based TIM should prolongs the application usage.

One key issue not adequately investigated so far is in-depth understanding of CNT-substrate interfacial region in these arrays, and the influence of those on physical and thermal properties of the final device. Underlying this region is essential for better understanding the controllability of CNTs growth on carbon substrate as well as the effect of buffer layer usage on carbon substrate for desirable CNT growth. This dissertation research is carefully designed to address some of the above issues by investigating factors that influence CNTs growth on carbon substrates and investigating the feasibility of using CNTs-Carbon hybrid materials as thermal management devices.
1.3 Scope and Objectives

The objective of this dissertation research was to investigate the synthesis of aligned dense carbon nanotubes (CNT) arrays/carpet on carbon substrate suitable for power electronic applications. The investigations were separated into four modules, which were grouped into background investigations and detailed investigations. These modules are highlighted below:

**Background Investigations:**

1. Comparison of different Chemical Vapor Deposition methods

   Several chemical vapor deposition (CVD) growth techniques were compared. The purpose is to find out if dense CNT carpets can be grown on sp$^3$ carbon materials that have high thermal conductivity and low electrical conductivity, such as diamond.

2. Comparison of Surface Modification Techniques

   For this module, the most suitable CVD technique was used as the CNT growth method. The purpose is to investigate the effectiveness of surface modifications techniques on CNT growth. Methods that increase the growth density of CNT carpet on graphitic substrates were identified.

**Detailed Investigations:**

3. Influence of Oxide Buffer Layer Materials
• The purpose of this investigation was to understand if and how different oxide buffer layer material influences CNT growth. Alumina (Al₂O₃) and silica (SiO₂) were selected as the oxide materials for this investigation. Advanced nano-scale coating techniques were used to deposit thin oxide films on flat standard carbon/Si samples. These standard carbon samples were fabricated in the lab, and they were used to provide better experimental controls for the investigation.

• This study module will answer the question, “How does oxide film thickness and growth time influence final CNT carpet height?” In addition, this investigation will reveal if CNT growth is controllable, which is highly desirable.

4. Thermal Properties Analysis

The goal of the final investigation is to see if samples made of CNT-carbon system are feasible for power electronic applications. Thermal diffusivity values of fabricated samples were measured using a laser flash apparatus, while the thermal properties of the samples were calculated. These investigations also show projections on how thermal resistance of the sample can be improved.
CHAPTER 2 Background

2.1 Background and literature reviews

The quest of making smaller electronic devices is one of the main driving forces behind nanotechnology. There is increasingly less room for generated heat to dissipate as electronic devices are reduced in size and weight, therefore, adequate thermal conduction through the nanomaterials becomes more critical. Improper thermal management of electronic systems can dramatically decrease the life expectancy of electronic components. Electronic components often fail at the interface due to thermal stress and mismatching thermal expansion properties between materials bonded together. One way to avoid this issue is to select materials that have similar thermal expansion properties, as well as high thermal conductivity values.

Early reporting of CNT has been on common semiconducting substrates such as silicon or silicon oxide, while other reports reference using loose CNTs incorporated into polymer or grease materials for study of thermal properties. Studies that report growing CNTs on lightweight material such as carbon substrates are less common. Some have reported growing CNTs on diamond seeds [1], diamond nano-rods grown from CNT [2], and simultaneously growth of CNTs and diamond [3]. However, none of these reported growth of CNTs on bulk carbon substrates.
Part of this research effort has been to identify the best ways to grow CNTs on carbon substrates. The investigation begins by summarizing different chemical vapor deposition (CVD) methods of CNT growth on substrates, such as freestanding diamond, that have high thermal conductivity values. Diamond substrate was chosen due to its high strength and high wearability, as well as its low coefficient thermal expansion (CTE), which matches closely with graphite. The CTE values are, 1, 2 and $17 \times 10^{-6} \text{ K}^{-1}$ for diamond, graphite, and copper, respectively \cite{4, 5, 6}. Once the CNT growth on diamond substrates was characterized, the investigation followed with CNT growth on various planar and porous carbon substrates for high-performance thermal applications. Finally, the last portion of the research was defined by thermal evaluations on the CNT-substrate samples grown. The thermal evaluation is very important, as it characterizes the thermal properties of an all carbon system used in this study. By doing so, it will demonstrate the feasibility of using an all carbon system as a thermal management device.

### 2.2 Significance of Carbon and Its Allotropes

Carbon is the sixth element on the periodic table and it has a molecular weight of 12.01g/mole. It resides in column IV of the periodic table. The carbon ground state electronic configuration is expressed as $1s^22s^22p^2$, and it has four electrons in the outer valence shell. Materials in nature tend to minimize energy in order to keep a balance and be in their most stable state. Therefore, it is natural to think that carbon will make four single bonds due to four available electrons in its unfilled outer shell. However, it was
found that carbon comes in a variety of molecular structures that consist of various types of carbon-to-carbon bonds [7], [8].

Hybridized orbitals are formed through the combination of 2s and 2p energy states into sp, sp$^2$ and sp$^3$ electronic configurations. The hybridization also determines the structure, bonding angle, bond energy, and properties of the resulting molecule. For example, carbon is able to form a variety of allotropic forms due to the hybridization of orbitals. Stable and meta-stable forms of carbon consist of graphite and diamond, respectively. The main difference between graphite and diamond is how the carbon atoms bond together. The carbon atoms in diamond are bonded via the sp$^3$ hybridized orbitals that forms a tetrahedral structure.

With sp hybridization, each electron in the 2s orbital hybridizes with one of the 2p orbital to form two sp hybridized orbitals in a straight line with bonding angle of 180°. Carbon structures in this configuration have a single bond and one triple bond with two nearest neighbors, such as ethyne. Next, sp$^2$ hybridization has one 2s orbital and two 2p orbital hybridized to form three sp$^2$ hybridized orbitals. In this hybridization state, orbitals align into a trigonal planar, where the carbon has one double bond and two single bond structures with a bonding angle at 120° and three nearest neighbors such as graphite and benzene. Finally, carbon uses one 2s and three 3p orbitals to form 4 sp$^3$ hybridized orbitals. In this configuration, carbon has four nearest neighbors each forming a single bond with bonding angle at 109.2°. This electronic configuration results in the
tetrahedral shape observed in diamond structures. Figure 1 illustrates several bonded carbon structure configurations.

Figure 1: Allotropic forms of Carbon (Figure from Wikipedia) a) diamond, b) graphite, c) lonsdaleite d) C_{60} buckminsterfullerene, e) C_{540} Fullerite f) C_{70}, g) amorphous carbon, and h) single-walled carbon nanotube

2.3 Diamond versus Graphite

Diamond and graphite are the two most abundant forms of carbon allotropes. Graphite is a stable and diamond is a meta-stable form of carbon. Let us take a closer look at the differences between diamond and graphite as these forms of carbon structures were used as substrates for CNT growth experiments. Diamond and graphite originate from the Greek words of adamas and graphos, which mean “invincible” and “to write” respectively. Although they are chemically the same, their properties are very different. Diamond is a sp^3 hybridized carbon structure, that has four nearest neighbors, tetrahedrally bonded at 109.5° from three other carbon atoms. This bonding structure
produces a regular three-dimensional array of carbon atoms. The carbon atoms in a diamond configuration are tightly bonded.

Graphite, on the other hand, is a $sp^2$ hybridized carbon structure that has three identical bonds that form in a planar configuration. The pi-bonds in this configuration bond cooperatively in plane, while the fourth electron on the graphite is de-localized. This configuration produces strong in-plane covalent bonds and weak de-localized bonds normal to the plane. The weak through plane bonds allow graphene planes to slide parallel to one another. This is why graphite is used as a dry lubricant on metallic locks, heavy machines and writing instruments like the number 2 pencil. In addition, the de-localized electron provides graphite’s electrical conductive property. These are some important fundamental differences between diamond and graphite. Figure 2 illustrates the lattice structure, bulk appearance and the similarities and differences between diamond and graphite physical properties.
2.4 Carbon Nanotube

The structure of CNT is similar to graphite. A single atomic layer (2-D sheet) of graphite is known as graphene. CNTs can be described as graphene sheets rolled up into a tube structure. Graphite is a layered structure, where each carbon atom has three valence electrons in plane making of a net of hexagonal “honeycomb” pattern. It also has a fourth valence electron that is located perpendicular to the hexagonal plane. Due to this fourth bond, each sheet of graphene is located at a distance of 3.35 Å apart in the interlayer direction \[8\], \[9\]. These graphene bonds are connected through weak Van der Waals forces that loosely stack the graphene sheets together. Because of this, the carbons planes can easily glide parallel to one another as well as being cleaved easily. The weak
out-of-plane bonding increases thermal and electrical transport resistances. As a result, graphene and CNTs are anisotropic when it comes to thermal or electrical conductivity. Since their discovery in 1991 [10], CNTs can arguably be considered as another natural allotropic form of carbon. There are two main types of CNTs, single wall CNT (SWNT) and multi-wall CNT (MWNT). This dissertation focuses on the latter. It was through the work of Endo et al. that people saw the first set of SWNT and MWNT in HRTEM images [11]. However, CNTs did not become a significant research topic until Iijima published his findings on tubular carbon structures. Soon after that, other groups published articles on different methods of synthesizing CNTs. Currently, CNTs can be fabricated using a wide variety of methods such as arc-discharge, pyrolysis, laser ablation, electrolysis and chemical vapor deposition (CVD) [8]. This research used CVD (more detail in Chapter 4) to grow CNTs. Several articles have reported theoretical calculations of CNT properties, and it was predicted that SWNTs had metallic or semi-metallic properties based on tube chirality and that MWNT were only metallic [7], [12]. MWNTs were mechanically tested and the results demonstrated that CNTs are much stronger and more flexible than carbon fibers. From these preliminary results and publications, CNTs soon become a leading research area. It was thought that the potential applications of combined properties of CNTs were endless. Some journal articles also identified different morphologies of CNTs, such as spaghetti, bamboo or coiled shaped ones, while others reported observation of cone shaped or bamboo-like shaped [14]–[17]. To make coiled tubes, defects such as pentagon and heptagon shaped rings must be formed. Dekker’s
group named the areas with pentagon or heptagons rings 5-7 defects [13]. These defects are the result of thermolytic processes with different growth rates or agglomeration. Dekker et al, also suggested that locations with pentagon rings exhibit higher residual strain and greater chemical reactivity than hexagonal areas [13]. CNTs are unique because they have a high aspect ratio, a hollow core, high tensile strength, and they are electrically and thermally conductive. Utilizing one or two physical properties, mentioned above, one can incorporate CNT in areas such as gas storage [18], field emission sources [19], high power capacitors [20], nano-switches [21], chemical sensors [22], composites [23], thermal interface materials [24], and the list goes on. However, it is necessary to understand CNT growth and control mechanisms to modify CNT properties to tailor them to a specific application. A portion of this dissertation focuses on understanding variables that affect CNT growth mechanisms and morphology. The proposed future work addresses how CNTs could be used to enhance properties for specific applications.

2.4.1 Physical Properties of CNTs

2.4.1.1 Electrical properties:

It was mentioned earlier that CNTs are a rolled up sheet of graphene. It was understood that CNTs can either be a single-wall SWNT or multi-wall MWNT. SWNTs can be further divided into one of the three types depending on how the tube is rolled up, and they are known as armchair, zigzag, and chiral [7]. According to Dresselhaus, the armchair type of SWNT is the only one that is considered metallic, the zigzag and chiral
types are semiconductors [25]. MWNT are predominately metallic due to its metallic outer shell. According to Kordrostami, a significant benefit of CNTs is that they contain long mean free paths in the micrometer range and can handle a large current density [26]. These are favorable characteristics of material properties for future electronic devices. Furthermore, it’s been suggested that the CNT preparations method can strongly affect the overall electrical property and performance [27].

2.4.1.2 Thermal properties:

Diamond and in-plane graphite exhibit extremely high thermal conductivity values. It has been reported that CNTs exhibit high thermal conductivity that is dominated by phonons at all temperatures along the tube axis. In graphite the phonon only dominates specific heat above 20 K [24]. Kim reported individual MWNT have higher recorded thermal conductivity value than diamond at room temperature with a value of 3000W/mK [24], [28], [29]. Due to the high thermal conductivity value, it may be beneficial to use CNTs heat sink and thermal interface applications.

2.4.1.3 Mechanical properties:

The carbon-to-carbon bond that exists in graphite is one of the strongest in nature. It has been published that CNTs are strong and flexible, which allow it to resist breaking upon bending. CNTs regularly demonstrate an average Young’s Modulus of $Y = 1$-1.8 TPa, which is much higher than carbon fibers with $Y= 800$ GPa [30], [31]. The high strength and flexible nature of CNTs are perfect for areas such as lightweight composites or even atomic force microscopy (AFM) tips.
2.5 Possible Applications with CNTs

It is easy to see that CNTs have the ability to be very versatile and useful in many future applications with the physical properties mentioned above. However, not all CNTs are created equal, due to wide variations in fabrication methods [arc discharge, laser ablation, chemical vapor deposition (CVD)]. To optimize CNT growth parameters a detailed study usually needs to be performed. However even with an optimal recipe developed for one system, it is possible that different tubes can be grown if a different system is used. Three different CVD processes were initially compared and one was selected as the growth method for the remainder of the investigation. The selected growth method was deemed most ideal to achieve the investigation need, while producing CNTs that are aligned and densely grown on the substrate. A detailed description on the different growth methods along with the recipes used is available in Chapter 4.

Using CNT’s high aspect ratio, one can use it to enhance applications in terms of providing more surface area without significant weight addition. Higher surface area allows more reactions to take place simultaneously, which can benefit applications that have reactions dominated by available surface area, such as in the case of catalytic reactions. Applications that can benefit from higher surface areas are scaffolds for cellular growth, cathodes for solid-state lithium ion batteries, and thermal interface materials (TIM). The proposed work for this dissertation focuses on CNTs use as a TIM to enhance heat dissipation for power electronic devices.
The interface is an important location; it is where two different surfaces come together and meet and where all of the interactions and reactions take place. Interactions, such as energy transfer, chemical reactions, diffusion, and physical adhesion/repulsion, are of great interest and are the basic foundation for this research. Understanding the different types of interactions taking place at the interface and how those interactions progress allows one to gain controllability for future designs. The ability to control a reaction allows one to design and engineer tailored products for a specific application. In this case, the application of interest is the thermal management of power electronics.

2.6 Carbon Materials for High Power Electronics Applications

2.6.1 $sp^3$ Carbon $\Rightarrow$ Diamond

Diamond has unmatched physical properties. It is durable, high in thermal conductivity and has the highest electric breakdown field. Due to these properties, diamond is said to be an excellent candidate for power electronics devices [32]. However, natural form diamond is expensive, and therefore hard to justify its use in commercial grade devices. In order to make diamond more affordable for high power electronic devices, studies have shown that laboratory grown diamond films are achievable [33]. One way to make power electronic devices more robust and to address thermo-mechanical stress is incorporation of CNTs with diamond substrate. Successful attachment of carbon nanotubes (CNTs) on diamond substrates can lead to unique/robust creation with superior thermal and mechanical properties. This concept has been demonstrated using modeling
analysis. Roy et al, has shown different geometric configuration how CNT and allotropic forms of carbon can be fitted together, however this was only demonstrated through computational modeling [34]. Some have reported the growth of CNT on diamond seeds [1] or diamond films [33]. However, research that grows CNT on diamond substrates is low. Chapter 4 addresses the inadequacies in the area of diamond-CNT growth research by investigating what growth techniques and growth parameters can be used to grow dense CNT carpets (without the substrates showing underneath) on diamond substrate. This was accomplished by using three CVD techniques to grow CNTs on polished diamond substrates.

2.6.2 $sp^2$ carbon ➔ Graphitic and Vitreous

Graphitic material is electrically conductive, whereas diamond is not. Certain high power electronic applications may find this property useful. In addition, graphitic material is lightweight and is available in a wider geometric selection such as bulk substrate, foam, and loose particulates. These features can be useful in areas such as aerospace, composites, and impact absorptions just to name a few. However, research that incorporates CNT with graphite also remains low, because the majority of CNT research uses electronic grade silicon as substrate. This investigation will address the limited information in areas of graphite-CNT by providing a systemic investigation for growing CNT on planar and porous carbon substrate and test the feasibility as a thermal interface management material.
2.7 History of Buffer Layer Usage for CNT Growth

This section highlights the history of buffer layer usage for CNT growth. It will show what material has been used as buffer layer and their successfulness in enhancing CNT growth density.

2.7.1 Background: Evolution of buffer layers

Although there was not a lot of information regarding investigation of buffer layer for CNT growth on carbon substrates, buffer layer investigation has been well reported for CNT growth on other substrates.

When CNTs were discovered researchers thought they could have great potential in thermal and electrical applications. Many of these applications require perfectly uniform contact at the interface in order to have a low (thermal or electrical) interface resistance. One approach originally used to create a low contact resistance was to grow the CNTs directly on metallic surfaces. Soon after, the research groups found that CNTs grown on metallic surfaces were of very poor quality. Mainly, the CNT growth was hindered by strong chemical activity between the catalytic particle and the substrate. The following sections illustrate some materials that researchers have explored to find the ideal buffer layer material for CNTs growth.
2.7.2 Pure Metallic buffer:

The study done by Du et.al, grew CNT directly on nickel substrate and the result revealed CNTs nucleated from fragmentation of nickel surface and the resulting CNTs were spaghetti like, low density and had poor controllability [35]. Another attempt was done by another group, by roughing up the surface with wet etching [36] or polishing [37] and ended with similar results. The next logical attempt was to grow on other type metal substrate, perhaps an alloy.

2.7.3 Alloy Metallic buffer:

Certain alloys have higher resistance to catalytic diffusion than pure metals, therefore some groups attempted to grow on alloys or alloy coated substrates. Researchers who attempted growth on alloys such as, stainless steel [38], [39], mumetal (Ni:Fe 77:14%) [40], and Inconel [41] did find an increase in growth density of CNTs forest. These improvements are said to be the cause of increased carbon precipitation rates when these alloys are used a catalyst particles. However, the resulting CNTs diameters are usually large and non-uniform.

Ternary phase diagrams are often used to provide a starting point for the researchers to select possible buffer layer material. These ternary phase diagrams would usually include metallic materials that are known to be good catalytic sources for CNTs growth. Figure 3 is a ternary phase diagram of stainless steel made from elemental Ni, Fe and Cr. Figure 4 shows the result of CNT growth when stainless steel alloys composed of Ni, Fe,
and Cr were used as catalyst layer, the result was reported from Hiraoka et al. [42]. The result indicated that Ni-based alloy with Cr or Fe are excellent for SWNT synthesis, while pure metals (Ni, and Fe) and alloys made with Fe-Cr produces both SWNT and MWNT types of CNTs.

Figure 3: An example of a ternary phase diagram for alloys [42]

Figure 4: An example of CNT growth on various alloy substrates [42]
2.7.4 Non-metallic buffer:

There are two main groups of non-metallic materials that have been tried as buffer layers. The first is the oxide group and the other is the nitride group. It wasn’t long before reporting of dense forest growth of CNTs using oxide based buffer layers. In addition the increasing the quantity of CNT, the morphology also becomes more aligned [43], [44]. Other non-oxide ceramics have also been used, such as nitrides, carbides, and carbonates. The results indicate that Al$_2$O$_3$ is one of the best buffer oxides for CNT growth. There are many ways to grow CNT, and it is important to keep in mind that a good quality of buffer layer should restrain the diffusion reaction between catalytic particle and the substrate, while minimizing the effect of this layer on the property of the device. Chapter 6 compares the influence that alumina and silica have on CNT growth. Section 3.3 listed some of the fundamental differences observed between the two oxides.

2.7.5 Critical buffer layer thickness:

Several research groups have suggested that in order to fully prevent catalytic particles from having a reaction with the substrate, a certain thickness of buffer layer must be used [45]–[47]. Since the activation energy required for reactions between two materials are materials dependent, the estimated oxide thickness will depend on which material are used. The thickness should be greater than the mean diffusion distance that catalyst material can travel during the growth time. This distance can be calculated using the diffusion coefficient equation (D), activation energy ($\varepsilon$), and temperature (t).
\[
D = D_0 e^{-\epsilon/kt}
\]

Equation 1: Arrhenius Equation

\[
\lambda = \sqrt{Dt}
\]

Equation 2: Diffusion Distance (λ)

Simmons et al. gave the following example, the diffusion coefficient of iron in silicon dioxide is \(D \approx 10^{-4} \text{ cm}^2 \text{ s}^{-1}, \epsilon = 2.8 \text{ eV}\) [45]. Therefore according to the equation, the diffusion length was 1.5 nm for iron, and 12 nm for Co, and 2.5 mm for Ni [45], Figure 5. However, the experimental observation of the diffusion was observed to be longer. The longer diffusion length was said to be due to higher concentrations of pinholes on the thin films. Figure 5 below summarizes the diffusion of different metals observed on silicon substrates.

<table>
<thead>
<tr>
<th>Metal</th>
<th>(D (\text{cm}^2/\text{s}))</th>
<th>(\epsilon \text{ (eV)})</th>
<th>(T \text{ (K)})</th>
<th>(\lambda \text{ (nm)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>(10^{-4})</td>
<td>2.8</td>
<td>900</td>
<td>1.5</td>
</tr>
<tr>
<td>Co</td>
<td>(10^{-7})</td>
<td>1.7</td>
<td>900</td>
<td>12</td>
</tr>
<tr>
<td>Ni</td>
<td>(10^{-9})</td>
<td>1.6</td>
<td>900</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Figure 5 Chart showing the diffusion distance for different metals on silicon at 900K, Simmons et al. [45]
CHAPTER 3: Materials and Techniques Used In This Investigation

The purpose of this chapter is to introduce the different materials, processes and techniques used in this project.

3.1 Materials used as substrates

3.1.1 Dense carbon (sp³) ➔ Diamond Substrates:

Diamond is a unique material that no other material can match in terms of thermal, mechanical, chemical or optical properties. It has been sought after as an ideal material for high power electronic applications. It has been reported that diamond has a high breakdown field strength of 10 MVcm⁻¹ as well as high thermal conductivity values >2000 W/m-K [1]. Although there are many different grades of natural and laboratory grown diamonds, a typical thermal conductivity value of a diamond substrate would have a value that is 2-5 times higher than a pure copper (385 W/m-K) and almost 4 -10 times higher than an aluminum nitride (140-180 W/m-K) [2]. To put it in perspective, Figure 6 shows the relative amount of diamond material required, comparing to silicon and other materials to block 10 kV. The figure shows that the amount of diamond required is less than 10% of what is required of silicon. Therefore diamond is thought to be an excellent candidate to be incorporated in electronic devices for thermal management. In addition, due to its wear resistant properties, diamond is thought to be an excellent material choice for use in harsh environments (corrosive and extreme temperatures.)
However, naturally formed diamond is very expensive so efforts have been made to produce diamond films in a laboratory setting. Currently, a wide variety of synthetic diamond is available for commercial and consumer purchases, including (loose diamond, diamond film, polished free standing diamond substrates).

Figure 7 is an Atomic Force Microscopy (AFM) image of the surface roughness of a purchased lab grown diamond substrate used in this study. The diamond substrate was purchased from SP3 Inc., and the measured surface roughness has a value of 14.35 nm.
3.1.2 Lightweight carbon ($sp^2$) materials ➔ graphite, CNT, carbon foams

The other carbon allotrope used in the investigation was of the $sp^2$ bonding configuration. These forms of carbon are lighter in comparison to diamond and are mostly graphitic, while some amorphous carbons can also have the $sp^2$ bonds. Graphitic carbons are electrically conductive and have an electrical conductivity value about $1 \times 10^5 \text{ S/m}$. The combination of lightweight and electrically conductive properties can be very useful for certain space industry power electronic systems. Below is an introduction on the physical properties of a variety of $sp^2$ carbon used in the investigation.

3.1.2.1 Pressed Graphite:

Industrial grade pressed graphite is commercially available and is used as heating strips in certain applications. Pressed graphite is formed by compressing carbon flakes under high pressure. Samples of this material were purchased from POCO Inc, with a grade of AUX-5. The orientation of the graphite flakes are random, therefore the thermal property of the material is isotropic. The material specification sheet is shown in Figure 8.
Figure 8: Material property of POCO graphite.

3.1.2.2 RVC foam:

Reticulated vitreous carbon (RVC) foam was purchased from Ultramet, Inc. According to the manufacturer, RVC foams is consisted of 97% open porosity, with three-dimensional interconnected network of solid struts. Each open cell can be modeled as 14-faceted polyhedral or commonly known as tetrakaidecahedron [4]. Due to the way these foams are manufactured, each strut has a triangular cross-section. Ultramet, Inc. provides carbon foams with various pore densities ranging from 10 pores per inch (PPI) up to 100 PPI. The pore diameter and relative density characterize each foam size. For this study, as received RVC foams have a measurement of 45 PPI and a specific surface area of $3\times10^3$ m$^2$/m$^3$ [5]. These foams are made up of amorphous glassy carbon that
provides high specific surface area, are easily machined, and are lighter than bulk carbon substrates. Figure 9 is a table from the manufacturer’s data sheet, and Figure 10 is an SEM image of a RCV foam, showing the microstructures of the struts.

<table>
<thead>
<tr>
<th>Reticulated Vitreous Carbon Foam, Ultramet Inc.</th>
<th>Thermal conductivity, W/mK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Size available</td>
<td>10, 20, 30, 45, 65, 80, and 100 ppi</td>
</tr>
<tr>
<td>Ash content</td>
<td>0.39 wt% at 10000 °C</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.045 g/cc</td>
</tr>
<tr>
<td>Ligament density</td>
<td>1.538 g/cc</td>
</tr>
<tr>
<td>Resistivity</td>
<td>0.75 Ω cm</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0.3 cal/g/ °C</td>
</tr>
<tr>
<td>Maximum use temperature</td>
<td>350 °C in air</td>
</tr>
<tr>
<td>Thermal expansion, ppm/ °C</td>
<td>at 950 °C</td>
</tr>
<tr>
<td>0-200 °C</td>
<td>1.15</td>
</tr>
<tr>
<td>0-500 °C</td>
<td>1.65</td>
</tr>
<tr>
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<td>Compressive Strength, kPa at 20 °C</td>
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<td>at 1000 °C in argon</td>
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Figure 9: Material property of Ultramet RVC foam.

