AN EXPLORATION OF THE FLAME SYNTHESIS OF SILICON DOPED
CARBON NANOTUBES

A Thesis in
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by
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ABSTRACT

Nanotubular structures have recently attracted a great deal of interest because of their high strength, high thermal conductivity, chemical stability, and unique electrical behavior. These properties suggest nanotubular structures may serve well in applications such as chemical sensing, temperature sensing, hydrogen gas storage, and polymer reinforcement. As it turns out, several materials, including silicon, carbon, and silicon carbide, all form this stable nanotubular phase; however, the variation of the material properties with the silicon and/or carbon content is unknown. To address this issue, an exploration of the flame synthesis of nanotubular structures composed of silicon and carbon in an unknown ratio or silicon ‘doped’ carbon nanotubes (SiCNTs) was completed.

This exploration was broken into two parts. The first included an ignition study to address the issues of safe handling and use of silane and to test its reactivity with carbon dioxide. Safe test procedures and equipment were developed and carbon dioxide was found not to react with silane after a series of ten tests. The second portion of this investigation involved the use of a laminar diffusion flame burner to synthesize nanotubes on an iron catalyzed stainless steel substrate. Nanotubular structures in the range of 10 to 20 nm in outer diameter were synthesized and characterized in a field emission scanning electron microscope although the chemical structure of these nanotubular structures was not determined. Equipment and procedures, however, were developed for use in further SiCNT synthesis exercises.
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Chapter 1

Introduction

1.1 Nanotubes: An Introduction

The first observation of a nanotubular structure occurred in 1959. While studying the products of a hydrocarbon flame, Singer and Grumer captured images of hollow filaments in an electron microscope [1]. The interest and study of these filamentous structures remained dormant until 1991 when Iijima conducted a thorough investigation and began the development of a true understanding of these structures [2]. In the days since this rediscovery, these nanotubular structures have been found to possess many unique properties, making them attractive for a large range of applications [3]. One such property is high tensile strength for their size. Another property is large electrical conductivity, which has the ability to carry large currents without a large resistance, leading to less heat generation and better component life. Still another property is high thermal conductivity. These properties make nanotubes an attractive alternative material in modern engineering applications.

In addition, a nanotubular solid phase is not unique to a single element. Carbon and silicon both form this solid phase. Likewise, silicon carbide (SiC), a compound of silicon and carbon, can also form this solid phase. These three compounds, even in their natural phases, exhibit a wide range of those properties previously discussed. For example, the cubic solid phase of each of these three compounds demonstrates a wide variation in thermal conductivity as displayed in Figure 1.1. This behavior in the cubic solid phase raised the
question of whether this variation occurs in the nanotubular solid phase of these materials as well. Consequently, the synthesis of nanotubes composed of a carbon/silicon ratio other than one (Si-CNTs) became the main focus in this research.

![Graph showing thermal conductivity comparison]

Figure 1.1: A comparison of the thermal conductivity of silicon, silicon carbide, and carbon in the diamond cubic solid phase (*Sources: Si [6], SiC[5], C[4]).

1.2 Literature Survey

As mentioned, the interest in Si-CNTs largely stems from the unique properties observed in the behavior of nanotubular structures in general. Therefore, it is necessary to better understand those behaviors and their origins. To do that, previous research involving silicon, silicon carbide, and carbon nanotubes must be investigated. It is important to understand their structure, properties, potential applications, and the synthesis processes
used to create them to fully realize their potential. However, it must be noted, though, that most of the previous research focuses on carbon nanotubes (CNTs).

### 1.2.1 History and Structure of Carbon Nanotubes

Iijima began by producing these carbon filaments on the negative end of a carbon electrode through discharge of a direct current arc in an argon environment [2]. Constructing the filaments in this manner revealed vital information about the atomic structure of the filaments after careful examination in an electron microscope. It turned out that the filaments were actually a sheet of graphite formed into a hollow cylinder. The lattice structure of this cylinder appeared to be helical with varying helix angles, depending on the position in the structure. At the same time, the filaments appeared to have more than one wall and varied widely in diameter (4 to 30 nm). Through these findings, Iijima had established a foundation for the study of carbon filaments or nanotubes.

In the years since Iijima’s initial work, the knowledge of these structures advanced considerably in multiple directions. First, according to Subramoney, researchers found that either successfully synthesizing or purifying carbon nanotubes would prove to be a serious challenge [7]. A proposed solution to this issue involved oxidizing all of the other carbon structures produced in the arc discharge method used by Iijima; however, this usually resulted in the destruction of 90% of the material before a pure sample was retrieved. Other methods surfaced, but it was clear that the arc discharge method would never provide adequate control for large scale production of carbon nanotubes. Eventually, a simpler
method of achieving higher purity came about through the well known chemical vapor deposition (CVD) process.

A second area of progress related to determining the mechanical properties of carbon nanotubes. Of course, once again, size posed a great challenge in completing such a task; however, tubes deformed by van der Waals interactions provided insight into their structure through electron microscopy [7]. More recently, advanced electron microscopy techniques indicated that carbon nanotubes have a very high tensile strength and Young’s modulus (at least in the hundreds of gigapascals for both). This information raised interest in carbon nanotubes for their promise as an ultra strong structural material.