Figure 10: SEM image of 45ppi RVC foam.
3.1.2.3 *Highly Oriented Pyrolytic Graphic (HOPG) from SPI, Inc*:

Highly Oriented Pyrolytic Graphic (HOPG) was purchased form SPI, Inc. HOPG is a carbon material that characterized by a preferred crystallographic arrangement of carbon sheets stacked in lamellar fashion where each layer of graphite is parallel to the surface of the substrate. According to company data, all of the sheets are within 1 degree of deviation from the surface. The lamellar structure provides a very strong force in the lateral direction of the plane and weak Van-der Waal forces between planes. The weak bonding between the planes allows samples to be cleaved easily from the bulk sample. HOPG is usually processed using a hot working technique, and then annealed under compressive stress at a high temperature near 3000K [6]. As a result, HOPG is high purity graphite, and contains ash content less than 10 ppm, Figure 11.

![Figure 11 HOPG from SPI](image-url)
The HOPG substrates used in this study are a grade 3, and were purchased from SPI, Inc. The “grading” is defined by the manufacturer, which correlates with degree of alignment between the graphene sheets. Grade 1 is the highest grade, according to the company, with an $0.4^\circ \pm 0.1^\circ$ alignment between the graphene sheets, while Grade 3 is the lowest grade with an $3.5^\circ \pm 1.5^\circ$ alignment between the graphene sheets. According to SPI, Inc, this material consists of parallel oriented stacking graphite sheets, with a surface roughness measured to be 0.2-0.3 nm in steps. Each step contains approximately a dozen atomic layers of graphene. Due to its highly ordered stacking nature, the thermal property of this material is anisotropic. SPI quotes the thermal conductivity at 1800 W/m-K along the basal plane, and 8-10 W/m-K in the Z (through thickness) direction. This material can be used up to 500 °C in air, up to 2500 °C under vacuum, and up to 3500 °C in inert atmosphere. Figure 8 shows the surface roughness image taken from AFM. The AFM scan was taken from one of the HOPG substrate used in the study, and the average root mean square (RMS) value was $4.36 \pm 0.1$ nm.
3.1.2.4 Model carbon samples

The purpose of this step is to fabricate a surface that is made of same chemical composition as carbon foam, however, on a flat substrate. This process is simple, controllable, and repeatable. Manufacture of carbon layer on silicon was done using the following process, and the resulting sample is named Model Carbon Sample. The process began by cleaning the Si samples using a Radio Corporation of America (RCA) cleaning procedure, which is a standard wafer cleaning step. Shipley 1813 photoresist was used to graphitize the surface of a silicon wafer. Shipley 1813 is composed of electronic grade propylene glycol monomethyl, ether acetate, mixed cresol novloak resin, fluoroaliphatic polymer ether and proprietary trihydroxybenzophenone. These silicon samples were spin coated with Shipley 1813 photoresist at 5000 rpm for 35 seconds. The coated samples were cured at 150 °C on a hot plate for one minute. The samples were then annealed for 10 minutes in a horizontal tube furnace at 750 °C in Argon ambient at a flow of 2 SCF/hr (standard cubic feet per hour).
vitreous carbon layer pyrolyzed on the silicon wafer surface had an average thickness of 450 nm. Figure 13 is a schematic drawing showing the development of the Model carbon sample.

![Pyrolyzing Carbon on Si Substrates](image)

**Figure 13** Schematic drawing of model carbon sample preparation

### 3.2 Metals Catalysts Materials:

Iron and nickel were selected as catalyst sources for this study. These materials have been reported in the literature to be great catalytic sources for CNT growth [7]–[10]. Catalyst sources can be introduced differently, depending on the growth methods used or required. For traditional growth methods, iron or nickel catalysts are sputtered onto the growth substrates. For newer and more scalable methods, organometallic compound containing iron particles are injected into the growth chambers using a syringe pump. Ferrocene was used in this investigation as the iron catalyst source for the floating catalyst CVD growth technique.
3.3 Oxide Buffer Layer Materials and Comparison:

3.3.1 Oxide Materials for the Investigation

The two oxide materials that were used in this studied were alumina (Al$_2$O$_3$) and silica (SiO$_2$). The oxides were used as a buffer layer to promote CNT growth density and to enhance the CNT morphology. It was important to know the effects of these oxides have on CNT growth characteristics. Here are some of the fundamental differences between these two oxides. Figure 14 shows the physical properties of these two oxides, alumina and silica. The figure shows that the intrinsic property of the oxide can change, due to different defect concentration or network formers. It has been reported that different deposition methods can lead to the creation of oxides with different defect concentrations [11]. Therefore, it is important to compare the effect of oxide material differences and to compare effects associated with purity differences. The investigation for the influence of oxide buffer layers can be found in Chapter 6. Sections below introduce different oxide materials used in this investigation along with their deposition techniques.
3.3.1.1 Alumina (Al₂O₃):

Single alumina crystals have a corundum crystal structure and a density of 3.89 g/cm³. However depending on how the oxide films are made (deposition or growth techniques) alumina can be crystalline or amorphous. Alumina is a high dielectric material with a dielectric constant of 9.8 at 1 MHz, it has a thermal conductivity value that ranges from 18 - 35 W/m-K, and coefficient of thermal expansion (CTE) value about 8.1 - 8.4 range. A sapphire substrate was also used in one of the study; this substrate was purchased from University Wafers with a 001 orientation.

3.3.1.2 Silica (SiO₂):

Silica is made up of network formers, which means that the crystal structure is mainly amorphous. Silica has a dielectric constant of 3.8 at 1 MHz, it has a thermal conductivity value about 1.4 W/m-K, and a CTE value that ranges from 0.55-12.3.
A fused quartz substrate was also used in one of the studies; this substrate was purchased from Technical Glass Products, Inc.

3.3.2 Formation of Oxide Buffer Layer Materials

This investigation used several different deposition techniques to obtain the desired thin film materials. The information about each thin film type is listed in this section.

3.3.2.1 Thermal Silica:

Silicon wafers were used to support this study because they are a standardized commercial material that is readily available to the electronic device community. The silicon wafers were sold with a layer of thermally oxidized silica layer on top measuring $1 \times 10^{-6}$ m in thickness. Samples used in this investigation were purchased from University Wafers with a 001 orientation.

3.3.2.2 Alumina by Atomic Layer Deposition:

Trimethylaluminum ($\text{C}_6\text{H}_{18}\text{Al}_2$) is an organometallic compound used as a precursor chemical during the atomic layer deposition process (ALD). This compound is primarily a dimer at room temperature. Its chemical structure is made up of two aluminum atoms and each atom is attached by two free methyl groups and two shared bridging methyl groups. In this study, this precursor, when used in an ALD process reacts with the surface O-H functional groups and deposits an aluminum monolayer. Next, the
aluminum layer reacts with water vapor molecules to form an aluminum oxide layer while simultaneously releasing a methane molecule back into the environment.

3.3.2.3 Silica by Atomic Layer Deposition:

Tris(dimethylamino)silane ((CH₃)₂N)₃SiH is an organosilicon compound used as a precursor chemical in ALD to deposit SiO₂ thin films. This chemical is considered to be a toxic organic liquid and is a pyrophoric open air. Its chemical structure consists of a silicon atom sitting at the center of the molecule; it forms one bond to a hydrogen atom and three separate bindings to (dimethylamino) groups. The silica ALD process is a four step process that involves saturating the surface with a thin layer of O-H groups, followed by purging the excess chemicals through a self-limiting process. However, the chemical process rate at which silicon oxide happens is much slower than aluminum oxide. Therefore, a longer precursor residence time is required to deposit a monolayer of silicon oxide.

3.3.2.4 Microwave Plasma Silica:

Another type of silica coating used in this study was deposited by a method called microwave plasma enhanced chemical vapor deposition (MPECVD or MPD for short). The procedure used in this study was the one developed by Dr. Pulikollu as part of his dissertation work. Early CNT growth studies has stated that CNT growth density tends to increase when a layer of oxide was deposited on graphitic carbon or carbon foam[12]--
[14]. Below is the recipe used in this investigation, but developed by Dr. Pulikollu and Dr. Barney for their dissertation work [15], [16].

The silica coating deposition uses gas phase precursors in microwave plasma CVD reactor. The reactor repeats three different steps in order to build up oxide thickness.

The three steps are as follows:

1. Pure oxygen, \( \text{O}_2 \) (99.99%) gas, was introduced into the microwave plasma chamber for 180 seconds. The gas has a flow rate of 50 mL/min. The chamber pressure was 48 Pa, and the microwave power was 225 W.

2. Pure oxygen, \( \text{O}_2 \) flow at 50 mL/min in 56 Pa. Hexamethyldisiloxane (HMDSO) flowing at a rate of 2 mL/min with microwave power of 250 W for up to 300 seconds. This step deposits the silica layer so the timing is important.

3. To stabilize the oxide coating, \( \text{O}_2 \) carrier gas flow at 50mL/min in 48 Pa was introduced into the chamber at a microwave power of 150W for 60s.

The oxide coating thickness can be varied by modifying step 2, in the recipe.

In Dr. Barney’s dissertation, he mentioned that the coating grows by island formation and coalesces after 1 minute to form a uniform layer. At 1 minute of deposition, the film is measured to be about 4-5 nm with a roughness of less than 1 nm. The MPD method deposits silica as an amorphous layer. This silica chemically bonds to carbon surface as a Si-C bond at the interface.
3.4 Material for floating catalyst CVD growth

3.4.1 Xylene:

Xylene (C₆H₄(CH₃)₂) is an organic solvent. Its chemical structure consists of two methyl groups attached to a benzene ring. The location of the methyl group can vary in one of the three available positions on the carbon thereby making isomers [ortho-, meta-, and para- xylene]. The xylene used in this work is meta-xylene (m-xylene) from Sigma-Aldrich. The purpose of the xylene is to dissolve ferrocene powder and to act as a vapor carbon source during CNT growth. Xylene has a boiling point of 138 – 139 °C, and is a clear liquid at room temperature.

3.4.2 Ferrocene:

Ferrocene (Fe(C₅H₅)₂) is an organometallic compound. Its chemical structure is made up of two cyclo-penta-dienyl rings attached with an iron atom in the middle. Ferrocene can easily be dissolved in organic solvents, such as one used in this study, m-xylene. At room temperature, ferrocene is stable and appears as a yellowish orange powder. The ferrocene used in this investigation is Acros Organic 98% with given melting temperature of 173 – 176 °C, boiling point of 249 °C, sublimation point at 100 °C, and molar mass of 186.04 g.
3.5 CNT growth Techniques

In this investigation chemical vapor deposition (CVD) was used to grow CNTs. The cost effectiveness and scalability of CVD make it ideal for systematic investigations. However, it is worth mentioning some of the other techniques that can be used for CNT synthesis. To grow CNT, a carbon source, a catalyst source and a heat source are all that is required. Because of this simple ingredient, there are many techniques that can be used to grow CNTs. As a background, this section will mention some of the major techniques used to grow CNT, and then introduce different CVD techniques used in this investigation, follow by the growth recipes used in this investigation.3.5.1 Growth Methods Not Used in this Investigation

The reviews published by Terrones et al. and Kumar et al. outline the different methods that are available for CNT growth [17], [18]. Namely they are: electric arc-discharge, laser ablation, and chemical vapor deposition (CVD).

3.5.1.1 Arc-discharge:

The first CNTs were discovered while using the arc-discharge method [22]. This method uses direct current (DC) to produce an arc between two graphite electrodes that are spaced about 1 mm apart in an inert gas filled chamber at low pressure. The electrodes are usually cylindrical in shape and the arc is usually very high temperature, ~4000 °C. The resulting CNTs from this process are usually very graphitic with minimal
defects; however, the entire batch may contain products that are not CNT, such as soot or fullerenes. To obtain CNTs, catalyst sources were needed, without catalyst sources only soot was formed [23]. Common operating parameters include a DC current between 50-100 A, and 20 V [24]. The arc discharge vaporizes the surface of one graphite electrode and deposits the result onto the other electrode.

3.5.1.2 Laser ablation:

This method uses a laser pulse to ablate and to evaporate high-purity graphite targets at high temperature [22], [25], as a result, highly graphitized CNTs are able to grow on a sample surface. However, the production yield is very low and aligned growth is difficult. The benefit of this method is its ability to produce good quality single wall CNT (SWNT). The production of SWNTs using this method can be controlled by controlling parameters such as target composition, temperature and pressure.

3.5.2 Growth Methods Used in this Investigation

Information regarding CNT growth on carbon surfaces is very limited. Therefore, different growth methods were explored to determine the feasibility and ease of production. Three CVD growth techniques were tested to determine the feasibility of growing CNT $sp^3$ structures. Out of which one growth technique was selected for the remainder of the investigation to produce readily comparable CNTs.
Since their discovery, CNTs have been fabricated using numerous growth techniques and recipes, as mentioned above. However, that doesn’t mean that the resulting CNTs the same intrinsic properties, due to resulting morphology differences. To start the CVD investigation, recipes used to grow CNT in this investigation were adopted from published literatures that were demonstrated to be a successful in producing CNTs. The growth recipes were first replicated by using the CVD equipment, used by this investigation, to grow CNTs on electronic grade silicon substrate with thermal silica oxide layer. After successfully validating the CNT growth on the silicon substrate, the process was repeated on the purchased diamond substrate. This investigation of CVD growth on diamond substrate is discussed in Chapter 4. The results from Chapter 4 allowed for the down-selection of the growth technique for the remainder of the investigation. Exploring successful methods of growing CNT on $sp^2$ carbon can be found in Chapter 5. The section below provides a description of each of the three CVD methods used in the investigation along with a description of the growth recipe used in the investigation.

3.5.2.1 Chemical vapor deposition (CVD):

This method is one of the more preferred methods used to grow CNTs due to its low set up cost, large CNT yield, and ability to be optimized [18], [26]. There are several different types of processes available and this investigation has chosen 3 CVD methods for further investigation. Namely the thermal CVD (TCVD), microwave plasma
enhanced CVD (MPECVD), and floating catalyst CVD (FCCVD). Generally speaking, a CVD process starts with passing a hydrocarbon source (methane, acetylene, acetone etc.) through a horizontal tube furnace that contains a substrate with metallic catalytic material at high temperature (500 – 1200 °C). The catalytic material decomposes the hydrocarbon into the carbon source needed for CNT growth. The CNTs nucleate from catalytic particles. CNT synthesis using this method requires controlling the following parameters very closely; carbon source, temperature, pressure, catalyst, feedstock gas, substrate, buffer layers and growth time. This method is known to grow both aligned and, non-aligned CNT carpets with, high and low yields, it can facilitate tip and root growths, as well as SWNT and MWNT. Depending on the application, certain CNT morphologies can be more desirable then others. The benefits of CVD growth technique is that it is versatile so that one can work to optimize the system in order to facilitate the growth of desired CNT morphology.

3.5.3 General and Specific Growth Recipes

3.5.3.1 Thermal (CVD):

Thermal CVD (TCVD) is one of the traditional growth techniques. This technique consists of a furnace, feedstock gases, and an optional vacuum attached at the exhaust end. TCVD is a two-step process where deposition of a catalyst layer is required prior to CNT growth. Before the metallic thin films can be used as catalyst, a heat treatment step
is required to coalesce the catalyst particles from the metallic films. Once the catalyst particles are formed, passing of carbon and feedstock gas into the tube furnace, in the growth temperature range, can facilitate CNT growth over time.

3.5.3.1.1 Referenced TCVD Method

For the thermal CVD process, prior study by Varanasi et al. reported growing CNT on diamond film using alloy Ni-Fe-W has shown success when using acetone + Argon (10%:90%) mix bottle, and feedstock gas H$_2$ + Argon (5%:95%) flowing at 400 and 300 standard cubic centimeters per minute (sccm), respectively [27]. With a growth temperature ranged from 750-800 °C. The growth was performed at a pressure of 90 Torr, with a growth time that ranges from 10 – 20 minutes.

3.5.3.1.2 Specific TCVD Recipe Used in this Investigation

As stated above, TCVD has a wide growth temperature range; after several growth attempts it was decided that the following setup was most suitable for this investigation. The growth parameters used in this investigation are as follows: To minimize the contaminants in the growth chamber, after the samples are loaded, the system was evacuated to less than 10 mTorr and held there for at least 15 minutes. After which, Ar+H$_2$ was allowed to flow for 15 minutes at 90 Torr to remove any remaining contaminates. The chamber is heated to 800 °C while keeping the gas flow and the chamber pressure at 90 Torr. After the temperature reaches 800 °C, an annealing time of 10 minutes was used to allow catalyst particles to coalesce. Next a C$_2$H$_2$ + Ar (10% +
90%) mix was introduced into the chamber with a growth time of 20 minutes. After which, the carbon source was terminated from flowing into the chamber. Finally turning off the power source to the heating element, the chamber was cooled to room temperature with a constant flow of Ar+H₂ gas.

Other growth temperatures (700-850 °C) were briefly explored using electronic grade silicon substrate with thermally grown oxide layers, but it was found that 800 °C provided the most uniform CNTs.

3.5.3.2 Microwave Plasma Enhanced (CVD):

MPECVD is also a traditional growth technique. This technique has two energy sources, one is a heating stage, and the other is H₂ plasma generated from a direct current, radio frequency (RF) or microwave power supply. The plasma generated can dissociate the carbon sources required for CNT growth at a lower temperature and pressure than most other CVD. Similar to TCVD, this technique is also a two-step process where deposition of a catalyst layer is required prior to CNT growth. A heat treatment process is required to coalesce the catalyst particles from the metallic films. In general MPECVD system use up to 1kW of microwave power transmitted from the generator through a wave-guide to a microwave coupler that emits the radiation via the antenna into the CVD chamber. When the ideal parameters are reached, plasma is formed, centered over the substrate to facilitate CNT growth for samples. Since the size of the plasma can be controlled it is
possible to grow CNT over an area that is larger than 10 cm\(^2\) [28]. The following parameters are necessary to control the plasma: microwave power, chamber pressure, gas source, flow rate, and chamber temperature.

3.5.3.2.1 Referenced MPECVD Method

For the MPECVD process, Crossley et al. and Wong et al. reported growing CNT on SiO\(_2\) coated silicon sample and showed success in using a two-step process where a heat treatment step was performed at a lower temperature followed by growth temperature at a higher temperature [28], [29]. In this process, after samples were loaded into the growth chamber the chamber is evacuated below 10 mTorr. Then the graphite stage and substrate are heated to 400º C in a hydrogen atmosphere of approximately 20 Torr. A catalyst pretreatment phase was started after the system reached steady state to allow thin catalyst films to coalesce into catalyst/nano-particles, necessary for CNT growth. The pretreatment phase exposed the catalyst layer to a H\(_2\) plasma induced by 400 W of microwave power for 5 minutes. The microwave power was terminated at the end of the pretreatment phase and the temperature was increased to 650º C at the same gas flow and pressure. The growth phase occurred for 2 minutes at 650º C, 1000 W of microwave power, with a hydrogen and methane (CH\(_4\)) mix. After the growth stage the microwave power and the heating stage were terminated, allowing the system to cool to room temperature while maintaining the hydrogen flow and chamber pressure.
3.5.3.2.2 MPECVD Recipe Used in this Investigation

To take a full advantage of MPECVD’s capability to produce CNT at lower growth temperatures, the growth temperature was limited to 650 °C during this study. After the substrates were loaded, the chamber was evacuated below 10 mTorr to ensure growth chamber cleanliness and to minimize potential contaminants. Then the graphite stage and substrate were heated to 400 °C in a hydrogen atmosphere of approximately 15 Torr. Once the system reached a steady state, the catalyst pretreatment phase coalesced from a catalyst metal film into nano-particles necessary for CNT growth. The pretreatment phase exposed the catalyst layer to a H$_2$ plasma induced by 400 W of microwave power for 5 minutes. The microwave power was terminated at the end of the pretreatment phase and the temperature increased to 650 °C while maintaining the same gas flow and pressure. The growth phase occurred for 2 minutes at 650° C, with hydrogen and methane (CH$_4$) mix, and 1000 W of microwave power. The microwave power and the heating stage were terminated after the growth stage, while maintaining the hydrogen flow and chamber pressure the system was allow cooling back to room temperature. Other parameters such as pressure range from 5 – 25 Torr, while growth temperatures (400-600°C) were briefly explored. However, these parameters were not used due to difficulties in creating or maintaining plasma or resulting in CNT growth.
3.5.3.3 Floating Catalyst (CVD):

The growth system was very similar to TCVD, where 1 inch diameter, horizontal furnace tube was used. The furnace used reaches a maximum temperature of 1200°C. The main advantage the FCCVD process is that it is a one-step process, which introduces the carbon and the catalyst source simultaneously into the growth zone.

3.5.3.3.1 Referenced FCCVD Method

For the FCCVD growth method, the investigation used the optimized procedures reported in in Barney’s dissertation [30], where substrates were first coated with plasma silica prior to CNT growth. The carbon and catalyst source used in this investigation was xylene to ferrocene. The xylene acts as the carbon feedstock while ferrocene decomposes at high temperatures to provide the catalytic iron particles required to nucleate for CNTs growth[31] To prepare solvent solution for this task, 0.12 g of Ferrocene was dissolved in 10 mL of xylene to be delivered into the growth chamber. Carrier gas used was Ar and H₂ from independent gas bottles flowing at a ratio of 100/50 sccm, respectively.

3.5.3.3.2 FCCVD Recipe Used in this Investigation

To prepare the growth chamber for CNT growth and to eliminate as much contaminants as possible, after the samples were loaded, the carrier gas Ar and H₂ was introduced into the chamber flowing at 100/50 sccm, respectively. This carrier gas was used through the entire FCCVD growth process, from initial stage of preparation of the growth chamber,
to elevating temperature to growth temperature of 750 °C, and finally cooling the chamber back to room temp. The carbon and catalyst source were only introduced after the temperature reached a steady state of 750 °C, and this source was injected at a rate of 3mL/hr for 20 minutes. The default growth time for this study was 20 minutes, however, other studies had growth times that varied based on the required experimental conditions and are noted in the results.

3.5.3.4 Sample Recipe Comparisons:

Figure 15 compares the list of ingredients and the growth parameters used for the three different types of CVD. Each growth technique has pros and cons regarding usability and production quality. However, the goal was to see which growth techniques could produce dense CNT growth on carbon substrates, and determine the most suitable method for this investigation. To read more about the background study that compares the resulting CNT using the recipes below please see Chapter 4.

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<th>Newer Approach</th>
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3.5.4 Growth mechanisms

It has been observed and published that CNTs have two growth modes, a tip growth and a root growth mode[32]. It has been reported that particles greater than 5 nm favor tip growth when grown on silicon, while particles greater than 5 nm favor root growth when grown on silica [33]. Both of which can produce CNTs that are highly crystalline in the (002) plane. In the tip growth mode, decomposed carbon feedstock reacts with the top portion of metallic catalytic particle and results in H$_2$ and C$_n$ species. The carbon species diffuse through the metallic particles followed by precipitation of CNT from the opposite end of the catalyst particle. This process is continued until metallic particles no longer react [34]. The root growth mode occurs when carbon moves through catalytic particle from the surface of the substrate, and precipitates from the top of the catalytic particle, while remains anchored at the surface of the substrate.

There are two types of CVD process, a traditional method and a newer more scalable method. The traditional require a two-step process for CNTs growth and the newer technique is a one-step process. Both types were explored in this dissertation. Although, CNT growth mechanisms are still a highly debatable topic and regardless which type of growth process is used. The general consensus, however is that the following must take place in order for CNTs to grow: (1) Hydrocarbon vapor is carried by inert gas into the growth zone that is at a significantly elevated temperature. (2) The presence of catalytic
particles in the growth zone will decompose the hydrocarbon into a carbon source. (3) Carbon sources diffuse through the metal particles. (4) Formation of graphitic structures at the apex (side farthest away from the substrate) of the catalytic particle is achieved through nucleation or precipitation [18], [34]–[36].
3.6 Surface modification methods

It was observed that growing CNT directly on $sp^2$ carbon surfaces was challenging. Therefore, some surface modification steps were taken to see which ones were effective in enhancing CNT growth density. The following is a description of the different surface modification techniques that were used in various parts of the investigation, with a majority of the comparisons made in Chapter 5. It is placed here as a reference if required. The treatments are separated into two groups. The first group covers the surface oxidation method by adding oxygen containing groups to the carbon surfaces. The second group covers the deposition of oxides onto the carbon surface. In addition, reactive ion etching (RIE) was used in order to provide surface roughness variation. This was done as a secondary surface modification technique.

3.6.1 Surface Oxidation Techniques

3.6.1.1 Nitric acid:

Nitric acid was used as another surface modification method. It was demonstrated that nitric acid can create surface defects on carbon, it was reported that such defects can enhance CNT growth on carbon surfaces [37], [38]. This treatment used 50 mL of 70% nitric acid at 100 °C for either a 4 hr or an 8 hr interval. The samples were dried in a vacuum furnace at 100 °C for 24 hours.
3.6.1.2 Oxygenation:

This investigation explored the use of oxygenation treatments as a way for surface modification. The purpose of an oxygenation treatment is to create surface defects (such as voids); it was believed that these defect sites could enhance the growth density of CNT. Oxygenation treatment was conducted on RVC foams. According to Ultramet, Inc. RVC foams can withstand air up to 350 °C. This means that a portion of carbon will be burn off due to combustion, at temperatures above 350 °C. This study first investigated if surface defects were created by the oxygenation process. A study was designed to determine the effectiveness of defect sites in assisting CNT growth on carbon surfaces. RVC samples were first cut into samples sizes measured at 5 mm x 5 mm x 10 mm blocks. The oxidation treatment took place for 1 hour at each of the following temperatures: 350 °C, 400 °C, 450 °C, and 500 °C. The horizontal tube furnace was first pre-heated at the set treatment temperature for 30 minutes. Pure oxygen gas was flowing at a rate of 1 L/minute. The pre-treatment and post treatment weights were measured to determine how much carbon was lost in the heat treatment process. The weight loss is due to combustion taking place between oxygen and carbon materials at high temperature. Figure 16 shows the result from Thermogravimetric analysis (TGA) used to quantify mass loss and validate the weight measurements. Figure 16 shows the percent of carbon weight loss as a function of temperature. This is good information to have, since it shows
that around 500 °C, about 10 wt% of carbon has been burned off. This indicates a
dramatic increase in defect sites on the surface of the carbon foam.

3.6.3.3 Bis(trimethylsilyl)amine (HMDS):

Figure 17, is a chemical structure of bis(trimethylsilyl)amine (HMDS). HMDS is a
color-less organosilicon liquid often used as an adhesion promoter for photoresists in
lithography steps. Samples were cleaned with a two-state substrate cleaning process to
minimize contamination and to enhance solvent wetting. Acetone removes organic
impurities; a subsequent rinse in isopropyl removes the contaminated acetone thus avoiding striations.

HMDS is usually applied on a substrate followed by soft bake on a hot place. When used, HMDS fragments into smaller groups by chemically bonds its Si atoms to the oxygen of an oxidized surface while releasing ammonia and methyl groups. The HMDS methyl group forms a hydrophobic layer on the substrate surface, thereby enhancing the wetting and adhesion of resist solvents. As a result, a silica coating forms on the surface of the substrate. Chapter 5 shows the investigation for the effectiveness of HMDS coating for CNT growth.

![Chemical structure of HMDS](image)

Figure 17 Chemical structure of HMDS

3.6.2 Deposition Techniques

3.6.2.1 Microwave Plasma Deposition (MPD)

The methodology of silica coating using microwave plasma CVD was adopted from the same growth conditions that was documented in detail in Pulikollu et al. [12]. To achieve silica coating, a mixture of hexamethyldisiloxane (HMDSO) and O₂ were used
sequentially in a magnetron generated microwave plasma coating system. The process was repeated several times to build up the silica coating until the desired thickness were achieved.

3.6.2.1.1 Plasma Silica Deposition Rate

Discrete deposition times were used to build up different silica film thicknesses to measure the plasma silica deposition rate. Figure 18 shows the oxide thickness versus deposition time results. The deposition of plasma silica is linearly related to the length of time used for film deposition. The first point on the chart was measured during a previous investigation conducted by this research group. This data point with 1 minute of deposition, which resulted in 4 nm of film thickness has been published earlier by Mukhopadhyay et al. [14].
3.6.2.2 Atomic Layer Deposition (ALD)

ALD is a vapor phase self-limiting thin film deposition method where the reactions take place between precursor gas molecules and the surface of the substrate. The resulting thin film is typically pinhole free and conformal to the surface of the substrate [39]. The precursor used for deposition of Al₂O₃ was trimethylaluminum, and SiO₂ was trisdimethylaluminum, both precursors alternated with water vapor during the deposition process. The thin film growth process was carried out at 200 °C with a deposition rate of 1 Å/s and 0.5 Å/s for Al₂O₃ and SiO₂, respectively.

Figure 18 Plasma silica deposition vs time, the first point (~4 nm) is a reference point from Mukhopadhyay et al.[14]
3.6.2.1 ALD Alumina Deposition Rate

In order to measure the deposition rate of the ALD Al₂O₃, discrete cycles were deposited to build up different alumina film thicknesses. Figure 19 shows the resulting oxide thickness versus deposition cycle. The result shows that the deposition of ALD Al₂O₃ is linearly related to the number of deposition cycles.

![ALD Al₂O₃ Deposition Time vs Oxide Thickness](image)

Figure 19 ALD alumina deposition versus cycle

3.6.2.3 Sputtering:

Sputtering is a technique used for thin film deposition. In this study the sputter is used to sputter thin film of nickel or iron to be used as the catalyst source for TCVD and MPECVD CNT growth techniques. The substrate receiving the deposited material is
placed in a vacuum chamber filled with an inert gas, such as Argon. A negative charge is applied to the target material in the sputter chamber causing a plasma plume to form. The free electrons from the target source will then collide with outer electronic shell of Argon gas. The positive charged Argon ions will then be attracted to the negative charged target material at a very high velocity that “sputters off” atomic size particles of the target material. The thin films are formed by the atomic particles that are knocked off of the bulk material and condense on the sample surface.

The sputter system used in this investigation has the following settings; 345V with 150 mA and Ar gas flowing at 20 sccm to keep the pressure at constant $5 \times 10^{-2}$ Torr.

3.6.3 Surface Roughing Techniques

3.6.3.1 Reactive Ion Etch (RIE)

Certain model carbon samples used in the investigation require a variation in surface roughness. One way to accomplish this requirement is to use reactive ion etch (RIE). RIE uses gas sources, typically oxygen or argon, to create plasma. This plasma can be used to etch the surfaces of a substrate material, thereby altering the surface morphology in terms of surface roughness or dangling bonds. The operating parameters to accomplish this for the RIE are as follows: 50 mTorr, 5.8 sccm O$_2$ flow, 13.56 MHz, 0.71 W/cm$^2$, and the direct current bias voltage was between -500 and -540 V. The chuck cooling water was set to 20°C. The sample was not bonded to the stage.
3.7 Instrumentation Used for Characterization, Testing and Evaluation

3.7.1 Scanning Electron Microscope (SEM):

Scanning electron microscope (SEM) is a type of electron microscope. This equipment produces images by scanning the surface of the sample with a focused beam of electrons. When electron hits the surface of the sample it interacts with the atoms on the sample and produces secondary electrons that can be detected to form a high magnification image. The signal contains information about the sample topography and/or chemical composition as well. For this study FEI SIRION SEM and JEOL SEM equipment were used to capture images using the secondary mode. This equipment provides high resolution topographical images up to 100-200k magnification. However, if the sample is not highly conductive it can limit the magnification and the imaging quality.

3.7.2 Energy-dispersive X-ray spectroscopy (EDS):

Energy-dispersive X-ray spectroscopy (EDS) is an elemental analysis tool often used in conjunction with SEM. The scanning electron beam excites atoms causing them to emit X-rays and give off unique signature peaks in the x-ray spectrum. The incident beam excites the electron in an inner shell of the sample and causes an ejection of an electron leaving the other electrons behind. The energy difference between the higher energy shell and the lower energy shell shows up as a signature peak on the x-ray chart.
3.7.3 Transmission electron microscopy (TEM):

Transmission electron microscopy (TEM) is another form of electron microscopy. The specimen used here are ultra-thin (<80 nm). From the incident beam the electron is passed through a specimen and an image is formed on the other side of the specimen by an imaging device. The TEM can magnify and focus the image on a fluorescent screen. Compared to SEM images, TEM images are typically taken at significantly higher resolution and magnification. In optimum conditions the TEM can achieve images of a single column of atoms.

3.7.4 Focused Ion Beam (FIB):

Focused Ion Beam (FIB) is an instrument that uses an electron beam for sample imaging similar to an SEM. It also has an ion beam column that can be used for thin film deposition and/or ablation of materials. This equipment is critical in TEM sample preparations.

In order to view a sample using the TEM, the electron beam needs to be able to transmit through the sample thickness. The thickness for “electron transparency” is usually targeted to be roughly around 75 – 150 nm; however a sample that requires atomic resolution may require a thickness around 10 nm. The term foil is used when describing samples being viewed under TEM. The sample specimen was nicknamed “foil” due to
the work done historically with TEM material came from material made of metal foils [40].

There are multiple methods to prepare a TEM foil, with advantages and disadvantages associated with each of the methods. Traditionally TEM foils were made from thinning of bulk material to sub-micrometer dimension using mechanical cutting, grinding, and polishing with progressively finer diamond abrasives. This process is non-trivial and can be very time consuming. In addition, during the sample preparation process there are possibilities of introducing artifacts and damages to samples. With practice, these effects can be minimized, however, it is important to choose the appropriate sample preparation method for specific sample composition for a particular data collection. One of the goals for this study was to analyze the cross sections of the grown CNT samples. Since the foil has a specific orientation that needs to be maintained, it makes the FIB an ideal method for sample preparation. The cross-sectional foils prepared in this study were prepared by using FIB techniques described below.

FEI DB235 is a dual-beam FIB system capable of switching between electron beam mode, used mainly for imaging, and ion beam mode used mainly for surface modification. The ion beam output ranges from 5-30 keV. The grown CNTs samples are mounted on a SEM pin stub using a carbon double sided sticky dot to stabilize the sample. This configuration allows the user to transfer the mounted sample from SEM to FIB without needing to re-mount the sample. This minimizes the possibility of damaging the sample
through the imaging process. Figure 20 outlines the procedure used to thin the cross-sectional sample from bulk CNT grown sample. Figure 20a and Figure 20b show the surface sample tilted at 52° with respect to the electron beam. Figure 20a was imaged with an electron beam (E-beam) source while Figure 20b was imaged with an ion beam (I-beam) source. The difference between taking images and etching material while using an I-beam is the amount of current required. The larger the current the more damage the I-beam can do to the material in the viewing area. Figure 20c and Figure 20d show the surface of the sample with a protective cap made of platinum and carbon. The protective cap prevents ion damage to the cross section foil, which is the area of interest. Figure 20c shows trenches that were cut on the front and the back face of the foil. The next step undercuts the foil to release it from the main substrate. This undercut slices across the thickness of the developing foil. This step is followed by the insertion of a tungsten needle called an Omniprob 3000. The purpose of the Omniprob is to first lift out the loose foil, followed by the attachment of the foil to a TEM grid. The attached foil is shown in Figure 20e (I-beam) and Figure 20f (e-beam). The final process involves thinning a section of the foil to electron transparency, about 100 nm range. The foil should then ready for initial TEM analysis. From this first analysis, the user can gauge the foil thickness, and see if subsequent thinning using a Fischione NanoMill 1040 is required. Figure 20 g-i show increased magnification TEM images of the foil.
3.7.5 Table Top Stylus Profilemeter:

Oxide deposition rates need to be established in order to investigate the surface modification treatments that allow the deposition of oxide thin films. The oxide
deposition rate was measured for ALD Al$_2$O$_3$ and plasma silica, respectively. Knowing the deposition rate allows the deposition of desirable oxide thickness. This will help in the investigation of CNT growth characteristics associated with oxide thickness.

The oxide thicknesses were measured using a table top stylus profilemeter. Figure 21 shows a screen shot of the data from the profilemeter. The thickness of the film was taken from the difference measured from the height of the film and the baseline.

![Figure 21 screen shot of profilometer](image)

**3.7.6 Atomic Force Microscopy (AFM):**

The Quesant© model Q-Scope 250 was the AFM unit used in this dissertation. Atomic force microscopy (AFM) is an instrument that uses a cantilever beam with a scanning probe that gently surveys the sample surface. Depending on the setup, as the probe scans across a surface, it provides a feedback in the form of electric potential or current. AFM can be operated under three different modes and they are contact mode, non-contact
mode and tapping mode. Depending on the scanning mode, the AFM can measure force in the form of contact force, Van der Waals force, chemical bonding, magnetic force, and even electrostatic forces. The probe tip is commonly made of silicon nitride or silicon with a tip radius of curvature in the nanometer range.

It is important to be able to compare the surface roughness of the growth samples, because it is believed that surface roughness has an influence on CNT growth in terms of density and alignment. The reported surface roughness values in this dissertation were obtained using a 1 Hz scan rate with 400 points per inch sampling resolution. Please see Chapter 6 for more information regarding surface roughness measurements and the effect it has on CNT growth.

3.7.7 Raman spectroscopy:

This instrument uses a laser source to interact with phonons and electrons of a sample resulting in an energy shift of the reflected photons. Raman shifts are recorded in wavenumbers (cm\(^{-1}\)). The shifts can provide information about the vibration modes, chemical information, and crystalline quality of the sample. In the case of CNT, Raman spectroscopy is used to identify distinct signature modes that are commonly referred to as D-peak (I_D) and G-peak (I_G) corresponding to “disordered” carbon and “graphitic” carbon [41]. The G-peak and the radial breathing mode (RBM) are 1\(^{st}\) order Raman scattering peaks that result from scattered phonon energy measurements. RBM is strong feature of
SWNT. It is a unique phonon mode, where all carbon atoms in the sample move coherently in the radial direction. The presence of this peak, located at (200 cm\(^{-1}\)) means that SWNTs are present. The D-peak results from 2\(^{nd}\) order Raman scattering measurements. Both G-peak and D-peak are the results of Raman scattering, therefore they are formed by the Stokes process as opposed to the anti-Stokes process where the phonons are absorbed. Raman spectra plots are formed by measuring the intensity of the scattered light as a function of frequency. The Raman spectrographic equipment used in this study was a DeltaNu ExamineR 532.

3.7.8 Sonication:

Many reported works involving the use of CNTs, state that the CNTs are in a loose powder-like form. However, in order to fully benefit from CNT’s high thermal conductivity, a strong attachment between the CNT and a substrate is required. One such configuration is to grow CNT directly on a substrate. A sonication test can be performed after the growth is complete in order to compare the quantitative attachment strength of the samples. In this investigation, a Branson 3210 sonicator bath was used. This sonication device uses a frequency of 42 kHz with an output of 100W. Grown CNTs samples were sonicated in water for 5 minutes.
3.7.9 Laser Flash Analysis:

The laser flash apparatus (LFA) technique was first developed in 1961 by Parker et al. [42], and has been well established and widely accepted as a thermal measurement technique. This instrument measures the thermal diffusivity of a material. The measurement set up is easy, and requires a small sample size. This method requires the specific heat and density of the tested material to be known before the test is conducted. Sometimes these two values are not readily available. This method uses a short laser pulse to heat the front side of the plane-parallel to the sample. The pulse is usually in the millisecond range, and the intensity is usually in several kilowatts per square millimeter range. The heat absorbed from laser propagates through the sample which causes the backside of the sample to rise in temperature. An infrared detector located on the other side of the sample (opposite to the laser) detects the sample change in temperature. The entire experiment was kept in an inert environment with a constant flow of Argon gas at 60 sccm. The output from LFA is the thermal diffusivity (α) value measured. In many cases the specific heat (\(C_p\)) of the sample can also be measured simultaneously. The thermal conductivity (\(\lambda\)) can be calculated using the equation below if the density (\(\delta\)) of the material is known.

\[
\lambda(T) = \alpha(T) * C_p(T) * \delta(T)
\]

Equation 3: Thermal Conductivity

Thermal diffusivity is defined by Parker’s equation below and has units of (m\(^2\)/s)
\[ \alpha = 0.1338 \times \frac{d^2}{t_{1/2}} \]

Equation 4: Thermal Diffusivity
Equation 4 accounts for the material thickness and the time at which the rise in temperature has reaches half of the maximum \((t_{1/2})\), see Figure 22 for a plot from a typical scan.

Figure 22: Half time rise of a diffusivity chart from Netzsch equipment manual.
The laser flash system used in this study was built by Netzsch, their MicroFlash©457 model. This instrument has a high accuracy and repeatability, ±2% for standard materials and ±3% for most materials measured. It has a wide temperature testing range of -125°C to 1100°C. It also uses a non-destructive non-contact technique, and it has multi-layer sample measurement and analysis capability. A functional diagram of the system provided by Netzsch is shown in Figure 23.
Figure 23: Drawing of a Laser Flash system
The image shows the LFA 457 is equipped with a laser, a furnace, sample stage and an
IR detector, which are controlled by a built-in data acquisition system. The sample stage
can rotate and hold up to three samples. To take measurements using the LFA 457
system, the sample needs to be opaque to infrared. It is recommended that samples with
low emissivity values can be coated with a thin layer of graphite to achieve blackbody
radiation characteristics. It is also suggested that an additional coating of a thin layer of gold be applied if better heat signal absorption is required. The samples are usually 10 mm$^2$ by 0.1 to 6 mm in thickness. It is important that the sample be as flat as possible to achieve optimal signal detection. Ideally, the laser should enter the sample at a 90 degree angle to allow heat to flow through the sample uniformly. The thermal analysis conducted with LFA is presented in Chapter 7.
Section II: Background Investigations
CHAPTER 4: Background Investigation Part I: Comparison of Chemical Vapor Deposition Methods

It was mentioned earlier in Section 3.5, that CNTs can be fabricated using a variety of growth techniques. However, it is known that the resulting CNTs are not always the same. For example some techniques are better at growing SWNT over MWNT, while others can produce coiled CNTs or vertically aligned CNTs. Due to cost effectiveness, scalability, and laboratory accessibility, this investigation selected CVD growth techniques for investigations of CNT fabrication on carbon substrates. A great majority of CNT reported thus far was done using electronic grade silicon. Growth on carbon substrates such as diamond or graphite remains low. Therefore it was not clear which of the CVD methods was are suitable at growing CNTs. Therefore, it was decided that background studies should be done to compare the effectiveness of using CVD methods to grow CNTs on diamond substrates. The following two chapters will be used for background information related to this investigation.

The background study conducted in this chapter has two purposes. The first purpose is to see if dense CNT growth (full coverage of the substrate) is achievable on diamond substrates when CVD growth technique was used. The second purpose is to provide general comparison among the three CVD growth techniques and their effectiveness of growing CNTs on diamond substrate. This background study will serve as a building block allowing more detailed studies to be conducted. The findings here will help in
narrowing down selections of suitable growth technique to be used for the reminder of the research.

Due to laboratory availability three different kinds of CVD fabrication method were used. Two of which are described as traditional growth methods, TCVD and MPECVD, while FCCVD is a newer and more scalable approach. The resulted grown samples were compared and characterized for CNTs growth density and tube morphologies, technique successfulness, and relative mechanical properties.

4.1 Objective (Grow CNTs on Diamond)

The objective of this chapter is to find out if CVD methods can be used to grow CNT on diamond substrates, in addition to compare the characteristic of the resulting tube. To accomplish this, the approach is to grow CNTs on diamond substrate using three different kinds of CVD methods, two traditional CVD methods and one newer CVD method. The results and the findings are presented below.

4.2 Preliminary Investigations: Suitable Catalyst Source For Traditional Growth Methods

The main difference between traditional growth methods and the newer and more scalable growth methods is the number of steps required for CNT growth. The traditional growth is a 2-step process where metallic catalyst thin films need to be deposited
independently and a heat treatment step is often required to coalesce the metallic films in order to form catalytic particles. This creates a unique opportunity to allow investigation of the behavior of catalyst particles using the traditional method. The newer and more scalable CVD process introduces catalyst and carbon source at the same time, while heat treatment step is not need, therefore was not included in the heat treatment comparisons step.

It has been report that transition metals are excellent catalyst source for growing CNTs. However their effect in supporting CNT growth on carbon substrate, more specifically diamond substrates, has not been well understood. Due to the laboratory availability two metal sources, iron and nickel, were simultaneously investigated. Using the traditional growth methods, their effects as catalyst sources on diamond substrates were compared.

4.2.1 Thermal CVD (TCVD) – Successful Catalyst Investigations:

TCVD is a well-established technique. It has been reported that this technique is successful at growing CNTs. Several published work stated that transition metal are an excellent source for CNT growth [3], [73], [104]. However many reported studies were ones investigated using silicon as substrate. It wasn’t clear if the result in terms of CNT morphology, crystallinity or areal density will be the same if diamond substrate was used. To address this uncertainty, investigations using iron and nickel as catalyst sources were conducted.
Diamond substrates were first sputtered individually with 10 nm nickel films or 10 nm iron films. These samples were grown at the same time to see which catalyst is most suitable for CNT growth. The growth parameters used for the initial TCVD investigation are listed in Section 3.5.3.1.2. Figure 24a shows the result when 10 nm nickel thin film was used for CNT growth. The SEM image shows a dense amount of CNTs were grown on the surface. Figure 24b shows the result when 10 nm iron thin film was used for CNT growth. The SEM images show that the surface did not produce anything that resembles closely to a CNT tube. These images show that using this growth parameter, nickel was better at growing CNT between the two catalyst sources. One possible reason for the differences between the results might be associated with the growth temperature and the catalyst source used. At 800°C, the temperature is above the eutectoid point for Fe-C, which is 727°C, but still below the eutectoid point for Ni-C, which is at 1326°C. This suggests that it is possible that at the CNT growth temperature, the iron thin films coalesce into nano-particles, and these particles reacted with diamond substrates or the carbon gas source. As a result, some form of carbide was more favorably formed instead of CNT. However since the eutectoid temperature is much higher for Ni-C, carbon was able to use nickel as a catalyst and precipitate CNTs out from the catalyst particles.
4.2.2 MPECVD – Successful Catalyst Investigations

Microwave plasma CVD also is a well-established CVD process; it is often used in low temperature processing of microelectronic. For CNT growth, the plasma in the reaction chamber usually dissociates the precursor even before they interact with the catalyst particles. Thus it has been reported by Robertson et al. and Cantoro et al. that low temperature (300 °C) CNT growth was achievable when grown on substrate with alumina support [105], [106].

Diamond substrates were first sputtered individually with 10 nm nickel films or 10 nm iron films for MPECVD investigation. These samples were grown at the same time to
see which catalyst is most ideal to initiate CNT growth. Growth parameter is shown in Section 3.7.2.2. Figure 25a shows the result when 10 nm nickel thin film was used for CNT growth. The SEM image shows a sparse growth of CNT on the surface. Figure 25b shows the result when 10 nm iron thin film was used for CNT growth. The SEM images show dense amount of CNT growth resulted on the surface. These images show that using this growth parameter, iron was better at growing CNT between the two catalyst sources. One possible reason is that at 650 °C, the temperature was too low to allow proper growth to take effect for samples using Ni catalyst. As a result, there was only a low CNT growth yield. Higher temperature was not explored since the goal is to take advantage of low-temperature processing technique provided by MPECVD.

Due to the results from this preliminary investigation it was determine that nickel catalyst will be used as the catalyst source for TCVD, and iron will be used as the catalyst source for MPECVD for the reminder comparison in this chapter.
4.2.3 Heat Treatment – Catalyst morphology comparisons

It is well established that the underlying catalysts play a big role in the structure and the morphology of the resulting CNTs [95], [107]–[109]. The results from Section 4.2.1 and Section 4.2.2 indicated that with the growth parameters investigated, different catalyst materials are required for the two different CVD growth techniques. In this section the heat treatment step was compared to investigate the underlying catalyst morphologies. The purpose of heat treatment is to allow the catalyst films to break up and coalesce into catalytic particles for CNT growth.

For TCVD and MPECVD growth methods, samples were brought to heat treatment temperature (800 °C for 2 minutes and 400 °C for 5 minutes, respectively) and held there for the heat treatment process. Instead of continue on with introduction of carbon source to allow CNTs to nucleate, the heat sources were terminated and bring the chamber back down to room temperature. After which, the samples were removed from the growth chamber and into microscopy chamber for surface feature analysis.

Figure 26a shows the result of TCVD thermal treated 10 nm nickel film after undergoing thermal treatment. The resulting nanoislands have an average diameters of 53 nm distributed uniformly across the substrate surface. Figure 26b shows the SEM surface analysis of a sample using MPECVD to thermally treat at 400°C. The image shows that the iron catalyst agglomerated into a continuous uneven film rather than coalesced into...
isolated nanoparticles.

Figure 26: SEM images of catalyst particles a) Ni catalyst after thermal treatment in TCVD. b) Fe catalyst after thermal treatment in MPECVD with hydrogen plasma.

4.3 Empirical investigation of 3 CVD methods for growing CNT on Diamond substrates

Now that the corresponding catalyst sources has been identified for the different growth methods a comparison of the resulting CNT using three different CVD methods were conducted.

For the growth parameters used for each of the corresponding CVD techniques please refer to the following sections. Section 3.5.3.1.2 for TCVD, Sections 3.5.3.2.2 for MPECVD, and Sections 3.5.3.3.2 for FCCVD.
In this investigation, catalyst particles size will be compared using microscopy techniques. Earlier reports of CNT growth on silicon stated that at some point CNTs will stop its growth due to inactivation of catalyst source. The inactivation of catalyst particles has been described as phenomena resulted in too much carbon built up that resulted in encapsulation of the catalyst particle. When encapsulation occurs, an immediately deactivation of the catalyst particle will occur [110]. Others mentioned that when catalyst particle changed from meta-stable phase to a stable phase it will lost its catalytic capability[108]. Furthermore, reports have shown that the catalyst activation can be extended if water vapor is introduced during growth [111]. Therefore by investigating the catalyst particles post CNT growth may reveal other notable information about the CNTs morphology and physical characteristics.

4.3.1 Characterization Methods

The grown sample resulting from each of the CVD methods were analyzed by microscopy, spectroscopy and sonication methods. FEI Sirion, a high resolution SEM, was used for microscopy analysis of CNT carpet height and nanotube morphology. In addition, to understand whether the CNTs were tip or root growth, cross-sectional TEM foils were prepared. Energy Electron Loss Spectroscopy (EELS) equiped by the TEM was used for chemical composition analysis. Raman spectroscopy analysis was used to provide the qualitative comparisons for the crystallinity characteristic of CNTs. The
Raman intensity ratio between the disorder peak (D-peak) and the graphite peak (G-peak) is used to determine the degree of crystallinity/purity of the CNT [112]. Finally, sonication test was performed for a qualitative analysis on the durability and mechanical strength of the bonding between CNTs and the diamond substrate. If CNTs are present on the surface of the substrate after a sonication test, it will suggest that the bonding between CNT and the substrate is strong. The grown CNTs samples were tested in a sonicator bath that uses a frequency of 42 kHz with an output of 100W. For details of sonication see Section 3.7.8.

4.4 Results and Discussion

4.4.1 Nanotube Morphology:

Figure 27 shows SEM images of the CNT layer formed on diamond film using the three different techniques. For TCVD nickel was the catalyst source, while MPECVD and FCCVD both uses iron as catalyst source. Figure 27a is the image of TCVD grown CNTs which have an average tube diameter of 61nm ±12nm, with uniform tubular structure. This correlates well with the uniform size distribution of nickel islands of similar sizes seen in Figure 26a.