The third and final area of progress in carbon nanotube knowledge deals with the structure itself. Besides knowing that the general makeup of the crystal lattice matches that of graphite, Dresselhaus et. al. postulated from a theoretical standpoint that the single walled nanotube has hemispherical endcaps that are essentially half of a $C_{60}$ or fullerene molecule [8]. They then further described the variations in the crystal lattice through two distinct variables. The first, and most obvious, was the tube diameter. The second was the chiral angle. This variable described the alignment of the graphite sheet with the tube central axis, after it was rolled into a cylinder. Consequently, this also determined the overall crystal structure of the nanotube.

Typically, this angle took on a value greater than zero and less than thirty degrees [8]. If this angle was zero degrees, the nanotube crystal structure was referred to as ‘zigzag’, while if it was thirty degrees, its structure was an ‘armchair’. Any angle between zero and thirty degrees earned the title of a ‘chiral’ nanotube. As it turned out these parameters affect the electronic conductivity as well as the vibrational modes of this structure. Dresselhaus et. al.
extended some of these conclusions to multi-walled configurations and suggested that improvements in experimental techniques would build upon this foundation of structural knowledge of the carbon nanotube. Knowing this information, the potential applications of carbon nanotubes began to emerge.

1.2.2 Potential Applications of Carbon Nanotubes

Their size, strength, chemistry, and electrical properties lend carbon nanotubes to a wide variety of applications. One such application is the storage of hydrogen for use in a fuel cell for transportation purposes [9, 10]. Their large surface area, variable crystal structure, and accommodation of dopants provide a potential environment for hydrogen absorption, which increases the hydrogen density without condensation or compression [9]. Condensation and compression of pure hydrogen are difficult and dangerous operations in mobile systems such as a vehicle making absorption into a carbon nanotube array an attractive alternative. A second potential application of serious interest is catalysis [11]. Not that the nanotubes are the catalyst themselves, but rather they serve as the catalyst support, placing the reactant in the reaction and allowing it to participate without affecting the overall chemical reaction itself.

A third possible application is the reinforcement of polymer substances [12, 13]. For instance, the presence of carbon nanotubes in petroleum pitches increased their strength 90% [12]. In another instance, the fracture strain of a carbon nanotube reinforced polymer measured as much as 18% [13]! Indeed, these are both remarkable improvements in mechanical properties of these materials.
A fourth and final application of carbon nanotubes involves their use in gas sensing [14]. Chemisorption of a gas on an array of nanotubes changes its capacitance or resistance depending on the type of gas present within that array. Consequently, the gas present at any one instant is known by the unique electrical conditions it creates in the nanotube array. The result is a simple, accurate, and robust gas sensor.

Each of these applications demonstrates the potential of carbon nanotubes and what they could mean to technology as a whole. On the other hand, many unanswered questions still remain regarding carbon nanotubes, including how to produce them in useful and meaningful quantities.

1.2.3 Flame Synthesis of Carbon Nanotubes

By their nature, the potential applications of carbon nanotubes demand highly pure, organized arrays of carbon nanotubes which, as previously mentioned, cannot be supplied by laser ablation or CVD techniques. Flame synthesis, however, is thought to have the potential to meet the demands of both quantity and quality according to Diener et. al. [15]. In an attempt to confirm this notion, many different flame arrangements ranging from a simple acetylene torch [16] to more complex two flame configurations [19, 20, 21] with different catalysts have been attempted.

One such arrangement was a premixed flame burning benzene or acetylene and oxygen in a low pressure atmosphere [15]. Through this flame flowed argon, carrying cobalt, iron, or nickel catalyst particles to initiate nanotube growth. The excess carbon needed to form the tubular structures was made available by operating the flame at an equivalence ratio
between 1.7 and 3.8 with fuel flow rates of either 1.25 SLPM for benzene or 3.75 SLPM for acetylene. The resulting products of this process passed through a filter where the catalyzed carbon nanotubes were collected.

In the end, this premixed flame produced mostly single walled carbon nanotubes (SWNTs) and some (~5% of the total nanotubes produced) multi-walled carbon nanotubes (MWNTs), which together comprised only approximately 1% of the total carbon material generated in the acetylene flame. On the other hand, the total carbon products of the benzene flame were nearly 10% MWNTs. This led Diener et. al. to the conclusion that the type of nanotube formed was mostly dependent on the chemistry of the particular hydrocarbon. Also, they suspected that, since benzene already possessed an aromatic ring, it would prevent the formation of SWNTs and promote the formation of polyaromatic hydrocarbons (PAHs). In turn, deposition of these molecules on a catalyst particle would lead to catalyst deactivation. As a result, the type of hydrocarbon chosen is vital to the nanotube synthesis process.