Figure 27b is an SEM image of MPECVD-grown CNT that indicates that the CNTs are not uniform and contain various defects as well as variation in diameters. This may be the result of the seed catalyst layer consisting of irregular-shaped particles. The
nonuniformity of individual tubes may also be influenced by defects developed during formation. The MPECVD method uses a hydrogen plasma that forms the growth process [27]. Some studies suggest that exposing growing CNTs to hydrogen-rich environments convert them into diamonds [28, 29]. Figure 27b shows the MPECVD CNTs tubes with defects similar to the ones reported by Behr et al. after exposure to the hydrogen-rich environment [113].

Figure 27c shows an image of FCCVD-grown CNTs. This figure indicates that the CNTs are uniform in diameter and grow as densely entangled forests. These CNTs have average diameters of 12 nm ± 1.8 nm, making them the smallest of the three growth methods. The image also suggests that there are particles residing on the outer surface of the CNTs. This is expected because the xylene/ferrocene mixture provides continuous source of iron particles throughout the entire process, some of which are expected to attach to the growing CNT surface. The diameter of the outer particles can provide an estimate of iron catalyst size, and they have an averaging diameter size of 12 nm ±2.2 nm.
4.4.2 Catalyst Distribution in the Final CNT-covered Diamond Structure

Figures 18–20 show high-resolution TEM images with Energy Electron Loss Spectroscopy (EELS). Figure 28 is the TEM and EELS analysis for the TCVD sample. Figure 28a is an EELS scan for elemental carbon, the lower portion of the figure have higher carbon concentration, therefore it was identified to be the diamond layer. The top portion of Figure 28a is highlighted by CNT. Since CNT and diamond are both made of elemental carbon the only way to tell the two apart is by comparing the pixel intensity. The whiter the pixel appears, the higher the pixel intensity for the scanned element. This is the same for Figure 29 and Figure 30. Using the pixel intensity comparison one can find the interface that separates the diamond substrate from CNTs.

Figure 28b is TEM image of the EELS scanned area, and Figure 28c is EELS scan for elemental nickel. These figures indicate that in TCVD, nickel particles are encapsulated with a layer of carbon, and CNT growth originates from the outer carbon layer. Since the
growth originates from the outer carbon layer, this image shows why the average CNT
diameter is slightly higher than the average catalyst particles diameter as shown in Figure
31. The encapsulated catalyst particle remains anchored at the diamond-CNT interface
implying the predominant growth mechanism is root growth. There are a few instances
where the catalyst particle moved several nanometers into the CNT length, away from
the interface. The interface is highlighted by the yellow dotted line. Growth patterns
similar to this indicate a small probability of catalyst lift-off.

The green dotted circle in Figure 28c, circles a nickel particle, and a red arrow shows the
location of this nickel particle in relation to CNT tubes in Figure 28b.

![Figure 28: TEM and EELS cross-sectional images of a TCVD CNT on Diamond sample a) EELS scan for elemental carbon, b) TEM imaged area, c) EELS scan for elemental nickel.](image)

Figure 29 is the TEM and EELS analysis for the MPECVD sample. Figure 29a is an
EELS scan for elemental carbon, Figure 29b is a TEM image of EELS scan area, and
Figure 29c is EELS scan for elemental Iron. It can be seen that iron particles in this case
do not reside along the interface, yellow dotted line, but rather move away from the
interface and into the CNT. Figure 29b shows that the CNTs produced using MPECVD technique were defected looking. As seen in Figure 27b and Figure 29b CNT resulted in this method looked more entangled, and tube diameter were less uniform along one tube and among the tubes. It was believed that the mobility of non-anchored catalytic particles at the interface may contribute to disordered CNT growth. It has been reported that CNTs resulted from tip growth mode produced CNTs that has bamboo-like features with more defects [114]. In addition it has been reported that the catalyst morphology can change when certain growth condition were used. Irregular catalyst morphology has been observed from the TEM images. Furthermore, it has been reported that as the particles migrate more stress is build up between the nucleated CNT and the catalyst particle, as a result kinks and defects are form during the growth process [115]. Therefore, it is also possible that when particles migrate during CNT growth, some stresses can build up coupled with irregular catalyst morphology the condition is more challenging to produce aligned CNTs. As a result CNT from MPECVD growth methods appears to be more defective. The green dotted circle in Figure 29c, circles some of the iron particles, and a red arrow shows the location of these iron particles in relation to CNT tubes in Figure 29b.
Figure 29: TEM and EELS cross-sectional images of a MPECVD CNT on Diamond sample, a) EELS scan for elemental carbon, b) TEM scan, c) EELS scan for elemental Iron.

Figure 30 shows the result from FCCVD growth method. Figure 30a is an EELS scan for elemental carbon, Figure 30b is a TEM image of EELS scan area, and Figure 30c is EELS scan for elemental Iron. Unlike the previous two CVD techniques mentioned, FCCVD technique deposited a layer of silica prior to CNT growth. These images show a high distribution of iron particles residing at the silica coated diamond CNT interface, yellow dotted line. The image suggests that silica layer has a high affinity for the iron particles. The large number of iron catalysts at the interface suggests that the silica film keeps catalyst particles anchored during CNT growth; as a result smaller and more uniform tubes were fabricated. Comparing with the previous growth methods without the silica layer, the catalyst particles appear to be larger and have higher mobility. It is believed that the oxide layer keeps the catalyst particles from agglomerating and migrating during CNT growth. In addition, Figure 30 shows additional iron particles found further...
away in the CNT forest. This is expected due to the continuous iron particle introduction throughout the CNT growth phase. Figure 30c, circles some of the iron particles, and a red arrow shows the location of these iron particles in relation to CNT tubes in Figure 30b.

![ TEM and EELS cross-sectional images of a FCCVD CNT on Diamond sample, a) EELS scan of elemental carbon, b)TEM scan area, EELS scan of elemental Iron.](image)

So far it was demonstrate that CNT can be successfully grown on diamond substrates. However, it was also observed that with the growth parameter used, different catalyst source were successful at growing CNTs. As a result, some features of CNT appear to be different, such as diameter and catalyst particles. These features are worth noting because they can have effects towards CNT’s intrinsic physical properties. For example, it was reported that CNTs with smaller diameters have higher thermal conductivity values \[116\]. Figure 31 shows the average particle size distribution taken with Image J software. This software provides quantitative values for the catalyst particle size and tube diameter comparison taken from the resulting TEM images. For TCVD, the average
catalyst particle diameter was measured to be 53nm ± 16nm, and the average tube diameter was 61nm ± 12nm. Thus, the catalyst diameters measured using TEM images are within the margin of error with the top view images seen by SEM. For MPECVD, the average catalyst particle diameter was 21nm ± 7nm, and the average tube diameter was 40nm ± 18nm. For the FCCVD method, the average catalyst particle size was 12nm ± 2nm, and the average tube diameter was 12nm ± 2nm. Cross-sectional TEM images provided additional information about particle location and concentration relative to the interface. It was expected that different growth techniques and different catalyst layer used will result in CNT morphology differences. Since the morphology of CNT is a dominating factor over the physical performance of the CNT. Investigating these results can reveal growth techniques required for desired CNT morphology.

It was observed that the CNT growth characteristics resulted from TCVD, was large catalyst particles that reside close to the interface. For MPECVD, the catalyst particles are distributed away from the interface. This migration may be due to the fact that they are smaller in size compared to ones seen produced from TCVD. It is possible that as CNTs nucleates it pushes smaller catalyst particles away from the interface, as a result tip growth mode more favorable in this condition [93]. However, size alone may not be the only reason why migration happened. Iron and nickel have different surface tensions (formation of particle) and surface stresses (wetting of the surface) and these could also be one of the possible reasons for migration of particles. For FCCVD growth, the images
indicate that the majority of the iron particles used as catalysts are anchored along the SiO$_2$ layer and the iron particles that arrived later reside outside the growing CNTs. The anchoring of smaller nanoparticles may be caused by the silica functional layer and may assist in uniform CNT growth. More investigation about the role of buffer layer can be found in Chapter 5 and 6. Figure 31 shows that the nanocatalyst particle size in each case correlates with the CNT diameters. This was also observed by SEM and TEM images, therefore it further validates the hypothesis that the CNT size is largely governed by catalyst particles.

![Average Catalytic Particle size and CNTs Diameter Distribution](chart.png)

**Figure 31: Particle size and CNTs tube diameter distribution chart**
4.4.3 Raman Spectroscopy Results:

Raman spectroscopy was performed on samples produced by the different growth methods. The results are presented in Figure 32. According to the Handbook of Raman Spectroscopy and Dresselhaus et al., Raman spectroscopy can be used as a guide to describe different carbon structures, such as diamond-like carbon which has C–C sp³ bonding, graphitic carbon which has sp² bonding, and glassy/amorphous carbon which has C–H and disordered mixed bonds [112], [117], [118]. The peaks found around 1350-1365 cm⁻¹ are called D-peaks, resulting from the disorderly network of sp² and sp³ carbon clusters, whereas the peaks found around 1580-1620 cm⁻¹ are called G-peaks as a result of graphite, and finally the peak found at 1332 cm⁻¹ is the diamond peak [117]–[119]. In this experiment, it was observed that samples produced uniform tubes resulted in lower \( I_D/I_G \) ratio, while ones produced in kinked looking tubes produced high \( I_D/I_G \) ratio. The \( I_D/I_G \) ratios are given as follows: TCVD = 0.30; MPECVD = 1.94; FCCVD = 0.84. Note that the TCVD has the lowest \( I_D/I_G \) ratio; its SEM images, Figure 27a, indicated that this tube structure looks the most uniform. In contrast, the \( I_D/I_G \) for MPECVD is the highest and its SEM images, Figure 27b, indicated that the tube structure appears damaged and full of defects. Earlier, it was stated that hydrogen may etch the CNT surface and introduce defect sites. The presence of the defects can raise the intensity of the D-peak. Another possibility that causes a high D-peak is when CNT is introduced to a hydrogen rich environment; the hydrogen alters CNT’s C-H bonding and
transforms them into diamond or disordered carbon [113], [120].

Since the CNTs were grown on diamond substrates, one might suggest that the high intensity of D-peak resulted from signals coming from the diamond substrate underneath. However, the recorded D-peak intensity lies around (1354 cm$^{-1}$), whereas known diamond -peaks are detected at (1332 cm$^{-1}$), indicating that the peak signal did not result from the diamond substrate. For confirmation, a razor blade was used to scrape away the CNTs from a sample and expose the diamond substrate underneath. The Raman spectra taken from the exposed diamond surface has a peak intensity at (1338 cm$^{-1}$), which closely matches the published Raman peak for diamond (1332 cm$^{-1}$). This additional test further indicates that the (1354 cm$^{-1}$) peak is indeed the -peak from the disordered CNT and not from the diamond substrate.
4.4.4 Sonication Results:

If the sample was used in a commercial device, it would be important to know if the CNTs had the strength to stay intact within the substrate. The sonication system was used in a brief comparison study to see if the resulting CNTs were strong enough to withstand volatile vibrational condition, which may be required in certain electronic packaging.

For the sonication test, SEM images were taken before and after the sonication treatment as shown in Figure 33. The images in the top row of Figure 33 were taken prior to sonication, and the bottom row images were taken after the test. Figure 33a were form the TCVD, Figure 33b were from the MPECVD, Figure 33c were from FCCVD, and Figure
33d were optical images taken from MPECVD sample. The before sonication image seen in Figure 33d can also be used to represent TCVD and FCCVD, because there were no visual differences observed after the sonication test. It can be seen that the nanotubes were intact even after sonication and that there were no noticeable differences seen in the before and after images from SEM. The low-magnification optical images show a difference for the MPECVD sample. Before sonication, all samples look identical at this magnification as seen in Figure 33d top image. The optical images after the sonication test were unchanged for TCVD and FCCVD which are also represented by Figure 33d top image. The MPECVD after sonication sample was different as shown in Figure 33d bottom image. While postsonication SEM images of MPECVD sample show that CNTs were present on the scanned regions, the low-magnification optical images show exposed diamond substrate on the corners of the sample. This indicates detachment of CNTs at the corners of this sample, implying that the bonding between CNTs and substrate may be the weakest in this fabrication method. It must be noted that because of the extremely high length/diameter ratio of the nanotubes, agitation in an ultrasonic bath produces concentrated stresses at the root of the CNT. Survival under these conditions indicates that these materials will be robust in many service conditions. Among the three samples, MPECVD specimen may be the weakest, and detachment begins to occur at the corners, which are the most vulnerable regions of the sample. Possible reasons that MPECVD growth technique resulted to be the weakest has to do with the fact that the CNTs
contains the most defects, kinked tubes, and another possible reason is that the catalyst particles were not anchored on the substrate as evident by TEM images represented by Figure 29.

![Figure 29](image)

Figure 33 (a), (b), and (c) are SEM images, and (d) is the optical image. The images in the top row were taken prior to sonication, and those in the bottom row were taken after the test. (a) is the TCVD sample. (b) is the MPECVD sample. (c) is the FCCVD sample, and (d) is taken from MPECVD Sample. There were no visual changes seen after the sonication test for the TCVD and the FCCVD sample. Therefore, the before image from (d), can also be used to represent before and after sonication test for TCVD and FCCVD sample

4.5 Overall comparison:

It is seen that very different types of CNT layers can be grown on diamond film by different techniques. It must be noted that TCVD and MPECVD are multistep processes that separate the catalyst deposition step from the CNT growth step. The catalytic particles in the TCVD growth are found to be the largest of the three types of growth for the conditions used. These particles were found to reside at the interface with minimal
migration into the CNT layer. The resulting CNT diameters were the largest, and were found to be uniform, with lowest Raman I_D/I_G ratio. The uniform structures are thought to be ideal since they have less defects, which means that the intrinsic property of the tubes have higher thermal and electrical properties. It was reported that defects in CNTs can reduce thermal conductivity values [121]. In addition, it has been reported that defects on the surfaces of CNT can decreases electrical conductivity and effectiveness of ballistic charge transport [122]. Furthermore, defects in CNT can degrade thermal properties, which affect the thermal dissipation in electronic packaging [123].

The SEM images show the CNTs that resulted from the MPECVD method contains kinks and defects on the individual tubes. As discussed previously the CNT defect may be a result of plasma etching [124], stress formed between CNT and catalyst particles during growth [115], or migration of catalyst particles due to tip growth mechanisms. Evidence of particle migration was captured from TEM images. It is believe that migration is a reason as to why those CNT structures are kinked. It can be proposed that as the CNTs are growing with the migrating catalytic particles, a straight path for growth was not provided, which resulted in a kinked-type growth. Furthermore, since the particles were found not anchored at the interface, the resulting sonication test shows CNTs can be knocked loose from high frequency conditions. Therefore, this approach which is suitable for large area growth or low temperature growth will be useful only in situations
where defective, kinked CNTs that have low mechanical bonding to the interface are acceptable. Certain post CNT growth processing such as surface functionalization of CNT might benefit from tubes that are more defective. The benefit of using FCCVD is that it is a one step process where catalyst and carbon source are introduced together. The resulting CNTs grown by this process had the smallest diameter, averaging 12 nm, with uniform and dense growth patterns. While this may be a very suitable approach in many applications, the technique also contains more iron particles arising from continuous catalyst deposition. This may be mitigated by modifying the process to cut off ferrocene during the latter part of CNT growth. This was not possible due to the configuration of the syringe used for the investigation. To investigate such hypothesis, one will require a different syringe adaptor else the growth procedure must be interrupted to accommodate syringe change. Since each method has its unique advantages and dis-advantages, these studies highlighting the fact that the selection of the CNT growth method is heavily influenced by the intended application.

4.6 Summary

In this empirical study, we compared the growth of CNTs forests on synthetic diamond substrates using three different CVD growth methods. The CNTs were characterized using electron microscope imaging (SEM and TEM), EELS, Raman spectroscopy, and the sonication test. Despite of different catalyst sources and interface composition used,
the SEM and TEM images were able to reveal CNT and catalyst particle diameter and morphology differences. Raman spectroscopic analysis showed that TCVD had the lowest disordered carbon to graphite intensity ratio of 0.3 followed by FCCVD of 0.83 and the highest by MPECVD of 1.94. TCVD also produces large diameter CNTs that are otherwise clean, with minimal tubular defects or additional catalytic contaminants. MPECVD is sometimes the preferred method for low temperature or larger scaled applications; however, the excess hydrogen plasma energy during growth may cause surface etching, and defective CNTs that may be detrimental to precision applications. MPECVD has the highest probability for catalytic mobility, the most defective CNT structure morphology, and the weakest interfacial bonding strength. It may be possible to improve this situation through processing parameter changes, but not certain. FCCVD has the advantage of being a one-step CNT growth method that does not need a separate catalyst deposition step, yet produces dense uniform CNTs. This technique provided the smallest CNT diameter, and intermediate diamond/graphite ratio in the Raman signal. It was mentioned earlier that the diameter of CNT is a factor that determines the physical property of CNT, where thinner CNTs has higher thermal conductivity values. In this investigation, FCCVD technique produces the smallest CNT in size, and the benefit of using this technique is its ability to produce carpet s of CNT with a uniform morphology. This method does produce some excess metal particles due to continuous catalyst nucleation. It has been reported that CNT are commonly contaminated by
excess metal particles, and a large research effort is say to be underway to develop a way to purify CNTs post processing [125]. Alternatively, excess metal particles can be useful for applications that require surface functionalization of CNT, but that is not the scope of this investigation. Furthermore, one possible way to minimize the amount of excess metallic particles is by stopping the catalytic source after a certain growth time. However this was not investigated due to requirement of different system configuration. Finally, this study validated there is a correlation between the size of catalyst particle and the CNT diameters when growing on diamond substrates, which can be very useful for future application design requirements. However investigation using diamond substrates was not continues due to cost and substrate limitation.
CHAPTER 5: \textit{Background Investigation Part II}: Comparison of Surface Modification Methods

In Chapter 4, it was demonstrated that CNT growth was achievable on SP\textsuperscript{3} carbon, diamond substrate. However, even though that diamond has excellent thermal properties, certain applications may favor substrates that are also electrically conductive. Therefore, CNT growth on SP\textsuperscript{2} graphitic carbon should also be investigated. SP\textsuperscript{2} carbons are lightweight, electronically conductive, and available in a wide selection of substrate geometries. The lightweight and conductive aspect of carbon substrate may be useful for some power electronic applications that are suitable for aerospace or composite industries. Substrate geometries of a particular interest are the ones that have high specific area, such as carbon foam. Carbon foam is a high surface area material. The increased surface area offered by carbon foam and attached CNTs would greatly benefit the thermal dissipation since the heat lost via convection is proportional to the surface area (and temperature difference).

In the previous chapter, it was observed that techniques such as TCVD and MPECVD would require a pre-deposition step for catalyst source prior to CNT growth. Such task may be difficult to achieve for complex structures that require equipment that is not limited to line of sight. FCCVD growth technique is simple, scalable, and able to fabricate CNTs with uniform diameter ranges from 10-20 nm. This technique is also the most feasible technique to grow CNT on complex structures, because it is not limited to
line of sight processing. Therefore this technique was selected as the growth technique for the remainder of the research.

In recent years, some research groups have identified ways to grow CNT without catalyst particles. However, the result often yields sparse CNT growth with controllability issues. The most common way to grow controllable and dense CNT still requires the use of catalyst particles. These catalytic particles are usually made of transition metals such as Fe, Ni, Pd and Au[73]. Growing CNTs directly on sp² carbon surfaces is challenging, and there are a few known solutions. First, it is possible that the selected transition metals will react with the carbon substrate. This leads to a formation of secondary carbide products. Some carbides have shown to inhibit CNT growth due to catalyst poisoning [126]. Secondly, certain growth conditions are favorable to many allotropes of carbon formation simultaneously. For example, different forms of carbon such as diamond, diamond-like carbon, and carbon nanotubes have been shown to grow simultaneously on a substrate [127]. Finally, catalytic particles may diffuse into the substrate during high temperature, and becomes unavailable for CNTs growth [128]. With all these known possibilities, investigation of surface modifications are needed in order see which modification are efficient in enhancing CNT growth on sp2 carbon substrates. This will then allow fabrication of better CNTs in terms of (growth density, growth morphology, and uniformity). Sections 3.6 have a description for each of the surface modification treatment used in this chapter.
The samples used in this chapter were reticulated vitreous carbon (RVC) foams. As received carbon foams were cut into sample size measuring 10 mm x 5 mm x 5mm. These samples were cleaned using sonication with a 42 kHz. Samples were first cleaned using sonication for 5 minutes in acetone followed by 5 minutes in isopropanol. After which the samples were taken out of the solution and an air gun equipped with Argon gas was used to blow dry the sample. For images of as-received RVC foams please see Figure 10. For each of the treatments described in the sections below, 3 samples were prepared. Each of the samples went through the surface modification treatment process follow by the CNT growth process. The growing process used was FCCVD process described in Section 3.5.3.3.2

5.1 Pre-experimental study: Direct Growth without modifications (Baseline)

In Chapter 4, it was demonstrated that the FCCVD recipe described in Section 3.5.3.3.2 was successful at growing dense CNT on diamond substrate. This was then used to see if dense CNT can grow on sp² carbon. To begin, a baseline growth was done, using as-received foam sample without any surface modification treatments. Figure 34 is SEM image showing that the growth was low and sparse. The CNTs were clustered and randomly orientated. This result shows that it is a challenge to grow dense CNT carpets directly on as-received carbon foams.
Due to this finding, it was believed that CNT growth on sp² carbon can be improved if proper surface modifications were performed. Surface modification that oxidizes the surfaces has been shown to be effective in enhancing CNT growth on loose graphite [98].

5.2 Objective: Surface Modification to Improve CNT Growth on Carbon Foam

The objective of this investigation is to demonstrate dense growth of CNT on porous carbon surfaces. The approach to accomplish this is to look into five different surface modification techniques and to see if any of the treatments options are effective. This is a preliminary comparison in order to differentiate methods that are effective and ones that are not. No optimization of the technique will be performed. A successful growth will be the one that allows dense CNT growth, coverage without substrate showing, on sp² carbon substrates. The surface modification includes two main types. In the first
approach, oxygen containing groups were added to the substrate surface using the following techniques; nitric acid, oxygenation, dip coating with Hexamethyldisilazane (HMDS). The second approach deposits oxide thin films on the surface of carbon substrate. The deposition techniques with corresponding oxides were plasma SiO$_2$, and ALD Al$_2$O$_3$.

5.3 Experimental: Surface Modifications Options

5.3.1 Surface Modifications

For each of the surface treatment options mentioned below, three test samples were prepared. After the samples receive surface treatments, CNT growth was attempted on the treated samples. Additional information about the surface modification techniques mentioned below can be found in Section 3.6.

5.3.1.1 Traditional Surface Modification Techniques

5.3.1.1.a) Nitric Acid

It has been report that nitric acid has the ability to break the strong covalent carbon bonds; thereby adding oxygen containing groups as well as creating defects on the surface of carbon substrates. It has been reported that such defects were successful at allowing CNTs to grow on graphitic particles[129]. The nitric acid treatment is a slow process. It
began by soaking batches of carbon foams, in a 70% concentration nitric acid, for either 4 hours or 8 hours at an elevated temperature of 120°C.

5.3.1.1.b) Oxygenation

Carbon starts to decompose in air when temperature rises above 350°C. Therefore one of the ways to modify the surface of the carbon foam is by exposing it to an oxygenated environment above the decomposition temperature. An experiment was setup to treat the carbon foam at various high temperatures (350, 400, 450, and 500°C) for 1 hour, in order to produce a range of defective surfaces on RVC foam. Treatments above 500°C were not pursued because the resulting carbon foam crumbles under normal sample handling.

5.3.1.1.c) Bis(trimethylsilyl)amine (HMDS)

The literatures have suggested that CNT grows very well on oxide surfaces such as silica or alumina[128], [130]. HMDS was used to modify the surface of carbon foam. When used, HMDS, bonds its Si atoms to the oxygen of an oxidized surface, thereby creating a silica layer on the surface of RVC foam. To create this silica coating on carbon foam samples, the RVC foams were dipped into HMDS solution and set off to dry on a hot plate at 100°C. EDS shows that there were 1 atomic % of silicon present on the foam surface after the coating process.
5.3.1.2 Advanced Nano-Scale Coating Techniques

Initial investigation uses carbon foam samples deposited with 4 nm of plasma silica and (2, 5, 10, 50 nm) of ALD alumina for comparisons. For oxide deposition parameters see Section 3.6.2, and for comprehensive investigation of the effect of oxide thickness on CNT growth see Section 5.4.2.2.a, and Chapter 7.

5.3.2 CNT Growth Parameters

FCCVD was used to grow CNT on the surface treated samples. The growth recipes used were ones from FCCVD mentioned earlier in Section 3.5.3.3.2.

5.4 Results and Discussion

5.4.1 Addition of oxygen groups on the surface carbon substrate (physisorption)

5.4.1.1 Growth on Nitric Acid modified sample

Figure 35 shows the image of nitric acid treated samples grown with CNTs. It was observed that clusters of CNT were present on the surface of the foam sample, however large area of substrate are still visible. As a result, it was determined that nitric acid treatment is insufficient at greatly enhancing CNT growth density on carbon foam.
Figure 35: CNT grown on nitric acid treated carbon foam. A) 4 hrs treatment, B) 8 hrs treatment

5.4.1.2 Growth on sample modified by oxygen at elevated temperature

Figure 36, shows the results of CNT growth on oxygenated carbon foams. These images show varying degrees of CNTs clusters grown on the surface of carbon foam. It can be seen that larger clusters of CNTs were grown on foams that were treated at higher temperature during oxygenated environment. However, it wasn’t clear if this was a result of more defect sites or larger defect sites created at those locations. Nonetheless, the overall growth yield remains low; therefore this method was not pursued further.
5.4.1.3 Growth on HMDS modified samples

The result of CNT growth on HMDS treated samples shown in Figure 37. As indicated by the figure, the result also did not show a significant improvement for CNT growth using this treatment, Figure 37 shows that the majority of substrate below is still visible. Perhaps denser CNT coverage can be achieved if thicker HMDS coating was provided;
however, this method was not pursued further at this time because other methods (oxide deposition) have shown to be more effective.

![Image of CNT growth on HMDS treated carbon foam]

**Figure 37**: CNT growth on HMDS treated carbon foam.

5.4.2 Deposition of Oxides

5.4.2.1 Growth on Plasma $\text{SiO}_2$ modified sample

Figure 38, shows the result of CNT growth on plasma SiO$_2$ coated samples. This image demonstrated that the qualities of growth (in terms of density, alignment, and tube uniformity) have finally increased significantly. It was the first time, in this investigation, that the results showed aligned CNT growth was achieved on the surface of the carbon foam. Earlier reports of CNT investigation conducted on electronic grade silicon, also reporting of CNT growth enhancement when oxide buffer layer were used [66], [68],
[130]. The enhancement observed from this preliminary investigation prompted interest to investigate CNT growth using this surface modification technique. Investigations using plasma silica treated sample along with effects of oxide thickness will be investigated further in Chapter 6.

Figure 38: CNT growth on MPD SiO2 modified foam.

5.4.2.2 Growth on ALD Al2O3 modified samples

Figure 39a, shows the result of a sample coated with 2 nm of alumina that received CNT growth, and Figure 39b is a sample coated with 10 nm of alumina also received CNT growth. Figure 39a shows that uniform distribution of CNT clusters can be seen throughout the carbon foam, however the growth was not dense nor aligned. When the alumina buffer layer was increased to 10 nm, it shows that CNT growth becomes dense and aligned. Therefore this demonstrates that proper selection of oxide thickness is
required to achieve desired CNT growth density and uniformity. Simmons et al reported that there is a critical oxide thickness required for CNT growth and enhancement, however this was conducted using electronic grade silicon [66]. With the results observed here, investigation using ALD Al₂O₃ treated sample will be investigated further in Chapter 6.

![Image](image.jpg)

**Figure 39**: CNT growth on ALD Al₂O₃ modified carbon foam. A) 2nm, B)10 nm

5.4.2.2.a. Extended Growth Investigation on ALD Al₂O₃ modified samples (thickness variation)

Samples with discrete oxide thickness were prepared and grown for investigation, (5, 10, and 50 nm). The 2 nm result shown in Figure 39 was too sparse, so it was not used. Figure 40 indicated that as the thickness of the buffer layers increases the carpet height also increases, currently with an oxide thickness of 50 nm the CNT growth observed was
also the longest. For SEM image see Figure 40, for plotted carpet height vs oxide thickness see Figure 41. However, it was observed that in certain areas alumina films were also “lifted-off” on these samples, highlighted by orange dotted lines, Figure 40. Note, the carpet height is measured from the entire visible length of CNT, including the lifted-off section. Therefore it wasn’t clear how the carpet height will change if “lift-off” did not occur. In addition these SEM images were taken on carbon foam samples. It was realized that theses height can change or inaccuracy in measurements can occur due to the viewing angel. Therefore it was decided that detailed study will be conducted on a flat substrate. Chapter 6 will address the “lifted-off” issue by trying other deposition procedures and to investigate growth on flat substrate so that better measurements and comparisons can be made.

Figure 40 Oxide thickness effect on carpet height, Al₂O₃ on RVC foam
It was interesting to know if CNT growth were achieved throughout the foam samples. Therefore, samples grown with CNT were sawed in half, width wise, resulting a sample size of 5 mm x 5 mm x 5 mm cube. The cut surfaces were investigated with SEM. Figure 42 shows a representation of the investigated area. The images from Figure 42 validated that CNT growth did take place well into the depth of the foam.
Figure 42 SEM of a broken interface, RVC foam sample saw in half

5.5 Summary

Surface modification techniques investigated in this chapter indicated that only ones that use oxide buffer layer were shown to be effective in improving CNT growth density on carbon foam. It was determined that surface oxidation methods such as nitric acid treatment, oxygenation, HMDS did not improve the CNT growth on the surface of carbon foam significantly as they were used. The improvement was only observed when oxide deposition was used on RVC samples. The results show when carbon foam coated with 4 nm plasma silica the CNT growth was improved in terms of growth density, alignment and uniformity. Similar growth improvement was observed when carbon foam was deposited with (>2nm) ALD alumina film deposition. At 2 nm the growth on alumina
was still sparse, however the amount of CNT cluster increased more uniformly throughout the foam. When thicker alumina was deposited, 10 nm, major improvement of CNT growth in terms of density, alignment and uniformity were observed. In addition, ALD alumina with a wider film thickness selection also show that as the film thickness increases the appeared carpet height also increased. However, it appears that certain growth using ALD alumina resulted in oxide film separation from the substrate, while the separation was not observed for sample deposited with silica with the three samples tested. However the separation issue will be investigated in a later chapter. Resolving the separation issue will allow better investigation to see the effect between oxide thickness and carpet height. The separation of the oxide film may be a result of CTE differences between the oxide layer and the carbon substrate. The CTE value for carbon is about $1.5 \times 10^{-6} \text{K}^{-1}$, for alumina is $8.1-8.4 \times 10^{-6} \text{K}^{-1}$, and silica is $0.55 \times 10^{-6}\text{K}^{-1}$. As the values suggest the CTE values between carbon and silica are much closer than the difference observed between carbon and alumina.

In this chapter it was observed that two different oxide materials were successful at enhancing CNT growth on carbon substrates. It was reported that similar buffer effects were observed when silicon samples were coated with an alumina oxide, where increases of CNT growth in terms of density were reported [130]. Therefore, it is essential to investigate the effect of different oxide material and their influence on CNT growth. This will be the scope for Chapter 6, influence of oxide on CNT growth.
Section III: Experimental

(Detailed Investigations)
CHAPTER 6: Influence of Oxide Buffer Layer Materials

The results of Chapter 5 show that in order to enhance the density of CNT growth on carbon foams, a pre-coating of oxide buffer layer material is required. In this study, two promising oxide materials, alumina and silica will be used to investigate their effects to CNT growth. In addition, different deposition techniques, alumina (ALD Al₂O₃, Sputtered Al₂O₃) and silica (thermally oxidized SiO₂, ALD SiO₂ and Plasma SiO₂), will be used to deposit the oxide buffer layers. It is suspected that oxide deposition via different deposition techniques results in oxide films with different stoichiometries. Figure 14 shows that oxide films made with different stoichiometries resulted in a large variation of intrinsic physical properties (thermal conductivity, density, CTE…, etc). Differences in intrinsic properties could potentially influence CNT growth, and therefore need investigation.

The study investigated in this chapter used modeled flat carbon substrates mentioned in Section 3.1.2.4, instead of carbon foams. The flat substrate geometry allows for better experimental control and more amenable microscopy comparisons for CNT growth characteristics on buffer layer variations. In addition, the flat carbon substrates have the same chemical composition as the carbon foam.
6.1 Oxide Buffer material for this investigation: $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$

Section 2.7 shows the history of buffer layer used to grow CNT on silicon substrate. Initially, it was thought that one of the ways to minimize interface resistance was to grow CNTs directly onto metals; however this method has resulted in a low growth density. As the studies progressed, using silicon as substrate, it was found that aligned CNTs can be grown on oxide buffer layer supported substrates. Simmons et al. reported that the use of iron or nickel as catalyst source for dense CNT growth, requires a critical buffer layer thickness about 4nm for $\text{SiO}_2$[1].

More recently, carbon has become an interesting material for substrate choice due to its lightweight and excellent thermal properties. Carbon has many great physical qualities that could be useful in future lightweight space material applications. However, growing CNTs directly on carbon is challenging due to several factors. First, during high temperature annealing, the metallic particles can diffuse into the substrate and, depending on the distance traveled, may no longer act as a viable catalyst to promote CNTs growth [2]. Secondly, carbon has low surface reactivity, which makes it difficult for other materials to bond to the surface, including many known transition metals regularly used as catalysts for CNTs growth[3]. There have been many attempts at surface modification to increase surface reactivity of carbon [3]–[7]. However, the most successful way is by modifying the carbon surface with an oxide buffer layer. This is because the oxide layer is an effective buffer that prevents catalytic particles from being absorbed into the
substrate; it also allows particles to agglomerate into islands that promote CNT growth [1], [8], [9].

In Chapter 4, it was demonstrated that CNT morphology is very sensitive to the combination of material selection and growth techniques used for synthesis. In this chapter, the goal is to investigate how oxide buffer layers play a role in CNTs growth mechanisms; it is important to keep in mind some of the observed growth behavior already reported. For example, it has been reported that, using TCVD growth method, samples coated with Al₂O₃ as a buffer layer have yielded the best grown CNTs in terms of tube density and alignment [2], [10]–[12]. This may or may not be true if a different growth method was used. With the success observed in the previous chapters, this investigation used the FCCVD method to grow CNTs. It is crucial to pay special attention to the metal particle and the buffer layer interaction, because the reaction taking place between the metal particle and the buffer surface can be altered due to slight changes in environment such as (temperature, and water vapor) [13]. For example, improper growth conditions, such as extremely high temperature, in certain instances, would result in excess amorphous carbon production. In other words, any alteration in growth conduction will require detailed investigation of the resulting CNTs. It has been reported that even when the same type of catalyst was used, on a different oxide buffer layer, the resulting CNTs was different [14]. For example, Amama et al. reported seeing a difference in growth characteristics when CNTs were grown using the same conditions
but upon different oxide buffer layers[11]. In addition, by comparing how the oxide buffer layers were deposited, sputtered versus evaporated, Ohashi’s group reported that CNTs grew better on sputtered oxide, which is attributed to it being more thermodynamically stable [12].

Recent studies reported by this group have shown that direct growth of CNTs on carbon is challenging and tends to result in sparse clusters [15], [16]. This is possibly due to the chemical inertness of graphite [3], [17]–[19], which results in a low affinity for the transition metal precursors that allow nano-catalyst formation [20]. In other words, transitions metals do not seed well on graphite surfaces [21], and as a result a very limited amount of catalyst particles were available on graphite surfaces for CNT nucleation. In an attempt to address this issue, this group recently studied the effect of several surface treatments on porous carbon foam, summarized in Chapter 5. It was found that buffer layers composed of either (5-50 nm) of alumina or 4 nm of silica largely enhanced the density of CNT growth on the foam surfaces [15], [16]. However, detailed studies have not been performed to determine the influence of buffer layer chemistry on carbon substrates with respect to CNT growth and controllability. Some general characteristics of a good buffer layer have been outlined by Rodriguez-Reinoso [20], but few additional requirements should be noted for growing them on carbon substrates: stability under reaction conditions, adequate mechanical properties, strong bonding to the substrate, and coating via a process that would not be limited by line-of-sight.
6.2 Objective: Understanding the Effect of Oxide Materials on CNT Growth

The objective of this study is to determine the suitability of oxide materials as buffer layers used for CNT growth. To accomplish this, oxides (Al₂O₃ and SiO₂) will be deposited on flat modeled carbon substrates.

It is hypothesized that different oxide materials influence CNT growth differently and oxide deposited using different deposition techniques would result in different oxygen deficiencies of the resulting oxide film. These deficiencies result in different oxide film quality and stoichiometry. Figure 14 shows those oxides result in different intrinsic properties when they have different stoichiometries. It is possible that these properties will influence CNT growth differently. It is the goal of this study to determine those effects. In order to study these effects, several different oxide deposition techniques will be used. The resulting oxide film will be compared for its influence on CNT growth and for its suitability as buffer layer. Here are the areas of investigation relating to the effect of buffer layers that will be investigated.

1. Surface roughness effect
2. Oxide thickness effect
3. Growth time effect
4. Oxide Material effect (Alumina versus Silica)
The influences of the different oxide materials and their surface interactions on CNT growth will be revealed in this study.

6.3 Experimental:

Model substrates of geometrically flat carbon were generated by pyrolysis of polymeric precursors on silicon wafers, Section 3.1.2.4. The vitreous carbon samples represent the same chemical structure as carbon foam but in simple planar geometry, which is much more suitable for quantitative analysis via microscopic and spectroscopic techniques. The alumina and silica were selected as buffer layer materials due to the observed results from Chapter 5, where CNT growth density and uniformity were both improved when these oxides were used. Microwave Plasma Enhanced - Chemical Vapor Deposition (MPECVD) and ALD were selected as surface pre-coating methods, and the FCCVD technique was selected to grow CNTs on the surface. This investigation uses the FCCVD growth technique found in Section 3.5.3.3.2 for CNT growth. However, the growth time has been modified to be either a 1 minute growth run or a 20 minute growth run.

6.3.1 Preparation of Vitreous Carbon on Si (model carbon substrate):

In order to effectively compare the resulting growth morphology of the CNT carpet, the substrate used should be flat (RMS < 5nm). This substrate requirement can be fabricated in the lab using the process described in Section 3.1.2.4. Essentially the carbon layer is
created by pyrolyzing a photoresist coated silicon sample. The vitreous carbon had an average thickness of 450 nm and average RMS value about 0.4 nm.

Some modeled carbon substrates were treated with reactive ion etching (RIE), Section 3.6.3.1, in order to provide the surface roughness variation needed to support the comparative analysis in this study.

6.3.2 Substrate and Buffer Layer Preparation

This study was conducted using flat substrates. This enabled a direct comparison between samples with various oxide deposition layers. Ideally, the results from this study could be applied in future studies, where carbon substrates with complex structures are preferred.

The majority of the oxide thicknesses deposited in this study was 5 nm. Certain studies investigate the effect of oxide thickness on CNT growth. In those studies, different oxide thickness will be used and the thickness will be specified, Section 6.4.4. The oxides deposited were as follows: ALD SiO₂ (ALD SiO₂), MPECVD SiO₂ (plasma SiO₂), ALD Al₂O₃ (ALD Al₂O₃), and sputtered Al₂O₃ (S Al₂O₃). In addition to these, several purchased commercially-available samples were used, and they are thermal SiO₂ (1 mm thick) on Si, sapphire substrate and fused silica. These commercially available samples were selected because their material characteristics were well understood and because
they have been used by various research groups to successfully grow densely aligned CNTs.

6.3.2.1 Atomic Layer Deposition (ALD) of Al$_2$O$_3$ and SiO$_2$:

ALD is a vapor phase, self-limiting, thin film deposition method in which the reactions take place between precursor gas molecules and the surface of the substrate. The resulting thin film should be pinhole-free and conformal to the substrate surface [22]. The organometallic precursors used for deposition of Al$_2$O$_3$ and SiO$_2$ were trimethylaluminum, and trisdimethylamino-silane, respectively. Water vapor served as the oxygen source for both films. The thin film growth process was conducted at 200 °C with deposition rates of 1.5 Å/cycle for Al$_2$O$_3$ and 0.5 Å/cycle for SiO$_2$.

In Chapter 5, it was discovered that certain sample areas demonstrated signs of alumina films “lift-off” post CNT growth. To address this point, some samples were deposited with the following modified ALD alumina recipes to determine if film adhesion improvements could be made.

1. Pre-oxygenation of the substrate surface followed by oxide deposition at 200°C.

2. Pre-anneal the sample at a higher temperature (500°C) in Argon for 3 minutes, prior to oxide deposition at 200°C.

3. Depositing the alumina films at a higher temperature (300°C).
*** However none of the treatments performed solved the “lift-off” issue, which was observed post CNT growth. As mentioned earlier there is a large CTE difference between C–Al$_2$O$_3$, and this difference is probably one of the main driving factors for film lift off. The lift-off issue can be undesirable for certain electronic applications, especially electrical or thermal applications, because it can disrupt transport properties at those locations. Other oxide deposition techniques may be able to produce films that have stronger adhesion to the substrate, but due to the complexity for certain substrate geometry, carbon foam; such deposition technique must not be limited to line of sight techniques. Therefore other suitable ways for improvements should be investigated in the future studies.

6.3.2.1.1 Oxide Thickness(Alumina):

ALD alumina technique mention in Section 3.3.2.2 was used to deposit the following alumina oxide thickness: (5, 10, 25, 50, 100, and 200 nm). In addition, a purchased sapphire substrate sample was used to represent a sample with infinite alumina thickness.

6.3.2.1.2 Reactive Ion Etch (RIE) with Oxygen Plasma:

In order to provide surface roughness variations, some standard carbon samples were treated with RIE prior to ALD alumina oxide deposition. RIE parameters used are ones mentioned in Section 3.6.3.1.
6.3.2.2 Microwave Plasma SiO$_2$:

MPECVD deposition technique mentioned in Section 3.3.2.4 was used for silica deposition. A mixture of hexamethyldisiloxane (HMDSO) and O$_2$ was flowed into a vacuum chamber equipped with an 850 W microwave generator with magnetron assist.

6.3.2.2.1 Oxide thickness (Silica):

Plasma silica technique mentioned in Section 3.3.2.4 was used to deposit the following silica oxide thickness: (4, 14, 23, 43, 70, 145, and 212 nm). In addition, a purchased fused quartz substrate sample was used to represent a sample with infinite silica thickness.

6.3.2.3 Sputter Alumina:

In order to provide alumina samples with different surface roughness, 5 nm of sputtered alumina was deposited. This resulted in a surface roughness RMS value of about 4 nm. The deposition technique used was mentioned in Section 3.6.2.3.

6.3.3 Samples

Section 6.3.2 shows the processing steps available for making the samples used in this investigation. This section will specify how those samples were used in the investigation. In addition, this information is shown in Figure 43.

In this investigation there are four growth baselines. In the first baseline growth, samples were grown on untreated carbon (standard carbon sample) to see if direct CNTs growth
was achievable. The second, third and fourth baseline growth was done with xylene alone (no ferrocene), on standard carbon, and oxide coated (ALD Alumina and Plasma Silica) standard carbon substrate. Using only xylene to grow CNT, it allows the study to determine if CNTs can grow without a metallic catalytic source.
Each sample set listed in Figure 43 was run several times in order to establish experimental uncertainties.

<table>
<thead>
<tr>
<th>Baseline Samples</th>
<th>Growth Chemicals</th>
<th>Surface Pre-Treatment Prior to Oxide Deposition</th>
<th>Growth Time (minutes)</th>
<th>Oxide Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Carbon</td>
<td>Xylene and Ferrocene</td>
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<td>n/a</td>
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<td>Standard Carbon</td>
<td>Xylene only</td>
<td>n/a</td>
<td>20</td>
<td>n/a</td>
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<tr>
<td>Standard Carbon w/ ALD Alumina</td>
<td>Xylene Only</td>
<td>n/a</td>
<td>20</td>
<td>5</td>
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<tr>
<td>Standard Carbon w/ Plasma Silica</td>
<td>Xylene Only</td>
<td>n/a</td>
<td>20</td>
<td>5</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Experimental Samples</th>
<th>Growth Chemicals</th>
<th>Surface Pre-Treatment Prior to Oxide Deposition</th>
<th>Growth Time (minutes)</th>
<th>Oxide Thickness (nm)</th>
</tr>
</thead>
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<td>1, 20</td>
<td>1000</td>
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<tr>
<td>Plasma Silica on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
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<td>4, 14, 23, 43, 70, 145, 212</td>
</tr>
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<td>ALD Silica on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>1, 20</td>
<td>5</td>
</tr>
<tr>
<td>Quartz</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>20</td>
<td>∞</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>1, 20, 40</td>
<td>5, 10, 25, 50, 100, 200</td>
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<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>Pre-oxygenation</td>
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</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>Pre-annealing at 500 °C</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>Oxide deposited at 300 °C</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>RIE 20 seconds</td>
<td>1, 20, 40</td>
<td>5</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>RIE 60 seconds</td>
<td>1, 20, 40</td>
<td>5</td>
</tr>
<tr>
<td>Sapphire</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>20</td>
<td>∞</td>
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### Baseline Samples
<table>
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<tr>
<th>Growth Chemicals</th>
<th>Surface Pre-Treatment Prior to Oxide Deposition</th>
<th>Growth Time (minutes)</th>
<th>Oxide Thickness (nm)</th>
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</thead>
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<td>Standard Carbon</td>
<td>Xylene and Ferrocene</td>
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</tr>
<tr>
<td>Standard Carbon</td>
<td>Xylene Only</td>
<td>n/a</td>
<td>20</td>
</tr>
<tr>
<td>Standard Carbon w/ ALD Alumina</td>
<td>Xylene Only</td>
<td>n/a</td>
<td>20</td>
</tr>
<tr>
<td>Standard Carbon w/ Plasma Silica</td>
<td>Xylene Only</td>
<td>n/a</td>
<td>20</td>
</tr>
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### Experimental Samples
<table>
<thead>
<tr>
<th>Growth Chemicals</th>
<th>Surface Pre-Treatment Prior to Oxide Deposition</th>
<th>Growth Time (minutes)</th>
<th>Oxide Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Silica on Si</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>1, 20</td>
</tr>
<tr>
<td>Plasma Silica on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>1, 5, 10, 20, 40, 60, 80, 100, 120</td>
</tr>
<tr>
<td>ALD Silica on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>1, 20</td>
</tr>
<tr>
<td>Quartz</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>20</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>1, 20, 40</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>Pre-oxygenation</td>
<td>20</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>Pre-annealing at 500 °C</td>
<td>20</td>
</tr>
<tr>
<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>Oxide deposited at 300 °C</td>
<td>20</td>
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<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>RIE 20 seconds</td>
<td>1, 20, 40</td>
</tr>
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<td>AID Alumina on Standard Carbon</td>
<td>Xylene and Ferrocene</td>
<td>RIE 60 seconds</td>
<td>1, 20, 40</td>
</tr>
<tr>
<td>Sapphire</td>
<td>Xylene and Ferrocene</td>
<td>n/a</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 43 Sample sets prepared for the investigation
6.3.4 CNT Growth Parameters

FCCVD was used to grow CNT on the surface treated samples. The growth recipes used were ones from FCCVD mentioned earlier in Section 3.5.3.3.2. However, the growth time was varied between 1-120 minutes for this study.

6.3.5 Sample Characterization:

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) techniques were used as part of the image analysis for this study. The catalyst diameters, tube diameters, and carpet heights were determined by measuring either the CNTs or the catalyst particles in the images. The SEM was a FEI model XL30 Sirion, operated at a 10 kV bias. SEM images were taken of at least three different regions of each sample. The TEM used was a Philips model CM200 LaB6, operated at 200 kV. The TEM samples were prepared by scraping the surface of each 20 minute growth sample with a clean glass slide. The scraped-off material was transferred onto a 200 mesh TEM grid. A grid sample was made for each of the sample types (Standard SiO$_2$, ALD SiO$_2$, Plasma SiO$_2$, and ALD Al$_2$O$_3$) after each run. Images were taken from at least three different areas per grid. AFM was used to quantify the roughness of pre-CNT growth surfaces of the various buffer layers, as well as the model carbon layer prior to buffer deposition. A Quesant© model Q-Scope 250 AFM was operated using the non-contact mode at a 1 Hz scan rate. All sample scan areas were 5 $\mu$m x 5 $\mu$m. Scandium and ImageJ v1.48
software was used for distance measurement analysis on the microscopy images. These software packages have tailorable pixel-to-distance settings and zoom functions for better measurement accuracy.

6.4 Results and Discussion

6.4.1 Baseline Study of CNT Growth

6.4.1.1 CNT growth on untreated carbon surface (baseline 1)

To establish a baseline, CNT growth was tested on the as-formed model carbon sample without a buffer layer. Figure 44a shows a cross-section view of a cleaved model carbon sample before CNT growth. The image shows the carbon layer residing between the two yellow arrows. Figure 44b and Figure 44c are aerial views of the model carbon sample taken after growth times of one minute and 20 minutes, respectively. Figure 44b shows that the surface of the sample contains a minimal amount of catalytic particles. Figure 44c demonstrated poor CNT growth, clearly showing that the growth was focused in a few random areas. The insert on the top right corner is a higher magnification image taken from the outlined square, and it shows that each surface particle is made of randomly-oriented CNT clusters.
Figure 44 (a) SEM images showing cross-section and aerial views of CNT growth on samples without oxide buffer layer. (a) cross-section of the model carbon sample, where the yellow arrows highlighted the carbon film. (b) high magnification of an aerial view of a sample after one minute of CNT growth. (c) sample after 20 minutes of CNT growth. The scale bars are.

Figure 44 shows that CNT growth directly on the model carbon surface was scant and disordered. This condition may be due to the fact that carbon surfaces are chemically inert and may not offer sufficient reactive sites for catalyst particle formation. Figure 44b shows that the surface was essentially bare and contained only a few identifiable patches of catalytic particles, and Figure 44c shows random clusters of CNT growth. Figure 44b suggests that metallic particles do not condense or nucleate readily on the carbon surface. In Figure 44c, the higher magnification insert shows that catalytic particles that do attach to the carbon surface may grow CNT in a random and nonaligned manner.

The nonaligned CNT growth is possibly due to low CNT growth density in the local area. This allows the CNTs to grow freely in any direction, instead of being forced to grow vertically [23]. In other words, the CNTs are not confined by adjacent tubes. This experiment validated the need for suitable buffer layers to grow densely aligned CNTs.
6.4.1.2 CNT growth without catalyst source (baseline 2, baseline 3, baseline 4)

Another baseline was established for the study by introducing only xylene (without ferrocene) during CNT growth period. This growth used Standard Carbon substrates with and without buffer layer. This was done to clearly determine if the metallic catalytic source were necessary on the buffer layers. After repeated CVD deposition without ferrocene and SEM imaging of the surface in each case, it was clearly determined that no CNT were growing on these samples.

The role of buffer layer and catalyst source for CNT growth on carbon substrate is important for this research. It has been reported [24]–[27] that SWNTs may grow directly on oxides such as alumina or silica without the use of metallic source. In those situations, the oxides are in the form of nanoparticles. However, in this study, the oxides deposited were in the form of thin films and the result indicated no CNT could grow without ferrocene. It is therefore important to note that the mere presence of oxide is not enough to support CNT growth. In other words, CNT growths can only occur in the presence of nanoparticle catalysts, which are provided by ferrocene in this study.

6.4.2 Surface Roughness of Buffer Layers

Figure 45 shows the AFM measurements of pre-CNT growth on the four buffer layers as well as the model carbon layer. It can be seen that the surface roughness RMS values vary from 0.201 nm to 3.861 nm. In order from smoothest to roughest, the samples fall...
in the following order: Standard SiO$_2$, ALD Al$_2$O$_3$, model carbon, ALD SiO$_2$, and then Plasma SiO$_2$.