In a later study, Height et. al. used a similar premixed flame consisting of acetylene and oxygen. This flame was diluted with argon at a concentration of 15 mol% and operated in a 6.7 kPa environment [17]. In this case, iron pentacarbonyl (Fe(CO)\textsubscript{5}) served as the aerosol catalyst via an argon carrier at a concentration of 6000 ± 500 ppm (molar). Samples of the product of this reaction were gathered on a transmission electron microscopy grid directly downstream of the flame in two separate experiments. The first involved varying the equivalence ratio of the flame between 1.4 and 2.2 and for each of these flames, collecting samples starting at 10 mm above the burner surface up to 75 mm above the surface. This yielded nanotubes at heights between 40 and 70 mm above the burner with rapid growth
appearing near 40 mm and tangled webs of nanotubes appearing closer to 70 mm. The second experiment entailed varying the equivalence ratio from 1.4 to 2.0 at a height above the flame of 70 mm. It produced nanotubes between equivalence ratios of 1.5 and 1.9 with better quality and higher quantity nanotubes appearing near the beginning of this range. This result demonstrated the effectiveness of iron pentacarbonyl as an aerosol catalyst for nanotube growth in a flame environment.

Even though it is a common practice, aerosol catalysis is not the only method used to catalyze a premixed flame. Vander Wal et al. used a fixed catalyst positioned over a chimney that directed product gases from a flat flame burner \[18\]. This fixed catalyst consisted of type 304 stainless steel mesh with 0.0009 in. wire diameter that had been coated with a layer of cobalt less than 10 nanometers thick through a physical vapor deposition process. The resulting catalyzed mesh appeared as a solid substrate with small “metal islands” on the surface when observed in an electron microscope. At this point, the catalyzed mesh was immersed in the product gases of the flat flame burner for a period of 12 minutes, then rapidly removed and placed in a flow of nitrogen (N\(_2\)) to cool the sample; thereby, preventing complete oxidation of it. The product gases were produced by a flame fueled by methane (CH\(_4\)), ethane (C\(_2\)H\(_6\)), propane (C\(_3\)H\(_8\)), ethylene (C\(_2\)H\(_4\)), or acetylene (C\(_2\)H\(_2\)). Equivalence ratios were typically varied for each fuel through the range of 1.5 to 2.0 by maintaining a constant air flow rate of 11.5 SLPM and adjusting the fuel flow rate.

From this experiment, it was shown that a fixed catalyst can also produce carbon nanotubes in a flame environment. At the same time, the impact of carbon to hydrogen ratio in the fuel on the carbon nanotube production came to light indicating that ethylene produced the best product gas environment. This information demonstrated that even fixed
catalysts can successfully capture carbon nanotubes and that hydrocarbon chemistry lends itself to producing environments highly conducive to carbon nanotube production in premixed flames.

Another way of using a premixed flame to synthesize nanotubes is to use its products as an atmosphere for a diffusion flame. Vander Wal and various coworkers [19, 20, 21] referred to this as a “pyrolysis” flame. Essentially, a diffusion flame supported by a small diameter tube (~1 cm) resided in the center of a flat flame or McKenna burner. Typically, then, the McKenna burner supported a rich C\textsubscript{2}H\textsubscript{2}/air flame while the diffusion flame was a combination of CO, H\textsubscript{2}, and He, C\textsubscript{2}H\textsubscript{2}, H\textsubscript{2}, and He, or some slight variation of these mixtures. In most instances, the catalyst was delivered to the flame through this flow as well. Thermophoretic (temperature driven) sampling of these flames disclosed information regarding the formation of the tubes themselves as well as the role of the catalysts.

Vander Wal and his coworkers remarked that there seemed to be a strong dependence on the amount of C\textsubscript{2}H\textsubscript{2} and CO present in the reactant stream of the diffusion flame and the SWNT yield. High concentrations of C\textsubscript{2}H\textsubscript{2} led to catalytic deactivation because of the formation of PAHs and deactivation of the catalyst particles. At the same time, the existence of both CO and C\textsubscript{2}H\textsubscript{2} in the flame promoted the growth of nanotubes, so long as their concentrations were not high enough to produce an amorphous carbon coating. At the same time, a high H\textsubscript{2} concentration removed carbon at a rapid rate from the surface of the catalyst particles, preventing SWNT growth as well. As a result, this flame arrangement provided a unique opportunity to further understand the development of carbon nanotubes in a flame environment.
Of course, there are alternative flame configurations to premixed. One such configuration involved the counter or opposed flow flame. Saveliev et. al., Merchan-Merchan et. al., and Xu et. al. all tested a similar counterflow flame where a jet of methane (\(\text{CH}_4\)), nitrogen diluted \(\text{CH}_4\), or a mixture of \(\text{CH}_4\) and \(\text{C}_2\text{H}_2\) flowed opposite a jet of diluted oxygen or air [22, 23, 24]. At the interface of the two jets, a stagnation plane supporting a stable flame existed that could either be sampled with a catalytic probe [22, 24] or through a thermophoretic method [23]. The catalytic probes employed in these experiments were either pure transition metals such as iron or nickel or they were an alloy of iron, nickel, and copper that remained in the flame for a number of minutes. For the thermophoretic sampling, a typical transmission electron microscopy grid was maneuvered into the flame on a probe to collect the sample and remained there for only 37 ms. This brief time period ensured the presence of a temperature gradient between the probe and the surrounding gases, but allowed adequate time for the solid particulate to deposit on the grid.