Figure 45 AFM images showing surface roughness of samples before CNT growth. Each image shows a scan taken from a represented 5µm by 5µm area at 1Hz. *Scale bars of the images are not uniform from one to another.

It is possible that surface characteristics such as roughness would influence CNT growth on carbon substrates. Therefore, surface roughness was measured for each type of buffer.
layer along with particle size, density and extent of initial CNT growth. Mock carbon samples were measured as a baseline reference, and the RMS value was found to be approximately 0.4 nm. The surface roughness increased with the addition of an oxide layer, with an exception of ALD ALD Al₂O₃, where the surface roughness actually decreased slightly. The roughness of the ALD Al₂O₃ was almost equal to that of the vitreous carbon layer, measuring at 0.405 nm. The roughness of the ALD SiO₂ layer was more than three times higher at approximately 1.45 nm. The SiO₂ deposited via MPECVD had the highest surface roughness value at approximately 4 nm; this was expected, because plasma-deposited SiO₂ films have been reported to grow as 3 to 4 nm islands, which merge to form complete films [28]. The Standard SiO₂ on silicon yielded the smoothest surface with an RMS surface roughness value of 0.2 nm.

The ALD method is expected to provide a conformal thin film morphology [35]. However, as stated above, the result shows that the surface roughness of ALD SiO₂ was about three times higher than the roughness of ALD Al₂O₃. This was attributed to the reaction between the ALD SiO₂ precursor and the carbon film for obtaining silica. The carbon film was degraded during the deposition process and as a result rougher surface was measured. Another possible reason might due to incomplete saturation of active sources on the substrate surface during film growth. As seen in Figure 47b, the ALD SiO₂ surface shows irregular holes in the top view SEM images. Furthermore, the carbon layer was not clearly distinguishable in the cross-sectional SEM imaging. To resolve this
issue, an additional test was performed in which the thickness of the vitreous carbon layer was measured by electron microscopy before and after ALD SiO$_2$ deposition. It was confirmed that a significant portion of the carbon layer does deplete during the ALD deposition process. This depletion may have resulted in surface roughening and void formation. It is not known if there are other possible ALD precursors for SiO$_2$ growth that prevent damage to the underlying carbon. The conclusion is that the present ALD SiO$_2$ precursor is of limited use in practical applications, since it causes noticeable degradation of the underlying carbon substrate.

6.4.2.1 Surface Roughness: Surface Variation for Alumina Coated Samples

In order to offer different surface roughnesses for oxide samples coated with alumina, a few standard carbon samples were modified with RIE treatment with oxygen plasma. The oxygen plasma created by RIE has the ability to etch the carbon surfaces within a few seconds of processing time, thereby creating a surface with different roughness. Since the ALD is a conformal deposition process, it should deposit an oxide film with roughness similar to the modified surfaces. Figure 46 shows the surface roughness of samples deposited with ALD Alumina post RIE treatments. The result shows the surface roughness increased from 0.45 nm – 0.70 nm when RIE etch time increased from 0 seconds to 60 seconds.
Figure 46 Surface roughness of RIE treated carbon sample that were coated with 5 nm of ALD Alumina. Sputtered alumina samples were also prepared; the film roughness was measured with an average RMS value of 4.44 nm. However, it was later determined from SEM images that the roughness was resulted from high number of voids present on the oxide film. These surface voids could potentially be unfavorable for certain electronic applications, as it will increase local thermal resistances. It was decided that samples with sputtered alumina will not be used in this investigation, but could be considered for future studies if a better deposition process was developed.
6.4.3 Growth of CNT arrays on oxide buffer layers

6.4.3.1 Brief growth: analysis of particle density, size, and CNT count

For this portion of the study, SEM images were taken of different oxide buffer layer surfaces after one minute of growth. The one-minute interval was selected to allow sufficient amounts of catalytic particles to be deposited onto the substrate. This interval prevents CNTs from growing too long and obscuring the catalytic particles. Figure 47 shows representative SEM images taken from all the samples with buffer layers after one minute. All of the images have a viewing area of 450 nm x 450 nm and were taken at 200k magnifications. These figures clearly show the particle distribution as well as the catalytic particle sizes. As seen in the Figure 47, CNTs had started to grow on the samples, but by varying amounts.
Figure 47 SEM images after one min growth. These images were processed with enhanced contrast. Figure 48 shows the measured values for catalyst particle densities, average particle diameters, and number of CNTs per square micron after one minute of growth as obtained from the SEM images in Figure 47.
Figure 48 Data collected after one minute growth, (a) particles per square micron observed after one minute for samples with different oxide buffer layers (b) average measured particle sizes after one minute and (c) number of CNTs present on the surface of each sample after one minute.

One important aspect of CNT growth is the areal density of the nanotubes. However, as the CNTs grow, they become entangled, increasing the difficulty in determining the absolute areal density from images. One way to compare CNT densities is to compare the number of catalytic particles on substrates before significant CNT growth. It has been suggested that each catalytic particle can produce at most one CNT [30], [31], hence particle count may provide an upper limit prediction of CNT density. Figure 47 shows an aerial view of the different samples. Figure 48 shows the average measured values as seen in the one-minute snapshots. These values serve as qualitative indicators of initial stages of growth, since it is expected that the actual quantities of catalytic particles will continue to change beyond the one-minute time frame. Figure 48 a and b suggest there were variations in terms of particle density on different buffer layers but no significant difference in particle sizes. In addition, it is important to note from Figure 48c that, even within the first minute, there were significantly more CNTs grown on ALD Al₂O₃ than on the SiO₂ samples. The presence of more CNTs suggests that iron particles stabilize on
the ALD Al₂O₃ surfaces more readily than on the silica surfaces, allowing for rapid nucleation and faster growth of CNTs. These differences may be attributed to the higher packing density of ALD Al₂O₃ and/or stronger catalyst-substrate interaction on the more ionic Al₂O₃ compared to SiO₂. Furthermore, Jadaun et al. suggested that the way that dangling bonds terminate on oxides surfaces would provide charge imbalances [32]. This may result in significant differences in the stability, surface charge densities, and chemical catalytic activities of the particles deposited on them. These atomic level differences on the oxide surfaces may be contributing to the differences in CNT nucleation.

Another way to compare the resulting information is by comparing the number of catalyst particle to surface roughness. AFM results shown in Figure 45, reveals that the three different silica buffer layers resulted in three surface roughness measurements. Using the data collected on the samples, a trend can be seen by plotting surface roughness from the RMS values versus particle count. Figure 49 shows samples that used SiO₂ shows a proportional increase between the surface roughness and the density of deposited nanoparticles. The fitted line has a R² value of 0.9721.
6.4.3.1.1 Brief Growth: RIE Treated Carbon Samples with ALD Alumina Coating

Standard carbon samples that were treated with RIE resulted in surface roughnesses that were proportional to the treatment times. One of the goals for this study is to see if an increase in surface roughness results in increased particle counts for samples that were deposited with ALD alumina. Figure 50 shows the SEM result of samples treated with RIE and coated with 5 nm of ALD alumina after 1 minute of CNT growth. It was observed that the CNT growth density increases for samples receiving longer RIE treatment times. In other words, samples that are rougher (longer RIE treatment times) result in denser CNT growth.
In addition, this SEM image shows that it is difficult to conduct particle count analysis on these samples due to the overwhelming presences of CNTs. Due to the overwhelming CNT coverage on the substrate surface, at this point, it is unknown if rougher surfaces contribute to higher number of particles received on the oxide surface, or if it contributes to a faster CNT nucleation rate. This might be an interesting area to investigate in the future study. From the results observed in Section 6.2.3, the higher surface roughness resulted in higher catalyst count, therefore it is hypothesized that rougher RIE treated surfaces also received more catalyst on the substrate surface. It is possible that the higher visual density observed in Figure 50 is a result of more CNTs grown simultaneously from higher catalyst density that is proportional to surface roughness.

Figure 50 1 minute CNT growth on alumina oxide coated (RIE treated) samples, CNT growth density increases with increase of surface roughness
6.4.3.2 Extended growth: analysis of tube diameter, carpet height and growth rate

In order to see the influence of different oxides have on CNT growth an extended CNT growth time of twenty minutes was used. Twenty minutes of CVD growth time was selected to allow for a detailed comparison of CNT carpet height on each buffer layer. Cross-sectional SEM images were taken from all the post-growth samples once they were cleaved in half. Figure 51a–d shows the side-by-side interface comparisons of the samples grown. SEM shows that that the carbon layer appears to be missing for Figure 51b and Figure 51c, however it was visible for Figure 51d. Using EDS, it was identified that indeed the carbon layer was not detected for Figure 51b, but was detected for Figure 51c. The inserts for Figure 51a–d show significant differences in the carpet height among the samples. The lower insert in Figure 51c is a low-magnification image showing the visible carbon layer for the plasma SiO$_2$ coated sample. Furthermore, the insert for Figure 51d shows a faint line in the middle of the CNT carpet, EDS identified this is a ALD Al$_2$O$_3$ buffer layer. This suggests that during CNT growth, ALD Al$_2$O$_3$ was detached from the interface.
Figure 51 (a-d) SEM images of 20 minutes growth samples; the highlighted scale bar is 500 nm
Figure 52a is a plot of the average height measurements, and Figure 51b shows the
proportional increase trend of carpet height versus particle count, measured from one
minute, for the silica samples. The linear relationship between the two can be seen from
the fitted line with a $R^2$ value of 0.9736.
Figure 52(a) average carpet height determined for each sample, and (b) correlation between particle count (value after one minute) and carpet height (value after 20 minutes) for all the samples. As seen in Figure 51, all of the samples grew self-oriented CNT carpets, much like those described by Fan et al. [23]. However, there were variations in carpet height. The results show a clear trend for the silica buffer-layer samples. Figure 51f revealed that as the particle count increased, the carpet height also increased. This observation is important because it points to the possibility that the packing density of catalyst particles can influence the carpet height obtained under identical conditions. In other words, for a given chemical composition of the buffer layer, increased particle density as a result of increased surface roughness can influence the carpet height of the CNT array. Earlier studies have mentioned that the surface roughness has been a factor for CNT growth efficiency and lengthening [33], [34]. In addition, Xu et al., mentioned that CNT alignment is a result of “crowding effect” [35]. However, some may argue that the length of the CNTs are the same, they just appear to be shorter because of the curliness difference from one batch of CNT compared to another. As a result, they are visually
shorter from one SEM viewing angle. Although this might be true, one possible way to prove this is to place the individual CNTs next to each other for comparison, however, isolating individual CNTs is not currently possible. Figure 51 shows the comparative cross-section images of CNT morphology. Note, it is difficult to determine the actual degree of alignment of the CNT carpet since the image capture occurred post cleaving, and there is no way to determine how much disturbance was done during cleaving.

6.4.3.2.1 Extended Growth for Surface Variation for Alumina Coated Samples

Extended growth studies were also performed on RIE surface modified samples. The idea was to see if rougher samples would produce longer CNT carpets for samples coated with ALD alumina. Figure 53 shows the result of extended growth runs (20 minutes) on samples treated with and without RIE followed by ALD alumina coating. It is unclear why samples receiving 20 second RIE treatments result in shorter CNT carpet when compared to sample that was never treated with RIE. However, when comparing samples treated with RIE times, 20 seconds versus 60 seconds, the samples that were rougher grew taller CNT carpets. This result is similar to what was observed when silica samples were used. However more investigation is needed to identify all of the effects from RIE treatments, in order to explain the possibility of negative impacts that RIE treated samples have on carpet height.
6.4.4 Thickness Effect

**6.4.4.1 ALD alumina thickness effect on modeled carbon samples**

In the earlier chapters, it was noted that certain growth, using ALD alumina would result in “lifted-off” oxide buffer layers sometime during CNT growth.

This lifting phenomenon raised concerns about the mechanical integrity of such structure. To address this issue, several pretreatment techniques were conducted to see if the “lift-off” issue could be corrected. The pretreatment techniques included the following:

1. Pre-oxygenation of the substrate surface
2. Pre-annealing the sample at a higher temperature (500°C) for 3 minutes
3. Depositing the alumina films at a higher temperature (300°C).

However none of the treatments performed solved the “lift-off” issue, which was observed post CNT growth. As mentioned earlier there is a large CTE difference between C–Al₂O₃, and this difference is probably one of the main driving factors of film lift-off. Furthermore, it has been reported by George et al., that the deposition of ALD alumina on CNT and graphitic surfaces is difficult, which is caused by the inert carbon surfaces [29]. However, there has been a report of successful film growth by Xuan et al. The location of the successful film growth took place along step edges, where the origin of nucleation site was believe to be located [36]. In this study, the substrate used is glassy carbon, therefore, it is possible that alumina oxides film only forms a weak bond with the carbon substrate, and results in the “lift-off” of the film that was observed post CNT analysis.

The lift-off issue can be undesirable for certain electronic applications, especially electrical or thermal applications, because it can disrupt transport properties at those locations. Other oxide deposition techniques might be able to produce films that have stronger adhesion to the substrate and should be investigated in future studies. Figure 54 shows the results from samples that were grown on samples deposited with various ALD Al₂O₃ thicknesses and grown for 20 minutes. These images show that the
oxide layers did lift-off in certain samples. However, the image does not indicate when the lift-off occurred during the CNT growth.

Figure 54 shows CNTs grown on various ALD alumina thickness deposited on standard carbon sample (unless specified otherwise), a) 5nm, b) 10 nm, c) 25 nm, d) 50 nm, e) 100 nm, f) 200 nm, g) Sapphire, h) 5 nm oxide on carbon foam. The orange dotted rectangle highlighted the alumina that lifted away from the substrate. Figure 55 shows the SEM images of two different locations from one sample. These images show that in some area of the sample the oxide film did not “lift-off” and in other locations the film “lift-off” did occur. However, when comparing the carpet height of un-lifted sample to just the top portion of the lifted sample, the carpet height was measured within one standard deviation of error. It was believed that the top portion of a “lift-off” sample received continued growth from the beginning, regardless if the oxide peeled off during the CNT growth. As a result, it was decided that by measuring the top portion of a “lift-off” sample, one can capture the effect of oxide layer thickness.
Figure 55 SEM images comparing the carpet heights: not lifted vs “lifted-off” sample locations

Figure 56 is a shows CNT carpet height as a function of oxide thickness. The feature of the graph shows that CNTs grew the fastest when oxide thickness is about 10 nm, and it resulted in tallest carpets when the same amount of time was use to grow CNTs. In addition, the images show that initially as the thickness of the buffer layers increased (up to 10 nm) the CNTs array height also increased, and as the thickness increased beyond 10nm a reduction in height was observed. The “lifted-off” portion of the film was highlighted with an orange dotted line rectangle in Figure 54 (a, b, d, and h). It was observed in Figure 56 that when a sapphire sample was used as a substrate, representing an infinite oxide thickness, the CNT carpet height reached a maximum around 3 µm. This result further validated that a thicker oxide thickness does not necessary yield taller CNT carpets in a given growth time. Figure 54h shows that the lift-off issue is not
limited to flat substrate geometry, it also occurs on complex carbon geometry such as foam. This observation was mentioned earlier in Chapter 5; however since it was more difficult to conduct detailed microscopy analysis on carbon foams, this investigation was performed using flat carbon substrates.

![Figure 56 Chart showing the CNT Carpet Height versus ALD Al₂O₃ Oxide Thickness.](image)

**6.4.4.2 Plasma SiO₂ thickness effect on modeled carbon samples**

Similarly, to investigate the effect of silica oxide thickness on CNT growth, samples with various oxide thicknesses were prepared using the plasma SiO₂ deposition technique. The ALD silica was not used due the creation of carbon surface defects mentioned earlier. Using the 20 minutes FCCVD growth parameter, the result of CNT carpet heights on those oxide thicknesses are shown Figure 57. The images indicated that the CNT array height increased as the oxide thickness increased, from 4 nm to 23.2 nm, however further increase in oxide thickness (> 23.2 nm) resulted in a shorter CNT array height. Figure 58
is a plot of CNT carpet height versus plasma oxide thickness. The feature of the graph shows that CNTs grew the fastest when oxide thickness was about 23 nm. This height resulted in the tallest carpets when the same amount of time was use to grow CNTs.

It was also observed in Figure 58 that when a fused quartz sample was used as a substrate, representing an infinite oxide thickness, the CNT carpet height reached a maximum around 3 µm. This result further validated that a thicker oxide thickness does not necessarily yield taller CNT carpets in a given growth time. This result is similar to the ones observed when alumina oxides were used for CNT growth.

Figure 57 CNTs grown on various plasma silica thickness deposited on standard carbon samples, a) ~4nm, b) ~14 nm, c) ~23 nm, d) ~43 nm, e) ~70 nm, f) ~145, g) ~212 nm, g) fused quartz.
It was observed that both alumina and silica buffer layers each have an optimal oxide thickness that allows CNTs to grow the fastest. For alumina this thickness is around 10 nm, Figure 56, and for silica it is about 23 nm, Figure 58. One possible reason that this optimal oxide thickness is different for different oxides may have to do with the particle sizes. In Section 6.4.3.1 and Section 6.4.6 the particles sizes for samples that used alumina were about 10 nm in diameter, while samples that used silica had an average diameter of about 19 nm. In addition, other factors such as bonding and CTE differences might also contributed to the optimal thickness difference. For example, alumina oxides are denser and more ionic than silica oxides. Furthermore, according to Ajayan et al. and In et al. the driving force for CNT nucleation is oxide material dependent [1], [2]. It is
possible these driving force differences resulted in different optimal oxide thickness. In Section 6.4.3, it was observed that different oxide materials have different nucleation rates, which supports the idea that the driving force is oxide dependent. The result shows that samples with alumina buffer layer nucleated CNT faster, and that the optimal oxide thickness is thinner than silica buffer layer. However, alumina samples were plagued with adhesion issues which are due to the large CTE difference between alumina and carbon. For this study, the weak adhesion is problematic for thermal applications, and therefore samples with alumina oxide will not be used for samples intended for thermal analysis.

This is not the first reported observation that CNT carpet height was influenced by oxide thickness. Several studies has reported that varying the thermally grown SiO$_2$ on Si from 3.5 nm – 24 nm resulted in carpet height differences [1], [3]. More specifically, it was reported that an oxide thickness of 5 nm is required for CNT to grow, and that as the oxide thickness increases so does the carpet height [1]. This investigation uses ALD alumina and plasma silica with oxide thicknesses that ranged from 5 nm to about 200 nm. In addition, quartz and sapphire were used to represent defect free infinite oxide substrate. It was observed that initially when the oxide thickness increased, the CNT carpet height also increased. Then further increase in oxide thickness resulted in decrease of carpet height. As a result the following hypothesis explains the possibility for this observation.

1. When the oxide was too thin
a. Catalyst particles can reach the substrate. When this happens, it can lead to catalyst poisoning. As a result the growth is terminated.

2. When the oxide was ideally thick
   a. Diffusion of iron particles into substrate was effectively blocked, which lead to full growth potential.

3. When the oxide was too thick
   It was observed that the CNT carpet height was reduced after reaching a certain oxide thickness. In order to find out the root cause one needs to investigate the following in future studies.
   a. The thickness of the oxide layer, beyond certain thickness, it might be possible that local thermal and electrical hot spots in some substrates become an issue. These hot spots might prevent efficient and effective CNT growth and should be considered for investigation in future studies.
   b. It is also possible that iron particles continue to diffuse into the depth of porous silica, as a result carbon sources can no longer react with catalyst particle to facilitate CNT growth. When this happens, CNT growth ceased to continue.
   c. Changes in film’s tension or internal stress
   d. Increases in defect concentration
Finally, the difference between Cao et al. and this investigation is the resulting carpet height. In Cao et al, samples were grown on epitaxy SiO$_2$ on Si, and observed that once the optimal oxide thickness has been reached, further increases in oxide thickness does not change CNT carpet height. However, in this study, it was observed if oxide thickness increases beyond the optimal thickness the CNT carpet height will be reduced. Further investigation is required to identify if growth on different substrates, silicon versus carbon, result in the different CNT growth behaviors or perhaps there are other influences that have yet to be observed.

6.4.5 Growth Time Effect

6.4.5.1 ALD alumina Growth Time Effect

Many studies have reported that, catalyst activity or poisoning, is one major factor in determining the duration of CNT growth and the ultimate carpet height achieved. In order to find out where the limitation is, CNTs were grown with discrete growth times of 20 minutes and 40 minutes on samples coated with 5 nm of ALD alumina. Figure 59 shows the result of ALD alumina coated samples that were treated with and without RIE prior to the oxide coating. It was observed that when the surface roughness is less than RMS $= 0.59$ nm, increase in growth time from 20 minutes to 40 minutes, results in increased carpet heights. However, when the surface roughness is $> \text{RMS} = 0.59$ nm
increase in growth time does not continue to increase in carpet height. This suggests that there is a limitation in growth time for samples that use 5 nm of ALD alumina.

Figure 59 CNT carpet heights on RIE treated/untreated samples with ALD Alumina, growth time variance

6.4.5.2 Plasma SiO₂ Growth Time Effect

Similarly, CNT growths were conducted on samples deposited with 23 nm of plasma silica, where the growth time parameter was changed from 1 minute to 120 minutes.
Figure 60 shows the cross-sectional SEM images of the samples grown at each corresponding time with each image shown at the same magnification. The measured carpet heights were plotted in a chart shown in Figure 61. However, this chart is missing the data point from 1 minute growth. The carpet height from 1 minute growth was too small to have a conclusive measurement. The result shows that the CNT array height increases linearly with growth time. In addition, the result shows that the growth continued for up to 120 minutes. Therefore, the physical height limit for this growth is currently unknown. However, it has been reported that CNT growth termination was due to a deactivation of the catalyst source. Therefore, it is possible that CNT growth termination will happen at some point. Furthermore, it might be possible to model this growth trend in a fashion analogous to population growth. Figure 60 shows that measurable growth did not happen until 5 minutes, which suggests that very little growth occurs within the first 5 minutes of the reaction. Growth times longer than 5 minutes follow the exponential rule until the carrying capacity is reached. It is unknown when and where the carrying capacity is for this growth, but once the carrying capacity is met the growth plateaus off. This investigation shows that time variables can be used as a controlling parameter for CNT growth.
Figure 60 X-section image of samples coated with 5 nm plasma SiO$_2$, grown for various growth times, samples shown are the same magnification with scale bar showing 200 µm.
6.4.5.3 Growth Mechanisms and Equations Discussed in the Literature

CNT growth mechanisms have been discussed extensively in the literature and there are ongoing debates on the exact growth mechanisms of different conditions of CNT growth. However, it is widely accepted that the overall process consists of the following steps.

1. The substrate or buffer layer provides a suitable surface to allow catalyst particles to anchor, while prevent clustering of particles
2. CNT nucleation takes place after the catalyst particles has seeded on the surface
3. The length of CNT grows with deposition time
4. Growth of CNT eventually terminates due to one of the following:
   - Catalyst poisoning
   - Catalyst inward diffusions
Entanglement and clustering of nanotubes with no space to grow

Several researches have formulated growth and kinetics related equations related to the above steps, few examples below.

Equation 5, and 6 below have been suggested by In et al. and P. M. Ajayan et al. to describe the rate of CNT growth during the linear stage of growth [68], [154].

**Equation 5: Rate of CNT growth, In et al.[154]**

\[
\nu_{CNT(growth)} = \frac{\Delta \mu}{kT} N_0 \omega \frac{N_0}{R_1 + R_2 + R_3}
\]

Where \( \frac{\Delta \mu}{kT} \) is oxide specific driving force for the reaction, and \( N_0 \) is the initial concentration of catalyst active sites, \( \omega \) is kinetic coefficient and \( R_1 \) is growth resistance related to diffusion of gas/molecules through the growing CNT forest to the catalyst sites, \( R_2 \) is growth resistance related to carbon adsorption and catalyst deactivations, and \( R_3 \) is growth resistance related to CNT nucleation.

**Equation 6: Rate of CNT growth, P.M. Ajayan et al.[68]**

\[
\nu_{CNT(growth)} = \frac{C_0K_s}{N}
\]
Where $C_0$ is the carbon concentration at the growth front, $K_s$ is the reaction rate constant that is dependent on the oxide thickness, and $N$ is the density of carbon atoms in the CNT film.

Furthermore, Shanov et al. offers a different perspective as shown in Equation 7 below. This equation includes a catalyst-lifetime term, where CNT growth terminates when catalyst particle is no longer active. This phenomenon has been reported by few other authors, but it was not observed in within the growth conditions of this investigation.

**Equation 7: Rate of CNT growth, Shanov et al.**[156]

\[
L_{CNT,T,t} = L_f - r_{growth} (t_{catL} - t)
\]

Where $L_{CNT,T,t}$ is the length of CNT at certain time and temperature. $L_f$ is the final CNT height, $r_{growth}$ is the rate of growth, $t_{catL}$ is the catalyst life time, $t$ is time and $T$ is temperature.

It must be noted that the proposed variables from the different equations have their own merits within a given set of growth conditions, and care is needed in correlating or comparing variables from one case to another.

In this investigation the initial stage (first 10 minutes) shows minimal or very slow growth, probably during initial nucleation. Once nucleated the growth rate becomes
constant, and CNT array length grows linearly with time with no tapering observed up to 120 minutes. This indicates that catalyst life time is not a factor under these conditions.

6.4.6 TEM analysis: CNT and catalyst morphology

Figure 62 shows that CNTs grown in this study resulted in multiple walls regardless of the type of oxide used as buffer layers. Numerous articles have stated that catalyst particle size determine the tube diameter and growth rate for CNTs [30], [39], [40]. As seen in Figure 62, there were two different morphologies for catalytic particles: spherical or cylindrical. Spherical particles seemed to have less uniformity in terms of the size of residual particles and resulting CNT diameters, whereas cylindrical particles seem to yield more uniform CNT diameters. The images revealed that the samples made with silica favored the spherical shapes, while the samples made with ALD Al$_2$O$_3$ favored the cylindrical shapes. The white arrows in Figure 62 point to the catalyst particles, and the dashed white arrows points to a few of the larger CNTs shown in the inserts of the figures, located on the top right corners.
Figure 62 TEM images that show particle and CNT morphology for (a - c) SiO$_2$, and (d) Al$_2$O$_3$ buffer layer samples.

It was observed that after one minute the particle sizes on all the samples were relatively the same; however, it was later found that CNTs grown via the SiO$_2$ buffer layer had larger variances than ones grown with the Al$_2$O$_3$ buffer layer. It was also observed that the CNT initiation rate was different between the two oxides. This difference may be the
cause for the particle morphology differences observed in Figure 62, where samples grown using Al₂O₃ resulted in an elongated catalyst shape, while samples using SiO₂ had more spherically shaped catalyst. CNT growth initiated earlier in samples with the ALD Al₂O₃ buffer layer had particle sizes that remained smaller and more uniform in size. The early nucleation process may have stopped the nanoparticles from enlarging, but it may have elongated the particles.

It is unclear if the morphology of the catalyst particle is formed prior to CNT growth or after. However, the study done by Schaper et al. showed that particle morphology can change during CNT growth, due to the catalyst particle being in a quasi-liquid state.[41] Therefore, even if the starting catalyst particles at 1 minute are similar in shape and size, it is possible that the morphology of the particles changes during CNT formation and growth. Several papers have suggested that it is possible to have nanometer size transition metals in a liquid state even if the temperature is several hundred degrees below the bulk melting point.[14], [42] Compounding this with the possibility that the catalytic particles can be in the form of a carbide, instead of α-iron, which also lowers the melting point temperature. If too much carbon was introduced during CNT growth, this may lead to supersaturation of carbon with carbide formation [41]. Although it is not possible to determine if any of the iron particles were in the liquid phase or in a carbide form, Figure 62 shows that the catalytic particle morphology is different when different oxide compositions were used.
The particles that are elongated have similar cross-sectional areas. As a result, samples that grew with elongated particles have tube diameters that are comparable in size. However, for the SiO\textsubscript{2} samples, the CNT nucleation took longer to initiate, which could allow the catalyst particles to continue to grow. In other words, it is possible that the delayed CNT growth on SiO\textsubscript{2} surfaces allowed the catalysts more time to grow in size, resulting in larger variations in catalyst size and CNT diameter. Figure 63 schematically indicates two possibilities that would allow iron particle sizes to enlarge on the SiO\textsubscript{2} buffer layer. The particles can grow by agglomeration with nearby particles, or by absorption of iron from the condensed catalytic source. In a floating catalyst technique, where the catalyst source is present in the precursor gases, it is not possible to separate the contribution of each of these possibilities. It is possible that both are occurring simultaneously to create larger catalytic particles on SiO\textsubscript{2} buffer layers.
6.4.7 Summary table

Table 1 below summarizes the observations of this study. The different categories compared are as follows: surface roughness of the oxide buffer layer, CNT nucleation rate, carpet height achieved after extended growth, tube diameter uniformity, buffer layer to model carbon layer strength, and other noticeable characteristics. This is a comparison; therefore, the descriptions used in each column are what were observed when comparing...
one sample to another sample in the study. It is important to point out that the observations may be specific to the chemicals and the deposition performed in this study, and that if other chemicals are used the outcome may be different.

| Table 1 A comparison table highlighting some of the characteristics observed in this study |
|-----------------------------------------------|-------|-------|-------|-------|
|                                | BL SiO₂ | ALD SiO₂ | Plasma SiO₂ | ALD Al₂O₃ |
| **Surface Roughness** (low (0.21 ± 0.034 nm)) | mid (1.469 ± 0.256 nm) | high (3.861 ± 0.136 nm) | low (0.405 ± 0.017 nm) |
| **(CNT Count) / CNT nucleation rate** (15/μm²)/slow | (40/μm²)/mid | (49/μm²)/mid | (454/μm²)/fast |
| **Carpet Height** Shortest (15.03 ± 0.91 nm) | Mid (21.46 ± 0.64 nm) | Tallest (34.71 ± 1.81 nm) | Mid (20.82 ± 0.47 nm) |
| **Comments** The buffer layer was on Si substrate without carbon, and CNT diameters were observed to have large variances | Carbon degradation by precursors was observed, and CNT diameters have some variances | Most promising and scalable method with good buffer layer to carbon adhesion and low CNT diameter variances | Oxide detachment issues were observed in some areas, but CNT diameters were very uniform |

6.5 Conclusions

It was observed in Chapter 5 that oxides can enhance CNT growth density. This chapter identified how oxides influence CNT growth in an effort to determine factors that affect growth controllability.

Two different oxide compositions, alumina and silica, have been compared, and the results show that oxides influence CNT growth in the following ways: CNT nucleation rates, CNT growth rates, and nano-catalyst particle morphologies. It also shows that CNT growth is controllable through growth time modification. In addition, the study shows that certain features associated with surface morphology, such as surface roughness and oxide thickness, influence CNT growth density and carpet height.

Furthermore, the study identified that due to CTE mismatch, certain oxides have adhesion
issues associated with the substrate, which can be important depending on the intended application.

The study result shows that samples with an Al$_2$O$_3$ buffer layer resulted in faster CNT nucleation and elongated residual nano-catalyst particles. In contrast, those with SiO$_2$ buffer samples showed a slower nucleation rate and more spherical particle morphologies. The study shows that the surface roughness of the sample is an important parameter and should be considered in sample design. It shows that catalyst particle density increased linearly with surface roughness, and that surface roughness can proportionately increase the CNT carpet height. It was observed that oxide thickness has an effect on the CNT growth rate, and that there is an optimal oxide thickness if the fastest CNT growth rate is desired.

It was demonstrated that samples that use alumina oxides have growth limitations after 40 minutes, while samples that use plasma SiO$_2$ experience continued growth through 120 minutes with no tapering observed. Therefore, the resistance associated with growth ability is larger with alumina oxide than silica oxide. The growth rate was related to equation 5, where it shows that the growth kinetic is driven by oxide specific driving force. Furthermore, this study shows that growth time can be used for growing controllable CNT array height when plasma silica was used.

This research emphasizes that growing CNTs on carbon substrates requires careful selection of the oxide buffer layer. Depending on the actual application, a carefully
engineered buffer layer should be able to provide control over CNT growth density and array characteristics. Among the buffer oxides investigated in this study, the ALD Al$_2$O$_3$ buffer layer provides the fastest CNT nucleation and most uniform catalyst size distribution, but samples with this oxide were plagued by adhesion issues, which may limit future applications. This issue should be further investigated in future studies. Perhaps other oxides that are more suitable and provide better substrate adhesion for the application can be found. Plasma SiO$_2$ offers a slower initial nucleation rate, but appears to be the most stable, controllable and scalable, which is why Plasma SiO$_2$ has been selected as the buffer layer that will be used for growing samples used for thermal analysis in the next chapter.
CHAPTER 7: Thermal investigation

It was established earlier that buffer layer material is required in order to enhance CNT growth on graphite substrate. Then it was demonstrated that CNT array height is linearly related to growth time, Section 6.4.5.2. This means that CNT carpet height is controllable by controlling the growth time.

This opens up the opportunity to design samples with tailorable carpet heights, which would be essential for investigation the effect of CNT length/carpet thickness on the thermal properties of the sample. Thermal property investigations involving CNT has shown improvements in thermal conductivity when loose CNTs (in a random orientation) were added into the matrix [159]. It was believed that configuration with aligned carpets of CNT attached directly to carbon substrate would further improve the thermal performances by minimizing contact resistance. Therefore samples configured with aligned CNT carpet directly grown on HOPG substrates, were prepared for the thermal investigation. As a result of this thermal investigation, parametric modeling equations, Equation 9 and Equation 10 in Section 7.4.7, were created to better understand how the variables affect the thermal resistance properties of CNT carpets. The variables include the following: CNT array height, density, and diameter.
7.1 Objective: Evaluate the thermal properties of CNT array

The objective of this study is to understand how some of the controllable CNT variables have on the thermal property of the CNT array. To accomplish this, CNT array of different heights were fabricated and tested using laser flash apparatus.

7.2 Background

One of the driving forces behind nanotechnology research is the potential to miniaturize electronic devices. As these devices shrink in size and enable more components to be packed into smaller spaces, efficient dissipation of waste heat generated through smaller volumes becomes more challenging. Excess heat, if not rapidly dissipated away from the nanoscale electronic components, can lead to signal instabilities and/or premature device degradation. One common issue is failure at the device/substrate interface due to thermal expansion mismatch between different material compositions. Therefore, optimizing mechanical compliance with better thermal transport through the interface is necessary to ensure stable performance. Hence, new strategies are needed for integrating emerging materials and/or material combinations for future thermal management devices.

Commercially available thermal interface materials (TIM) products, such as solder and thermal grease, have known thermal resistance (R) values around 7 and 14 mm²K/W, respectively [160]. However, these materials have limited use in many future aerospace applications due to their high densities, tendency to harden and crack after prolong usage,
and/or environmental degradation [19], [161]. Therefore, it is becoming very important to investigate lightweight and robust architectures for TIMs that can support the emerging power electronic devices for aerospace use.

Graphene and carbon nanotubes (CNTs) are potential candidates for future microelectronic device packaging materials due to their excellent thermal and mechanical properties. These carbon materials are tailorable and can be fabricated into highly flexible films that support mechanical compliance between electronic packaging materials [162], [163]. Carbon materials have coefficient of thermal expansion (CTE) values of $1.1 \times 10^{-6}$ m/(m-K), which closely matches silicon’s CTE value of $2.6 \times 10^{-6}$ m/(m-K), a commonly used semiconductor material use in electronics packaging. Copper, on the other hand, is a very commonly used semiconductor attachment substrate with a CTE value of $16.6 \times 10^{-6}$ m/(m-K) and has significant CTE mismatch and interfacial mechanical stress, a major cause of packaging failures. This shows that carbon materials can address failures due to CTE mismatch while adding mechanical strength and flexibility to the components. In addition, components utilizing these carbon materials may withstand prolonged thermal cycling and would be less prone to failure due to interfacial delamination. Furthermore, carbon materials are chemically inert, which allows these components to operate in more extreme conditions such as corrosive environments.
Thermal analysis involving CNT arrays has been reported extensively, but there are currently no uniform testing standards due to a lack of standardization in CNT fabrication. The reported data on thermal conductivity varies over a wide range. For example, using a dynamic modeling technique, the thermal conductivity (κ) value of a single walled CNT (SWNT) was reported to be 6,600 W/m-K [164]. Others have reported κ values ranging from 8 to 10,000 W/m-K [1], [165]–[170] for SWNTs, and 0.145 to 3000 W/m-K for multi-walled CNTs (MWNTs) [2], [22], [50], [165], [168], [171]–[174]. The wide range of values is a result of differences in the morphology of CNTs tested, and the testing techniques or conditions used. Furthermore it has been reported that the diameter of CNT can also change the thermal conductivity of CNT, where increasing the CNT diameters results in lowering the thermal conductivity [175].

From an electronics packaging standpoint, an understanding of the thermal transport properties of an array of CNTs orientated in the same direction is more applicable than those of an individual CNT or masses of randomly orientated CNTs. Thermal conductivity values of free standing CNTs arrays have been reported to be 1.9 W/m-K for SWNT arrays [165], and 3 to 15 W/m-K for MWNT arrays[172]. Thermal analysis on free standing CNTs array may be ideal, in terms of determining the intrinsic thermal properties of the CNTs; but in practical devices, CNT arrays will need to be attached to a substrate that supports the device. Therefore, a thermal analysis of samples comprised of
CNTs arrays attached to their growth substrate is more realistic, but is also more challenging.

The majority of reported CNT array growth is on electronic grade silicon substrates, and reported thermal conductivity (κ) values range from 8.3 to 15 W/m-K [2], [176]. Others have reported values of 27 W/m-K with the addition of a metallized bonding layer on the CNT array[173]. More recently, studies have reported success with growing CNT arrays on graphite substrates [19], [136], [177], [178]. It was suggested that three-dimensional structures consisting of CNTs joined perpendicular to graphene may be suitable as a high performance TIM [2]. This study involved CNT arrays of a fixed 25 µm length grown on thin graphite foil. Laser flash analysis (LFA) was used to measure the thermal resistance of the CNT layer. The CNTs were reported to be branched and having bamboo-like structures. Assuming their thermal conductivity to be 7 W/m-K, interfacial resistance was estimated to be 6 mm²K /W, which showed promise for future applications.

The objective of this investigation was to perform thermal measurements on a series of precisely controlled CNT arrays of set carpet lengths that were grown on highly oriented pyrolytic graphite (HOPG) substrates coated with a thin silica buffer layer. Success of this growth technique and details of CNT array quality have been reported in earlier publications [22-24]. In this study, LFA was used to measure the thermal transport properties of these samples in the through thickness direction. To the best of our knowledge, this is the first study reporting on the thermal analysis of varying length CNT
arrays. A 1-D thermal resistance model was incorporated to investigate the influence of CNT variables (diameter, array height, and density) on the thermal transport properties of an all carbon system for aerospace electronics packaging applications.

7.3 Experimental

7.3.1 CNT Growth:

Floating catalyst chemical vapor deposition (FCCVD), mentioned in Section 3.5.3.3.2, was used to grow CNT array films on (1 x 1 x 0.1 cm) highly oriented HOPG samples purchased from SPI, Inc. The growth time was varied from 60 min to 120 minutes in order to produce CNT with various carpet heights. The HOPG substrates were first coated with a thin film of SiO$_2$ (< 200 nm) as a buffer layer. Using methods similar to the ones documented in Pulikoll’s dissertation[23], the SiO$_2$ was deposited using a microwave plasma CVD, where the silicon source was hexamethyldisiloxane. The resulting samples were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and LFA. In this investigation, even though the thermal analysis testing temperature ranges from room temperature to 110 °C, for the analysis and comparisons portion of the study, only the diffusivity values measured at room temperature was used to calculate thermal conductivity value, and ultimately the thermal resistance values. Table 2 show the samples prepared for the investigation.
Table 2: Sample properties

<table>
<thead>
<tr>
<th>Samples</th>
<th>units</th>
<th>Bottom Layer</th>
<th>Cap</th>
<th>Top Layer</th>
<th>1 cm x 1 cm (nominal sample size)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>mm</td>
<td>HOPG 1</td>
<td>HOPG 2</td>
<td>HOPG 3</td>
<td>CNT I (482µm)</td>
</tr>
<tr>
<td>y</td>
<td>mm</td>
<td>1.23±.01</td>
<td>1.37±.01</td>
<td>1.42±.01</td>
<td>1.15±.01</td>
</tr>
<tr>
<td>z</td>
<td>mm</td>
<td>0.2518</td>
<td>0.3060</td>
<td>0.3148</td>
<td>0.2363</td>
</tr>
<tr>
<td>Weight</td>
<td>g</td>
<td>2.16±0.1</td>
<td></td>
<td></td>
<td>0.091</td>
</tr>
<tr>
<td>(Average Sample Density)</td>
<td>g/cm³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SEM and TEM analysis was performed to characterize the CNTs in relation to morphology, packing density, and interface composition. The TEM foils were prepared using focused ion beam (FIB) extraction and thinning techniques described in Chapter 3. The samples were protected with a layer of sputtered platinum in order to help preserve the CNTs and the cross-sectional area of interest. The resulting foil was extremely delicate and easily damaged by the high intensity TEM beam. Hence, images of regions of interest had to be quickly taken after all the focusing adjustments were made on an adjacent area of the specimen. Electron energy loss spectroscopy (EELS) was used for iron and silicon identification at the CNT/HOPG interface, Figure 65.

7.3.3 Raman spectroscopy analysis:

Raman spectroscopy data was collected and it was found that the samples did not have a peak at (200 cm⁻¹), therefore the CNT samples grown were MWCNTs.
7.3.4 Thermal analysis:

A Netzsch LFA 457 laser flash apparatus was used to measure the thermal property of the samples. Samples were loaded into 1 cm$^2$ sample holder and were placed on the testing stage. Essential data values (dimensions, density, weight, specific heat, and testing temperature range) were entered into the system prior to testing of a one layer sample. The system only measures the diffusivity value of one unknown layer at a time. To measure the diffusivity value of a multi-layer sample, data values mentioned above plus the diffusivity value of the known layers must be entered prior to multi-layer analysis.

LFA measures the thermal diffusivity value of the unknown layer as a function of temperature. The thermal diffusivity, $\alpha$ (mm$^2$/s), was first defined by Parker et al. [103] for laser flash analysis as

$$\alpha = 0.138 \frac{l^2}{t_{1/2}}$$

or

$$\alpha = \frac{k}{\rho \cdot c_p}$$

with a unit of (mm$^2$/second), shown in Equation 4.

where $l$ is the length/thickness of the specimen and $t_{1/2}$ is the time needed for the rear surface temperature to reach half its maximum value. The equipment can measure the diffusivity of a sample that ranges from 0.01 to 1000 mm$^2$/s with reproducibility of ±3%. The values reported in this study uses one $\sigma$ standard error.

In this work, single, and two-layer analysis were conducted to analyze the thermal diffusivity values for HOPG substrates, and CNT array films. Such sample is constructed
with CNT on HOPG substrate as lamellar composites. The thermal resistance of each layer and each interface was calculated using a 2-step testing procedure, as shown in the results section. For details of calculation please see Appendix D.

7.4 Results and Discussion

Figure 64a is a 3-D representation of the 2-layer sample, while Figure 64b shows a side-view schematic of the 2-layer samples used for thermal analysis. As seen in the figure, the CNT array and interface is labeled as the top layer and the oxide coated substrate as the bottom layer. Equations that correspond to the thermal resistance contributed from each layer are shown. $R_{HOPG}$ is the thermal resistance of the substrate layer, and $R_{array}$ is the bulk thermal resistance of the CNT array. $R_{oxide}$ was determined to be negligible as discussed later. $R_{interface}$ value can be considered as a combined thermal resistance value that incorporated the following: thermal resistance of the catalyst particles and the thermal resistance resulting from the interface between the oxide and the substrate. The physical properties of the HOPG layer and the CNT layer are listed in Table 2. The weights of CNTs were obtained by weighing the HOPG samples before and after CNT growth. These physical property values were entered in the laser flash system for the thermal analysis.
7.4.1 Microscopy and characterization:

As mentioned, an overall measure of CNT content in the samples was obtained from the weight, i.e. the difference in weight before and after CNT growth on the substrate. In order to assure that CNT growth was only on the top surface and not on the sides, the sides of the HOPG substrates were masked off prior to deposition of the oxide buffer layer. It has been clearly demonstrated in the past that there is minimal CNT growth without a buffer oxide layer on the surface [135], [136], [178], [179].

More details of CNT growth, such as number of nanotubes per unit area of substrate, CNT diameter, and length (array height) were obtained from the SEM images. The CNT growth density can be estimated by using the SEM image depth of field and counting the number of CNTs visible in the image area. In this study, the number of CNTs was measured to be $77 \pm 6$ CNTs/$\mu$m² or $7.7 \times 10^9$ CNTs/cm². In comparison, CNT density
values has been reported to range from $8 \times 10^9$ to $5 \times 10^{11}$ CNTs/cm$^2$ [139], [165], [180], which show a wide range from about $8 \times 10^9$ to $5 \times 10^{11}$ CNTs/cm$^2$. It must be pointed out that this is an estimate only, and there is a possibility of underestimating the total number of CNT in a given area. Namely, because a SEM image can only capture objects within the line of sight, this can lead to some unaccounted CNTs that fall outside of the field of view or are obscured. Secondly, it is assumed that the number of CNTs stays the same from the interface of the sample to the CNT tips. This may not be true, since it is possible for new CNTs to grow some distance away from the interface. Therefore, using SEM to estimate the CNT count leads to a value that represents the minimum number of CNTs in an area. This value was used in the parametric modeling analysis, Equation 9.

Each component within the thermal interface can affect the thermal transport, and perhaps increase the overall thermal resistance. Therefore it is important to examine the interface in order to determine if any obstructions are in the thermal pathway. Figure 65 is a set of TEM images taken from the CNT/HOPG interface. The inset in Figure 65b is an SEM image prior to the TEM alteration, and shows that the CNTs used for thermal measurements were uniform and aligned before FIB processing. Figure 65e is a merged image that shows the location of the Fe catalyst particles in relation to the oxide at the interface. In theory, the particles should have some thermal resistance contributions; however due to their size being small in scale (10 nm), it is expected that the contribution
would be small as well. Hence, these particles were not treated as a separate component/layer in the thermal analysis portion of this study.

To make TEM foils, FIB process was used. This technique requires pre-coating the area of interest with sputtered platinum, thereby filling the voids between CNTs and coating the CNT during the process. Once the coating is in place, an ion beam was used to etch away excess material, allowing the area of interest to be lifted for TEM and electron energy loss spectroscopy analyses. Figure 65b is a representation of unaltered CNTs with a higher magnification image as an insert. This image shows that the CNTs used for thermal measurements were uniform and aligned before FIB processing.

![Figure 65 SEM and TEM images of the CNT/HOPG interface, the TEM uses EELS technique to find the oxide layer and the iron catalyst particles.](image)

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7.4.2 Raman spectroscopy:

Based on the absence of a peak in the radial breathing zone (~200 cm\(^{-1}\)), it was concluded that the bulk of CNTs were multi-walled. The D-peak to G-peak ratios were measured and the values ranged from 0.46 to 0.79. Hence, the grown CNTs have more graphitic structures than defects sites. The Raman values suggested that CNTs has good morphology, more graphitic features, which should correlates to high thermal conductivity values.

7.4.3 Thermal Analysis:

The LFA system uses a laser pulse to deposit energy on the front face of a sample, and a detector measures the temperature response of the rear face. LFA uses validated models from literature to determine the thermal diffusivity, \( \alpha \), of the sample or layer in question. Once the diffusivity is determined, both the thermal conductivity (\( \kappa \)), and the thermal resistance (\( R \)), can be calculated. To calculate the thermal conductivity of the sample, equation 2 can be used

\[
\kappa = \alpha \times \rho \times C_p
\]

where \( \rho \) (g/cm\(^3\)) and \( C_p \) (J/g °C) are density and specific heat, respectively. The specific heat for the sample was validated using differential scanning calorimetry (DSC). To
determine the thermal resistance value (R) of an area, Equation 8 is used. This thermal resistance equation is more favorably used for thermal interface material. As seen from the equation, the thermal interface layer is independent of area.

\[
R = \frac{1}{\kappa}, \quad \text{with the unit of} \quad \frac{m^2K}{W}
\]

Equation 8 Thermal Resistance, Dewitt et al. [160]
where \(l\) is the thickness of the thermal layer within the sample.

7.4.4 Thermal Analysis of the Substrate (HOPG):

The HOPG sample is an excellent sample to be measured by the LFA system because it is made of graphite and nontransparent to the IR detector. Figure 66 shows the average thermal diffusivity values of HOPG samples measured over the temperature range of (25 - 100 °C).
7.4.5 Thermal Analysis of Substrates with a Buffer Layer:

Diffusivity values were also obtained for HOPG samples coated with a SiO$_2$ buffer layer. It was determined that the oxide layer was too thin for the LFA system to measure the diffusivity contributions. Namely, the measured diffusivity value for the SiO$_2$ coated HOPG samples were essentially the same as those measured for the baseline HOPG samples, Figure 66. Using a referenced thermal conductivity value for silica, 1.4 W/m-K, the thermal resistance of the silica oxide layer was estimated. It shows that the thermal resistance value for the silica buffer layer is indeed expected to be several orders of magnitude smaller, $5.21 \times 10^{-8}$ m$^2$K/W, than that of the HOPG substrate layer about 2.5 x
Therefore it is safe to assume that the oxide buffer layer has negligible thermal resistance contribution, as indicated in Table 3.

7.4.6 Thermal Analysis of Substrates with a Buffer Layer and CNT Array Film:

In this investigation, CNT arrays were grown as a uniform film on the oxide coated HOPG samples. The oxide coated HOPG substrate was considered the bottom layer of the composite, and the CNT film and the corresponding R_{interface} were treated as the top layer. The previously obtained thermal diffusivity value and corresponding physical properties of the bottom layer of each sample (HOPG 1, 2 and 3) was first entered as a known value in the Netzsch LFA two-layer analysis. The resulting average diffusivity values for the top layer of each sample (CNT I (482 µm), II (199 µm), and III (75 µm)) are listed in Table 3. The thermal diffusivity value for the top layer was converted/calculated to thermal resistance value using Equation 3 and Equation 8, in order to compare the thermal resistance contributions from each of the layers.

Table 3: Thermal Analysis Results

<table>
<thead>
<tr>
<th>Samples</th>
<th>units</th>
<th>Bottom Layer</th>
<th>Top Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG 1</td>
<td>3.864±0.06</td>
<td>4.053±0.08</td>
<td>4.177±0.09</td>
</tr>
<tr>
<td>HOPG 2</td>
<td>6.099±0.04</td>
<td>3.088±0.04</td>
<td>0.558±0.03</td>
</tr>
<tr>
<td>HOPG 3</td>
<td>0.351</td>
<td>0.199</td>
<td>0.087</td>
</tr>
<tr>
<td>HOPG 1</td>
<td>2.35E-04</td>
<td>2.48E-04</td>
<td>2.49E-04</td>
</tr>
<tr>
<td>HOPG 2</td>
<td>2.35E-04</td>
<td>2.48E-04</td>
<td>2.49E-04</td>
</tr>
<tr>
<td>HOPG 3</td>
<td>2.35E-04</td>
<td>2.48E-04</td>
<td>2.49E-04</td>
</tr>
<tr>
<td>R_{bottom} = R_{sub}+R_{oxide}</td>
<td>m² K/W</td>
<td>5.21E-08</td>
<td></td>
</tr>
<tr>
<td>R_{oxide}</td>
<td>m² K/W</td>
<td>5.21E-08</td>
<td></td>
</tr>
<tr>
<td>R_{array} = R_{array} + R_{interface}</td>
<td>m² K/W</td>
<td>1.37E-03</td>
<td>1.00E-03</td>
</tr>
<tr>
<td>R_{interface} (Figure 5)</td>
<td>m² K/W</td>
<td>7.59E-04</td>
<td></td>
</tr>
<tr>
<td>R_{array} (Figure 5)</td>
<td>W/mK</td>
<td>7.91E-01</td>
<td></td>
</tr>
<tr>
<td>R_{array}</td>
<td>m² K/W</td>
<td>6.09E-04</td>
<td>2.52E-04</td>
</tr>
</tbody>
</table>
Figure 67, $R_{\text{top}}$ is plotted and it is the value for the sum of CNT array and the $R_{\text{interface}}$. It can be seen that, there is a linear trend between $R_{\text{array}}$ and the height of the CNT arrays. Since all of the samples use the same growth parameters (other than growth time), it was assumed that the CNT/HOPG interface resistance, $R_{\text{interface}}$, for all samples were the same. Therefore, the contribution of $R_{\text{interface}}$ to the combined resistance of $R_{\text{top}}$ can be obtained by a linear line extrapolated to the y-axis intercept. Based on this y-intercept, inherent $R_{\text{interface}}$ was measured to be $7.59 \times 10^{-4}$ m$^2$ K/W. $R_{\text{array}}$ values for each of the three samples were calculated by subtracting $R_{\text{interface}}$ from the respective $R_{\text{top}}$ values. The thermal conductivity value of the CNT array was then calculated to be $7.91 \times 10^{-1}$ W/m-K, from the inverse of the slope of the trend line.