The results of these experiments indicated that the flame structure itself played an important role in determining the carbon structures synthesized. Typically, in the high temperature portion of the flame (1350 K) or the fuel side, only amorphous carbon formed [24]. Saveliev et. al. observed the formation of MWNT bundles in this region as well [22]. Then, in a range from 1300 to 1000 K the MWNTs appear, but in continuously changing diameter and quantity [24]. Finally, in the flame region where the temperature is less than 950 K, nanotubular structures no longer appear, likely due to the lack of nanoparticle catalyst formation. A variety of other structures such as helical and ribbon like nanofibers were also discovered within these flames [22]. Therefore, these flames appear to create carbon
Using this same flame setup, Merchan-Merchan et. al. investigated a novel idea of applying an electric potential to the sample probe and the burner injectors to address the quality and quantity control issue, on two separate occasions. In applying the electric potential, a radial electric field was created, surrounding the probe [25]. The field, then, changed the pattern of ion and electron transport within the flame causing a “floating potential” maintained near -300 mV for most of the experiment. In the presence of this electric potential, a uniform layer of vertically aligned carbon nanotubes formed on a catalyzed sample probe composed of 73% Ni, 17% Cu, and 10% Fe. After closer inspection, these tubes appeared to have a very small range of diameter variation with a mean of approximately 38 nm. Equally important to the creation of the array of vertically aligned nanotubes was the absence of other contaminants that appeared when the electric potential was not used. Of course, the quality and size of the nanotube arrays varied with position in the flame, but they did appear in different flame positions, further confirming the applicability of the electric potential in forming nanotube arrays.

In a later study, Merchan-Merchan et. al. tested this same setup once again, but with higher applied electric potentials. This time, the range of applied voltage stretched from 0.3 V to 30 V [26]. After varying the applied electric potential between 0.1 and 1 V in a similar flame position as the previous test, the array thickness (tube length) was found to experience a linear variation. At 3 V, the array became saturated causing helical nanotubular structures and eventually branched tubes. Then, once a 5 V electric potential was reached, the morphology of the catalytic particles changed, providing even more opportunities for
nanotube branching. An electric potential of 12 V created an array of variously shaped, branched nanotubes including those that have tree-like structures. Although its capabilities are limited, applied electric potential shows promise for controlling the morphology of flame synthesized carbon nanotubes as shown by Merchan-Merchan et. al.

Nakazawa et. al. used a wall stagnation flame configuration, similar to the counterflow configuration discussed above, to synthesize carbon nanotubes. Here a vertically oriented stainless steel tube with an inner diameter of 10 mm created a jet that impinged on a ceramic disk with a 76 mm diameter located 8 mm from the end of the tube [27]. Attached to the ceramic disk was a 0.1 mm thick nickel plate that served as the catalyst to support nanotube growth. From the tube flowed premixed ethylene and air that was diluted with nitrogen to create a “trumpet” shaped flame burning at an equivalence ratio of 1.6. This flame impinged on the nickel plate for a total of 10 minutes so as to allow sufficient time for carbon deposition. The result of this impingement was a donut shaped region of carbon deposition between radial distances of 10 and 15 mm from the center of the injector tube. Toward the outer extent of this region, MWNT layers were found regularly. The composing nanotubes typically had diameters in the range of 8 to 21 nm and were estimated to be over 1.0 micron in length. Nakawaza et. al. suggested that this process provides a robust, easily adaptable alternative to traditional flame synthesis techniques.

Equally robust, but more established is the diffusion flame. Both Yuan et. al. and Arana et. al. employed such a flame in an attempt to create carbon nanotubes [28, 29]. Yuan et. al. employed a 1.1 cm and a 5 cm diameter tube through which CH$_4$ flowed with a velocity of 16.3 cm/s and air flowed with a velocity of 63 cm/s, respectively [28]. Meanwhile, Arana et. al. used a burner composed of two concentric tubes of 11.1 and 101.6
mm with ethylene flowing at a rate of 4.6 cm$^3$/s through the center tube and air flowing at a rate of 713.3 cm$^3$/s through the outer tube [29]. To capture products from these flames, both groups used stainless steel either in a wire or wire mesh form [28, 29]. Arana et. al. also used platinum and nickel wires to sample the flame [29]. Both groups then allowed their substrates to remain in the flame for a period longer than 10 but less than 30 minutes [28, 29]. After analyzing their samples, it appeared that Arana et. al. were able to grow carbon nanotubes on the nickel substrate of approximately 5 nm in diameter and on the order of 1 µm in length in thick mats [29]. Yuan et. al. also formed some multi-walled carbon nanotubes with diameters of 20 to 60 nm, but found that the region in the flame that they formed was limited at best [28].

To examine the diffusion flame structure and its ability to form nanotubes further, Lee et. al. [30] and Xu with his coworkers [31, 32] created inverse diffusion flame arrangements. An inverse diffusion flame is one where the oxidizer is supplied via a central tube that is then surrounded by fuel [30]. This creates a unique situation in that the region normally isolated underneath the flame front in a regular diffusion flame can be sampled without penetrating the high temperature flame front. At the same time, this produced a situation where some of the hydrocarbon species in the fuel were also being pyrolyzed above the flame instead of oxidized within it, since the hydrocarbon fuel source was surrounding the flame instead of the oxidizer. Lee et. al. mixed ethylene (C$_2$H$_4$) with nitrogen and flowed them at a rate of 35 L/min to the flame through a 94 mm tube. Inside of that tube was an 11 mm tube that delivered air to the reactor at a rate of 0.8 L/min. This arrangement was then surrounded by a Pyrex chimney to isolate it from the ambient environment. Both stainless steel and nickel substrates were used to sample this 20 mm flame for dwell times of 120
seconds resulting in the nickel substrates being the most successful for creating nanotubular structures. Nanotubes with diameters ranging from 20 to 60 nm were found in regions of the flame between 800 and 1300 K in entangled mats on the surface of the substrate.

As mentioned, Xu et. al. used a similar set up to produce carbon nanotubes. Instead of using \( \text{C}_2\text{H}_4 \), \( \text{CH}_4 \), and nitrogen flowed at a rate of 14.2 L/min through the outer tube while air flowed at a rate of 0.8 L/min from the center tube [31]. A 50 mm long probe composed of Ni/Cu, Ni/Cr or Fe was used to sample the 15 mm high flames under an imposed electric potential similar to that previously described. Comparable to the results of Lee et. al., Xu et. al. discovered carbon nanotubes with uniform diameters near the high temperature regions of the flame on the nickel based substrates at 6 mm, 9 mm, 12 mm, and 15 mm above the burner. Of these heights, 12 mm seemed the best as even the iron substrate produced nanotubes; however, they were mixed with other carbon nanostructures as well. On the other hand, the nickel based substrates produced mats of vertically aligned carbon nanotubes at this height with uniform diameters between 15 and 20 nm that, after a dwell time of 30 minutes in the flame, were approximately 6 microns in length. This orientation and purity, Xu and coworkers mention in a later study of the same flame and conditions, was a direct result of the electric potential [32]. Its presence discourages soot and its precursors from preventing nanotube formation and reorganizes the ions in the flame product gases so they more readily produce organized mats of carbon nanotubes.

A final flame configuration was introduced by Vander Wal et. al. This involved a two stage configuration where a diffusion flame fueled by air and ashless filter paper soaked in iron nitrate supplied product gases laden with iron catalyst particles [33]. These flame products mixed with CO, \( \text{H}_2 \), He, and air to produce a premixed reactant flow. This flow
emerged from a 0.95 cm tube at a rate of 0.25 SLPM located in the center of a flat flame burner. The flat flame burner hosted an acetylene/air flame burning at an equivalence ratio of 1.6. This two stage flame was then sampled using an electrically controlled air cylinder holding a transmission electron microscopy (TEM) grid for flame dwell times of 10 ms. The resulting products collected on the TEM consisted primarily of single walled carbon nanotubes and a surprising lack of amorphous carbon likely due to the presence of the flame supported by the flat flame burner. Its presence eliminates the unsaturated pyrolysis products in the ambient environment that would typically be present in other flame configurations. These results were promising because this method demonstrated that nanotubes could be synthesized without contamination on a large scale.

After examining these flame synthesis techniques, a few distinct parameters that have a direct effect on the production of carbon nanotubes became apparent. First, regardless of the type of flame employed, the carbon source was important. This gas directly determined the flame product environment which either promoted or prevented nanotube growth. Second, the local temperature of the flame where it was sampled often indicated whether or not carbon nanotubes would form. Granted, the temperature range where nanotube formation was observed was quite large, but this range also varied with the carbon source and the resulting flame product gases. Third, the sampling technique employed including effects of the dwell time, electrical characteristics, and flame location had a direct role in determining the characteristics of the nanotubes produced. Fourth, and equally important, was the catalyst employed including effects of the type of material, the supporting substrate, and its interaction with any particular flame synthesis environment.
1.2.4 Carbon Nanotube Catalysts

As it turns out, catalysts do more than promote the formation of carbon nanotubes. Although the exact role of catalyst particles is unclear, it is known that they are required, at least for the synthesis of SWNTs, according to Height et. al. [34]. Generally, catalyst particles participate in carbon nanotube production through a three step process, regardless of the synthesis technique. First, the carbon deposits on the surface of the catalyst particle by way of one of three different methods shown in Equations 1.1 through 1.3. Equation 1.1 involves hydrocarbon ‘cracking’ where any hydrocarbons present in the gaseous atmosphere directly contribute to the carbon deposition. Equation 1.2 then presents the ‘reduction’ process where carbon monoxide (CO) present in the gaseous environment reacts with \( \text{H}_2 \) to form water and deposits carbon on the catalyst particle. Finally, Equation 1.3 displays the process of disproportionation of CO to form carbon dioxide (CO\(_2\)) and deposit carbon. Height et. al. remarked that in most environments where CO is the primary carbon source, the latter two reactions are thought to serve as the primary means of carbon deposition.

\[
C_xH_y \xrightarrow{\text{metal}} xC_{\text{solid}} + \frac{y}{2}H_2 \quad (1.1)[34]
\]

\[
CO + H_2 \xrightarrow{\text{metal}} C_{\text{solid}} + \text{H}_2\text{O} \quad (1.2)[34]
\]

\[
2CO \xrightarrow{\text{metal}} C_{\text{solid}} + \text{CO}_2 \quad (1.3)[34]
\]