Figure 67 also indicated two noteworthy points. When the carpet height is short, the dominating thermal resistance contribution is from the $R_{\text{interface}}$. When the carpet height becomes nominally tall the dominating thermal resistance contribution is coming from $R_{\text{array}}$.

One area to keep in mind when selecting optimal carpet height for the TIM application is to consider the balance between thermal resistance and the thermal mechanical compliance properties that CNTs can offer. On one hand longer CNTs can provide flexibility to a thermal interface that is otherwise rigid, on the other hand the length of CNT carpet can increase thermal resistance.
Figure 67: Thermal Resistance of samples with different CNT height

7.4.7 CNT Thermal Conductivity Analysis:

Using the array thermal conductivity calculated above, it is also possible to calculate the thermal conductivity value of a single CNT ($\kappa_{\text{CNT}}$). To accomplish this, an equation was formulated using simplified assumptions about the CNT array. It was assumed that all individual CNTs in the array are solid cylinders and they are all uniform in material composition (morphology, tube diameter, and height). In addition, the CNTs are in parallel with each other and occupy a certain volume fraction, 8.5\% in this case. Furthermore, the thermal conductivity value of each CNT in the array is equal to each
other and is constant along the length of CNT, Figure 68. If the number of CNTs per area and the diameter of the CNT are known, then the thermal conductivity value of a CNT, $\kappa_{\text{CNT}}$, can be calculated using Equation 9.

$$K_{\text{cnt}} = \frac{L}{R_{\text{array}}} - (\kappa_{\text{air}} \times \left(1 - \left(N \times \frac{\pi}{4} d^2\right)\right)) \frac{N \times \frac{\pi}{4} d^2}{N \times \frac{\pi}{4} d^2}$$

Equation 9 Thermal Conductivity of Parametric Comparisons
where $d$ is the average diameter of the CNTs and $N$ is the number of CNTs per area.

Using the SEM images, the average CNT diameter was measured to be 19 ± 5 nm, and the growth density was measured to be 7.7 ± 0.6 x 10$^{13}$ CNTs/m$^2$. Using equation 4, the thermal conductivity of a single CNT, $\kappa_{\text{CNT}}$, was calculated to be 35.09 W/m-K. Again, note that this is the average thermal conductivity assuming the CNT to be a solid cylinder. In reality, the CNT is a hollow cylinder having an approximate inner diameter of 7 nm and an outer diameter of ~19 nm. While this is not the highest thermal conductivity value reported for carbon nanotubes, it is within range for CNTs of this type. As discussed previously, the reported thermal conductivity of CNTs ranges from 0.145 – 3000 W/m-K.
depending on the quality of CNT, sample configuration and testing methods. For CNTs having diameter that ranges from 20-100 nm with similar testing structures (CNT carpet) the thermal conductivity values reported ranges from 7-20 W/ m-K [2], [19], [181]. From an engineering point of view, 35 W/m-K is superior to many commercially available thermal interface materials (thermal grease, or epoxy bond, etc.) used today [175]. Hence, the combination of CNTs on HOPG shows promise as a new TIM for certain electronic applications.

7.4.8 Thermal Resistance Analytical Model:

Equation 10 (parameter sensitivity analysis) was created, by rearranging Equation 9, to help to predict the effect of CNT morphology and growth density on thermal resistivity of the array

\[
R_{\text{array}} = \frac{L}{(N \ast \kappa_{\text{cnt}} \ast \frac{\pi}{4} d^2) + \left(\kappa_{\text{air}} \ast \left(1 - (N \ast \frac{\pi}{4} d^2)\right)\right)}
\]

Equation 10 Thermal Resistance of Parametric Comparisons
Figure 69 shows that if the number of CNTs per given area is increased, \( R_{\text{array}} \), would decrease, as expected. However there is a limitation on how much improvement can be achieved, since \( R_{\text{array}} \) converges to an asymptote. This suggests that once a critical CNT growth density is reached, any additional increase will not greatly improve the thermal resistance. There will also be a practical limit set by the density at which the individual
nanotubes touch each other and cannot be grown any closer together. The figure also shows that the effect of CNT length diminishes as the CNT density increases, this suggest that CNT growth density is the dominating factor that affects the thermal resistance. This simple model underscores that through CNT growth optimization, the thermal resistance of the array can be further reduced. Using the thermal conductivity value of 35 W/ m-K, the best possible thermal resistance achievable will be about $2 \times 10^{-6} \text{ m}^2 \text{ K/W}$ for the CNT array carpet, if pristine samples of CNTs with 90% growth coverage were fabricated. This value places TIMs comprised of a combination of CNTs on HOPG on par with many commercially available TIM samples.
Figure 69 shows how the variable (#CNT/area) would change thermal resistance using the model equation. The experimental values are marked in each of the lines. The uniqueness about this study is the sample substrate is made almost entirely out of carbon, which CNT was grown on HOPG. In this configuration, CNT on HOPG, thermal resistance of the interface $R_{\text{interface}}$ value was extrapolated, which are often missing when testing sample consisted of CNT bundles or single CNT. In addition, $R_{\text{array}} = 9.48 \times 10^{-5}$ m$^2$ K/W is the measure thermal resistance value for the shortest CNT carpet of 75 μm. This value is comparable with commercially available product such as solder, silicon grease, and epoxy, with thermal resistance value that ranges from $0.01 \times 10^{-4} - 7 \times 10^{-4}$ m$^2$ K/W. In addition this value is slightly higher then reported thermal resistance value (7-20 W/m-K) by others with similar test setup [2], [19], [181]. The model used in this study shows that an absolute minimum thermal resistance $R_{\text{array}}$ reachable, if ideal CNT
density can be fabricated, is $1.3 \times 10^{-6}$ W/mK. Furthermore, this study demonstrates this is one technique that one can use to provide precision control over the thickness of TIM used with uniform coverage, which is often a difficult task to accomplish when using commercial grade thermal grease.

7.5 Conclusion

In this investigation, films of carpet-like arrays of carbon nanotubes (CNT) were grown on oxide coated HOPG substrates. It was shown by high resolution TEM images that the catalyst particles were embedded in the oxide layer. Using the height of CNTs array as the variable, the thermal properties of these all carbon samples were determined. The result shows that $R_{\text{array}}$ is linearly related to the CNT array height, and $R_{\text{interface}}$ was extrapolated from the y-intercept of a plot of thermal resistance versus array height. Thermal conductivity value of the individual CNTs was calculated to be about 35 W/m-K. Furthermore, this investigation provided a simple analytical model to determine the effect of different CNT variables on thermal resistance. The model suggested that if pristine CNTs with maximum packing density can be achieved, an optimally low thermal resistance value of about $2 \times 10^{-6}$ m$^2$ K/W is obtainable in the array. This value places the thermal resistance of TIMs comprised of a combination of CNTs and HOPG on par with current commercially available TIM material. As an added benefit, the all carbon TIM system is strong, durable, compliant, and will not suffer from drying out or thermal
cycling issues. Future studies will explore reducing the thermal interface resistance created by the tips of CNTs and a mating substrate in an electronics stacking configuration: this area remains a major challenge.
Section IV: Future and Conclusions

(Ideas for Future Studies, and Concluding Remarks)
CHAPTER 8: Conclusion

Successful investigations have been conducted to understand synthesis-structure-property relationships of CNT arrays attached to carbon surfaces and their relevance to power electronic applications. The key takeaways are summarized in this chapter and the key results are highlighted in Figure 70.

Initial background investigations revealed that CNT carpets can be successfully grown on synthetic diamond substrates using three different CVD growth methods. Each method produces CNTs with a distinctly different diameter, morphology, graphitic purity, and interfacial characteristics. Of the different growth methods, FCCVD has the advantage of being a one-step CNT growth method that does not need a separate catalyst deposition step, yet produces dense uniform CNTs. In addition, this method provided the finest CNT diameter, and acceptable $sp^3/sp^2$ defect ratio as seen from the Raman signal.

Moreover, this technique is not limited to line of sight growth, which can be beneficial for growing samples in future having complex geometry. Because of these potential advantages, this technique was selected as the growth method for the remainder of the investigation. The background investigations also confirmed with repeatable results that one-step CNT growth is challenging on bare carbon substrates, and an oxide buffer layer is essential for growth, in terms of density, uniformity and nanotube alignment.

Based on these results, the first detailed investigation was designed to investigate the influence of different oxide material as buffer layers. Two different oxide compositions,
alumina and silica, were compared in the investigation. The results show different CNT nucleation rates, growth rates, and nano-catalyst particle morphologies that resulted from these different oxides. The samples with the \( \text{Al}_2\text{O}_3 \) buffer layer resulted in faster CNT nucleation, elongated residual nano-catalyst particles, and a uniform tube size distribution. However, this method is plagued by adhesion issues due to the oxide layer peeling off the substrate which may limit future applications. In contrast, samples with plasma-deposited \( \text{SiO}_2 \) buffer layers showed slower nucleation rates, more spherical nano-catalyst morphologies, taller carpet heights in the same growth time, and better oxide adhesion to the substrate. Furthermore, this investigation showed that surface roughness of the buffer layer is an important property that needs to be carefully controlled. The catalyst particle density increased linearly with surface roughness, which proportionately increased the CNT carpet height. These results emphasize that growing CNTs on carbon substrates requires careful selection of the oxide buffer layer.

Once a buffer layer composition and morphology is selected, it would be desirable to have the ability to grow controllable CNT arrays. To investigate if this is achievable; the second detailed investigation was designed to understand the influence of oxide thickness and growth time on the final CNT array. It was observed that the CNT carpet height initially increases as the oxide thickness increases to an optimal thickness and any further increase in the oxide thickness results in the decrease of carpet height. This effect was seen in both oxides, but the optimal thickness was different for each composition (10 nm
for Al₂O₃, and 23 nm for SiO₂). The possible mechanisms that may cause this effect were discussed in Chapter 6. It was also observed that the CNT carpet height follows a linear trend with growth time for a selected oxide buffer thickness. This result demonstrates that while inherent properties of the CNT array can be modified by selection of buffer layer parameters, CNT array height is tunable with growth time.

Finally, to evaluate the applicability of these materials in power electronic applications, the thermal properties of CNT arrays were evaluated using Laser Flash Analysis. The result shows that the thermal resistance of the CNT array, R_array, is linearly related to the CNT array height. This, along with structural information, could be used to estimate the thermal conductivity of the individual multi-walled nanotubes, which was found to be about 35 W/m-K. Furthermore, these investigations lead to a simple analytical model for predicting the effect of different CNT variables on thermal resistance, and suggested ways that the thermal resistance of the structure can be improved.

In summary, this investigation provides deeper insights into the fabrication, characterization, and applicability of lightweight multiscale components for advanced power electronics. The successful growth of dense aligned CNT arrays on two allotropes of carbon substrates was accomplished. The importance of an oxide buffer layer, its composition, thickness, and surface roughness on the final growth characteristics was investigated. Dense CNT arrays with controllable carpet heights were successfully grown and their thermal properties tested as a function of CNT array heights. This
provided the capability to directly measure the thermal resistance contribution from the substrate-array interface, which to-date has only been reported as indirectly estimated values involving many approximations. In addition, the thermal conductivity of the individual multi-walled nanotube could be calculated and found to be approximately 35 W/ m-K, and approaches for the further improvement of thermal resistance have been discussed.

In closing, as the demand for smaller electronics packages continue to grow, lightweight multiscale structures will be very desirable as future thermal-interface materials. This dissertation offers in-depth understanding of one class of material, and demonstrates that it is not only possible to design and fabricate them but also that they have significant potential to replace and outperform current state of art and commercially available products.
## Areas of Investigation | Key Takeaways
---|---
Comparison of Growth Methods | FCCVD: Simple, reliable, and most scaleable

Comparison of Surface Modifications | 1. Re-confirmed that oxide buffer layer is required, its ability to enhance CNT growth density is superior to other surface modification techniques investigated  
2. Oxides enhances growth density, and alignment

Influence of Oxide Buffer Layer Materials (with different oxide compositions and structures) | 1. Different CNT nucleation rate  
2. Different surface roughness, which effects growth density and carpet height

Influence of Oxide Thickness | Effects carpet height, and there is a optimal thickness for tallest CNT carpet

Thermal Properties Analysis | Thermal resistance is linearly related to carpet height. This allows the thermal interface to be calculated, and the thermal conductivity of CNT was estimated to be 35 W/m-K.

Figure 70 Key areas of investigation and the takeaways
CHAPTER 9: Future Studies and Applications

While conducting the investigation, some issues have been observed in certain portions of the study. These areas will require further investigations in order to understand the underlying causes. Such areas are mentioned here.

9.1 Oxide and Substrate Adhesion Issues

As mentioned earlier, a separation between the oxide buffer layer and the carbon substrate known as “lift-off” was observed, when CNT was grown with ALD alumina. This suggests that the bonding between ALD alumina oxide and the substrate is weak. Such weakness is a problem for many applications that requires strong attachment for efficient thermal and electrical transport. It would be useful to understand the atomic interaction at those interfaces.

9.2 Surface Functionalization to Enhanced Transport Properties

For future applications, the effectiveness of the device depends heavily on the efficiency of the electrical and thermal transport through the material interfaces. Enhance the tips of CNTs would allow better interface transport. A few initial investigations were done to explore the feasibility of surface functionalization of the CNT carpets.
9.2.1 Electroless plating of Nickel

The electroless plating method is a wet chemistry method where it requires multiple steps in order for the metal particles to adhere to the surface of CNT. The steps used was developed by Fan et al. [182], which includes the following steps: acetone wash, sensitization, activation, and coating. It wasn’t clear how fast the surface of the CNT can be coated with the metallic particles so the experiment. The experiment was stopped every minute in order for images analysis to be taken. The total metal deposition process was 6 minutes. Figure 71 showing the results gather from this experiment.
Figure 71: Electroless nickel plating at various time intervals. A) 1 min, B) 3 min, C) 5 min, D) 6 min. Figure 71 revealed that the earliest detectable nucleation process starts at around 5 minutes. The particle rapidly grows after that. It appears that the metal particles are much larger than CNT at 6 minutes into the coating process. The coating does not coat individual CNT, but rather taking up the void spaces between the tubes.
Pt coating using ALD

The ALD metal plating process uses (Trimethyl)methylcyclopentadienylplatinum(IV) and remote O$_2$ plasma to deposit the platinum thin film. The growth chamber was set at 270 °C with a deposition rate of 0.7 Å/cycle. Figure 72 shows the result after ALD pt treatment.

Figure 72: Metal coating using ALD platinum
The result shown in Figure 72 indicated two major noticeable differences between electroless plating and ALD coating method. First the alignment and carpet morphology
in the ALD sample is preserved, and second the particle sizes found in ALD are much smaller and actually coats individual CNT.

9.3 Future Device Applications

9.3.1 Thermal interface materials

An ideal thermal interface is the one that have two sides of material that forms a uniform connection with the opposite side. However these kinds of interface seldom exist. Therefore materials such as thermal interface material (TIM) are used in order to enhance the connection while filling in any voids created by joining of the two sides. Figure 73 is an image showing non-uniform contacts from joining two substrates, where the voids are created.

![Figure 73 cartoon representation of an interface](image_url)

To address the voids there are many commercial products available to help minimize these imperfections while increase thermal conductivities across two surfaces Figure 73.
However many commercial products available currently can suffer failure through environment contributions or shelf life. Therefore CNT provides an alternative to some of the commercial products. Figure 74 listed some of the advantages and disadvantages from some of the common TIM materials.

<table>
<thead>
<tr>
<th>TIM</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Grease</td>
<td>High thermal conductivity</td>
<td>Phase separation during thermal cycling</td>
</tr>
<tr>
<td></td>
<td>Thin joint with low thermal resistance</td>
<td>Messy to work with</td>
</tr>
<tr>
<td></td>
<td>No curing time</td>
<td>Dry out over time</td>
</tr>
<tr>
<td></td>
<td>No delamination</td>
<td>Hard to achieve uniform thickness</td>
</tr>
<tr>
<td></td>
<td>Low cost</td>
<td>Possible for excess greases</td>
</tr>
<tr>
<td>Filled Polymers</td>
<td>Not messy</td>
<td>Need curing time</td>
</tr>
<tr>
<td></td>
<td>Uniform application thickness</td>
<td>Lower thermal conductivity than greases</td>
</tr>
<tr>
<td></td>
<td>Good dielectric properties</td>
<td>Delamination problems</td>
</tr>
<tr>
<td></td>
<td>Low modulus</td>
<td>Permanent clamping needed</td>
</tr>
<tr>
<td></td>
<td>Easily cut to size</td>
<td>Higher cost than greases</td>
</tr>
<tr>
<td>Phase-changing material Polymeric</td>
<td>Easier application and handling</td>
<td>Surface resistance can be greater than greases</td>
</tr>
<tr>
<td></td>
<td>No curing time</td>
<td>Constant pressure required</td>
</tr>
<tr>
<td></td>
<td>No dry-out</td>
<td>Voids can result with thermal cycles</td>
</tr>
<tr>
<td></td>
<td>No delamination</td>
<td></td>
</tr>
<tr>
<td>Low Molding Wax</td>
<td>Easy to apply</td>
<td>Dry-out and crevices at the interface</td>
</tr>
<tr>
<td></td>
<td>all metal path</td>
<td>Intermetallic growth</td>
</tr>
<tr>
<td></td>
<td>No curing time</td>
<td>Oxidation/Corrosion at elevated temperatures</td>
</tr>
</tbody>
</table>

Figure 74 common TIM material and their comparisons
9.3.2 Lightweight composites

One of the benefits of exploring CNT growth on carbon substrates is the ability to create a lightweight composite. These composites can provide great benefits to space and aerospace industries, where weight saving is critical to the success of the mission.

9.3.3 Electrical applications

CNT is known to have excellent thermal, electrical and mechanical properties. In this investigation, only thermal properties were investigated extensively. It is possible that such carbon configuration can be beneficial for electrical applications as well.
References


1999.


Section V: Appendices
Appendix A: List of Publications

- Betty T. Quinton, et al. “Controllable CNT growth with SiO$_2$ buffer layer” submitting soon!


Appendix B: Preliminary Thermal analysis on carbon samples

B.1: Initial Thermal Testing

In addition to the thermal analysis conducted on HOPG samples, Chapter 8, thermal analysis were also conducted on other carbon structure samples. However, these samples were only evaluated initially and were never used in the later part of the investigation. Appendix B will show the result from the thermal analysis conducted on these samples. Before that CNT carpet can be controlled with confidence some thermal analysis was conducted as preliminary tests. These tests were conducted with two purposes. It was a way to understand how to operate laser flash equipment and to see if sample geometry is proper for the testing equipment. The thermal analysis investigations were conducted on different carbon substrates including: diamond, carbon foam and pressed graphite.

B.1.1 Laser Flash analysis (LFA) on Diamond

Figure 75 shows the thermal conductivity results taken from diamond substrate samples, using the LFA method. The samples tested for comparison are as the following: standard diamond sample, diamond sample coated with 5 nm nickel on diamond with CNT growth, and 10 nm nickel coated on diamond with CNT growth. The result shows that the samples with CNT did have a higher thermal conductivity value then ones that do not have CNT.
B.1.2 LFA on Foam

The porosity of the foam is usually filled by air, which is low in thermal conductivity and a poor measurement median. Therefore, in order to measure the thermal property of a carbon foam sample, with and without CNT, it was filled with epoxy prior to thermal testing. The samples shown in Figure 76 were tested as the following, a piece of epoxy, RVC foam filled with epoxy and RVC foam with CNT that is filled with epoxy. The result showed that samples with CNT did have a higher thermal diffusivity value than ones without.

Figure 75 LFA result on diamond samples
B.1.3 LFA on pressed graphite

The foam samples have complex geometry and high in porosity, therefore it is difficult to accurately measure thermal conductivity value contributed from the foam. One way to test thermal conductivity of the sample is by testing it on a flat sample with materials that are the same chemically. Hence pressed graphite substrates were chosen as a flat model for this test. Figure 77 shows the result measured on pressed graphite. The result shows the graphite sample with CNT have slightly higher thermal diffusivity value than samples without the CNT, however more test will be needed to see if it is significantly different.

Figure 76 LFA result on RVC samples

Figure 77 RVC Foam Diffusivity
It was envisioned that when CNTs are used in an application it will be in some forms of interface layer much like a thermal interface material. Because of this, sandwich configurations with CNTs imbedded in the middle was fabricated; see Figure 78 for a cross-section configuration. The samples (with and without CNTs) were fabricated with oxides and the CNT sides facing each other. This way the CNT layer will be the only changing variable for the evaluation.

Three different sandwiches were made and they are the following:

**SPI** = two SPI HOPG facing each other.
**SPI/Al₂O₃** = Two SPI HOPG each ALD with 10nm of Al₂O₃. The sandwich were made with Al₂O₃ facing each other.

**SPI/Al₂O₃/CNT** = Two SPI HOPG each ALD with 10nm of Al₂O₃ and CNTs were grown on the Al₂O₃.

The sandwich was made with CNTs facing each other.

![Diagram of SPI, SPI/Al₂O₃, SPI/Al₂O₃/CNT sandwiches](image)

*Figure 78 LFA results on HOPG sandwiches*
Appendix C: Thermal analysis challenges with short CNT carpets

It was thought that samples with shorter CNT carpets would have better thermal resistance value. Therefore, in addition to the samples tested in section 8.2, there was another sample made for evaluation. This sample has the shortest CNT array height among the entire sample tested. Using the growth time as the control variable, the height of the array fabricated on HOPG was only 23 µm in length. Due to the shortness of the sample, accurate analysis of the sample becomes a challenge. First the amount of weight gain cannot be measured with confidence. This is because the amount of weight gain was within the measuring error of the equipment (±0.3mg). The weight of the sample is crucial for the thermal analysis since it uses this value to find the density related to the sample. The density of the sample is used by the LFA equipment for thermal diffusivity measurement. Because of this relationship, the resulting thermal diffusivity values were not measured with confidence.
### Appendix D: Thermal Analysis Calculation

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Thermal Diffusivity</td>
<td>$\frac{mm^2}{s}$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific Heat</td>
<td>$\frac{J}{g\cdot ^\circ C}$</td>
</tr>
<tr>
<td>g</td>
<td>Mass</td>
<td>$g$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>$\frac{g}{cm^3}$</td>
</tr>
<tr>
<td>l</td>
<td>Length</td>
<td>m</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Thermal Conductivity</td>
<td>$\frac{W}{mK}$</td>
</tr>
<tr>
<td>$\kappa_{array}$</td>
<td>Thermal Conductivity of an array of CNTs</td>
<td>$\frac{W}{mK}$</td>
</tr>
<tr>
<td>$\kappa_{CNT}$</td>
<td>Thermal Conductivity of a CNT</td>
<td>$\frac{W}{mK}$</td>
</tr>
<tr>
<td>R</td>
<td>Thermal Resistance with normalized area</td>
<td>$\frac{m^2K}{W}$</td>
</tr>
<tr>
<td>$R_{HOPG}$</td>
<td>Thermal Resistance of the HOPG layer</td>
<td>$\frac{m^2K}{W}$</td>
</tr>
<tr>
<td>$R_{oxide}$</td>
<td>Thermal Resistance of the oxide layer</td>
<td>$\frac{m^2K}{W}$</td>
</tr>
<tr>
<td>$R_{array}$</td>
<td>Thermal Resistance of an array of CNT</td>
<td>$\frac{m^2K}{W}$</td>
</tr>
<tr>
<td>N</td>
<td># of CNT per area</td>
<td>$\frac{# CNT}{m^2}$</td>
</tr>
<tr>
<td>d</td>
<td>Diameter of CNT</td>
<td>m</td>
</tr>
</tbody>
</table>

**Measured**

xxi
• Thermal diffusivity
• Specific heat
• Mass
• Length

**Equations:**

- Established equations
  - $\kappa = \alpha \cdot c_p \cdot \rho$
  - $R = \frac{1}{\kappa}$

- Equation used for thermal resistance layers defined
  - $R_{\text{Top}} = R_{\text{array}} + R_{\text{interface}}$
  - $R_{\text{Bottom}} = R_{\text{HOPG}} + R_{\text{oxide}}$
– Equation related to the investigation
  
  \[ \kappa_{Top} = \alpha_{Top} \cdot c_{p_{Top}} \cdot \rho_{Top} \]

  \[ R_{Top} = \frac{1}{\kappa_{Top}} \]

  \[ R_{array} = R_{Top} - R_{interface} \]

– Modeled equations

  \[ R_{array} = \frac{L}{\left( N \cdot \kappa_{cnt} \cdot \frac{\pi}{4} \cdot d^2 \right) + \left( \kappa_{air} \cdot \left( 1 - \left( N \cdot \frac{\pi}{4} \cdot d^2 \right) \right) \right)} \]

  \[ \kappa_{cnt} = \frac{\frac{L}{R_{array}} \cdot \left( \kappa_{air} \cdot \left( 1 - \left( N \cdot \frac{\pi}{4} \cdot d^2 \right) \right) \right)}{N \cdot \frac{\pi}{4} \cdot d^2} \]