Once the carbon deposits on the catalyst particle, it is believed to diffuse either on or through the catalyst. Whether the carbon diffuses on the catalyst surface or through the catalyst itself typically varies from one nanotube producing situation to another. Factors such
as the catalyst crystal structure, the gaseous environment surrounding the catalyst, and the
temperature of the entire environment all influence this activity. However, Height et. al.
pointed out that comparisons of the characteristic diffusion time scale have been made by
others and the time scale for internal diffusion at 1273 K for a particle 10 nanometers in
diameter is on the order of 0.01 milliseconds, while at 1000 K the surface diffusion time
scale for a similar particle is on the order of 10 milliseconds. In addition, the crystal lattice of
the catalyst particle is believed to provide a structured diffusion pattern which would
influence the lattice structure of the carbon nanotube. If the majority of the carbon diffused
on the surface, it would probably result in an amorphous carbon deposit.

The final step in this general nanotube formation process is typically accepted as a
precipitation event. Once the carbon has diffused through the catalyst particle, Height et. al.
stated that the current belief among researchers is that one of two precipitation processes
occur [34]. The first process, as previously mentioned, involves the carbon diffusing through
the catalyst particle and the crystal structure acting as template for the crystal structure of the
carbon nanotube. So, the crystal structure of the catalyst particle actually controls the
diffusion process in a manner that produces a structured carbon nanotube. The second
process Height et. al. mention involves the catalyst particle becoming partially encapsulated
in carbon, forming a hemispherical cap. Then, the rest of the tube grows from this cap, away
from the catalyst particle.

With this generally accepted three step model of nanotube growth in mind, Height
et. al. formulated a more detailed model based on these three steps involving the interaction
of two catalyst particles tailored specifically to the flame environment [34]. They claimed that
the contact of two catalyst particles creates a region of low carbon concentration because it
is shielded from the gaseous environment that has a high carbon concentration. If this were not the case, they contended that the single particle would simply become encapsulated in carbon and no tubular structure would form. However, the presence of this region with a relatively low carbon concentration promotes the carbon diffusion through or on the catalyst particle necessary to form the tubular structure. Once this diffusion process is established, it will continue to provide carbon to the contact point between the two catalyst particles until the force from the precipitated carbon is sufficient to break the two particles apart. At this point the tube will continue to grow as carbon continues to diffuse through the catalyst particles and deposit from the gaseous environment. Height et. al. presented several situations that could then stop the growth of the nanotubes or prevent their growth altogether, resulting in the formation of a variety of different nanoparticles. They did, however, observe the presence of ‘dumbbell’ shaped nanoparticles in a flame synthesis environment, which supports this concept of tube growth. Although this model may not totally describe the role of catalysts in nanotube formation, it does aid in justifying their presence in nanotube growth.

As important as knowing the role of the catalyst in the formation of carbon nanotubes is knowing what substances can serve as a catalyst particle. According to Arana et. al., transition metals such as nickel, cobalt, and iron typically serve as catalysts for nanotube growth [35]. It turns out that these metals crack hydrocarbons well and readily form unstable carbides which permit them to rapidly diffuse carbon. These metals do not have to be in their pure form, however, to serve as catalyst particles. Arana et. al. successfully produced carbon nanofibers (a nanotube that is not hollow) on a stainless steel substrate, which is an alloy of iron. Also, they were able to produce carbon nanofibers on platinum, which was not
known to catalyze carbon nanostructure growth prior to their work. Thus it appears that transition metals in general may have the potential to catalyze carbon nanotube growth.

1.2.5 Carbon Nanotube Catalyst Application Methods

The application of a catalyst varies from situation to situation as described in the flame synthesis section. Typically, though, the application method belongs to one of five categories. The first of these includes vapor phase introduction of a catalyst [15, 17, 20, 36]. This usually implies that the catalyst either enters the reactor as a true vapor via a sublimation process or as part of a carrier gas such as iron pentacarbonyl. Instead of a true vapor, the second method introduces the catalyst particles in a solid phase while in a carrier gas, forming an aerosol [19, 21, 33]. Most of the time, this involves nebulization of a transition metal salt, such as nickel nitrate, suspended in an alcohol solution. The nebulized droplets are most often placed in an inert carrier gas stream for delivery to the reactor.

The remaining application methods use a stationary catalyst supported by an underlying substrate. The first of these methods comes in a probe or wire form [22, 24, 25, 26, 28, 29, 31, 32, 35]. In some instances the probe or wire is actually composed of the catalyst material either in its pure form or as an alloy. In other instances the catalyst coats the surface of the probe or wire, from which, the nanotubes are produced. The second of the stationary catalysts are catalyst coated meshes [18, 23, 30]. The only difference between this and a catalyst coated wire is that the wire is woven into a mesh prior to being coated with a catalyst. The last of the stationary catalysts involves a coated stationary substrate [16, 27]. This application usually involves the flame impinging on a coated, stationary metal plate in
stagnation flame synthesis configurations. Most catalyst applications are manifestations of one of these five basic types of methods.

1.2.6 Silicon Nanotubes

Silicon nanotubes (SiNTs) have a more recent history, having been synthesized for the first time in 2001. Prior to 2001, they were predicted to exist as stable structures through ab initio arguments in structures similar to carbon nanotubes with properties varying with the chiral angle [37]. However, they still showed great promise as their Young's modulus was expected to be in the range of 70 to 80 GPa. As a result, they too may serve in the applications set forth for CNTs besides being better suited for integration into existing silicon applications [38]. To create SiNTs for these applications, Tang et. al. used silicon monoxide mixed with deionized water in a reactor maintained at 470 °C and 6.8 MPa while being stirred 200 rev/min by a mechanical stirring mechanism. This mixture remained at these conditions for a period of one hour and then was allowed to cool. The result was an aqueous solution from which SiNTs were extracted and found to be 15 nm in outer diameter and 5 nm in inner diameter on average.

Alternatively, a chemical vapor deposition process was also used to synthesize SiNTs. Sha et. al. used a specially prepared, gold sputtered plate of Al₂O₃ containing small pores that was placed in a furnace under a partial vacuum maintained at 20 Pa [39]. The furnace was then heated to a temperature of 620 °C and a mixture of argon, hydrogen, and silane was injected at a ratio of 10:2:1 to achieve a new pressure of 1450 Pa. After the
deposition process was complete, the plate was removed and washed in a HCl bath. The pores within the plate then contained SiNTs on the order of 50 nm in outer diameter.

1.2.7 Silicon Carbide Nanotubes

The same year Tang et. al. first synthesized SiNTs, silicon carbide nanotubes (SiCNTs) were also being created [40]. These nanotubes are thought to be similar in form to carbon and silicon nanotubes, but ultimately composed of a different structure because of the presence of both elements on each lattice point [41]. As a matter of fact, two distinct structures have been studied. The first type involves alternating Si and C bonds where a single Si atom has three C atom neighbors. Alternatively, in the second type, each Si atom is bonded to two C atoms and a single Si atom. Ab initio studies found that the first type with alternating Si-C bonds was more stable than the Si-Si or C-C bonds in the second type. In spite of these studies, direct observations of the structure of a SiCNT have yet to be documented. Nonetheless, there is a high degree of confidence that SiCNT properties still vary with their chiral angle as in typical CNTs. Unlike CNTs though, the SiC composition is expected to give SiCNTs higher surface reactivity, better high temperature stability, and better performance in harsh environments when employed in similar applications to CNTs.

Despite no documented SiCNT observations, SiCNTs have been synthesized through various methods, many similar to those already presented for both CNTs and SiNTs. For instance, Pei et. al. used a hydrothermal method to synthesize SiCNTs that was almost identical to that used by Tang et. al. to construct SiNTs [42]. The main differences lie in the ingredients used. 0.625 g of SiC combined with SiO\textsubscript{2} in a ratio of 2 to 3 coupled with
49.4 ml of distilled water were used to make the 7 nm outer diameter SiCNTs. Taguchi et. al. also synthesized SiCNTs approximately 10 nm in outer diameter by combining Si powder with CNTs in an environmental chamber maintained at 1200 °C for 100 hours [43]. The CNTs and Si powder were not in contact throughout this process, but diffusion provided by the elevated temperature created a mechanism for SiCNT synthesis.

1.2.8 Characterization Techniques

Two types of characterization techniques are commonly used to investigate carbon nanotube morphology and chemical structure. First, as far as the carbon nanotube morphology is concerned, either field emission scanning electron microscopy (FESEM) [18] or high resolution transmission electron microscopy (HRTEM) [44] is used. This captures images and provides dimensional information regarding the carbon nanotubular structure. Then, to retrieve chemical structure information, spectroscopy techniques such as X-ray photoelectron spectroscopy are employed [44]. One particularly useful spectroscopy technique is Raman spectroscopy, which creates a unique response in carbon nanotubes. It turns out that Raman spectroscopy senses different carbon solid phases through changes in the intensity or width of the peaks in the carbon spectrum. Appendix C expands upon the application of Raman spectroscopy to carbon nanotube characterization.

1.3 Research Goals

Fagan et. al. recently showed through a first principles argument that the prospect of creating nanotubes with a ratio of Si to C other than unity or ‘doping’ of a CNT with an Si
atom, may be possible [45]. They also mention that, if Si doping does actually occur, it would create a strong bond site on the surface of the nanotube. The result would be a nanotubular structure with a higher reactivity because of its increased ability to maintain a strong bond with other molecules. Regular CNTs typically absorb molecules onto their surface, resulting in a weak bond and poor reactivity. However, the presence of the Si atom could lead to other doping procedures that would provide the opportunity to engineer the optical and chemical properties. Such modifications would create potential for the use of these nanotubular structures as chemical and temperature sensors along with the aforementioned applications such as gas storage. This potential, coupled with the previously discussed variation of interesting properties with Si to C ratio, creates the goal for the present research of synthesizing Si-C nanotubular structures where Si and C appear in ratios other than 1:1.

This goal presents a difficult challenge in selecting an appropriate synthesis method. Two particular challenges are more prominent than others in making this selection. The first challenge is the complicated process of actually combining Si and C in a single structure but not on a 1:1 basis. The second challenge then comes in the form of repeatability and scalability. Based on the prior success synthesizing CNTs, combustion synthesis seems to show promise in satisfying the second challenge quite well. As for addressing the first challenge, it also holds great potential because it provides an environment in which the chemistry, temperature, and pressure can be reasonably controlled while being simultaneously sampled and observed. Therefore, combustion synthesis will be used to synthesize Si-CNTs.

To complete this exploration, a series of experimental tests consisting of two major sections were arranged and conducted. The first section, which consisted of ten tests, was
termed the ignition study as it was intended to determine the combustion behavior of silane and its reactivity with carbon dioxide. This information then served as the foundation for the second section of testing referred to as the laminar burner tests. The first three tests in this section composed the equipment familiarization tests which were intended to develop the operating, sampling, and characterization procedures for the second portion of the laminar burner tests. This second portion of tests then consisted of the Si-CNT production tests where Si-CNTs were synthesized. The discussion of this approach follows in Chapter 2 beginning with the ignition study and progressing on to the laminar burner tests. Chapter 3 then contains and discusses the results from both series of tests. Finally, Chapter 4 summarizes the conclusions and presents recommendations for future work.
Chapter 2

Experimental Apparatus and Procedure

2.1 Preliminary Ignition Study

During the course of this study, two apparatuses were constructed. The first of these apparatuses enabled an ignition study of silane (SiH₄), which was selected because of its simple molecular structure and high reactivity. The purpose of this study was to meet the secondary goals set forth for this research. First, and of utmost importance, the combustion behavior of the pyrophoric silane gas was documented, mainly for safety reasons. Second, the reactivity of silane with carbon dioxide was investigated. Meeting these goals involved the design of a simple choked nozzle injector to deliver silane to the ambient atmosphere in a diffusion flame. Carbon dioxide was injected into the reactor vessel to establish its reactivity with silane; three different injector designs were used. Using this equipment, a series of ten tests were conducted at the Applied Research Laboratory’s (ARL) Steam Facility located near Pennsylvania State University’s University Park Campus. All gases and gas related equipment were obtained from GTS Inc. and all fittings and tubing were from Pittsburgh Valve and Fitting Co.

2.1.1 Burner Design

As mentioned, silane was injected from a choked nozzle into a simple reactor vessel that was recovered from a previous fuel study experiment. A photograph of the exterior of
this reactor vessel appears in Figure 2.1. Note that the top of the reactor vessel was removed for ease of access as well as improved visualization of the reaction. Figure 2.2 shows the interior of the reactor along with its various components. Here the choked nozzle silane injector appears below the thermocouple rake. The choked nozzle silane injector was fabricated on a horizontal lathe in a 3/16” stainless steel Swagelok plug. The other two injectors provide both compressed air and carbon dioxide (CO$_2$) to the environment within the reactor. Both an aviation ignitor and a nichrome hot wire ignitor were used to assist in overcoming any activation energy in the silane and CO$_2$ oxidation reaction. It is also shown in the Figure 2.2.

Figure 2.1: The exterior of the reactor used in the ignition study.
Equations 2.1 and 2.2 provided the pressure ratio (PR) and the mass flux, respectively, for a choked nozzle condition [46]. This condition implies that the flow velocity at the minimum flow area of the nozzle is equal to that of the local sound speed corresponding to a Mach number value of 1. Since Equation 2.2 calculates the mass flux for a given Mach number, downstream pressure, and temperature, which are the standard temperature and pressure of 298.15 K and 101.325 kPa in this case, the nozzle area was open for selection. Consequently, it made sense to select a diameter to minimize the use of the expensive silane gas, which implied using the smallest diameter as practically possible on a horizontal lathe. The result was the fabrication of a nozzle with a 0.015” minimum flow diameter and a mass flow rate of 1.68 gm/min. A schematic of this nozzle can be seen in Figure 2.3.

\[
PR = \left[ 1 + 0.5(k - 1)Ma^2 \right]^{\frac{k}{k-1}} \tag{2.1}[46]
\]

Figure 2.2: The interior of the reactor used in the ignition study after a test run.
Unlike the silane injector, three different types of carbon dioxide injectors were used throughout the duration of the ignition study. For the first four ignition study tests, the curved ¼” Swagelok tubing shown in Figure 2.2 served as a simple carbon dioxide injector. The intent of this design was to immerse the silane flame in a carbon dioxide environment within the reaction chamber, so the flow rate of carbon dioxide was not necessarily of utmost importance as long as it was nonzero. Since ¼” Swagelok stainless steel tubing was used to deliver the carbon dioxide, this was the most convenient choice to construct an injector to test CO$_2$ reactivity with silane. For the ignition study tests four through seven, the carbon dioxide injector design changed to that shown in Figure 2.4. Here, a piece of 3/16” stainless steel capped a piece of 5/8” Swagelok stainless steel tubing. Near the stainless steel plate, carbon dioxide flowed from a series of four horizontally directed holes creating a layer of carbon dioxide gas throughout the base of the reactor and totally submersing the silane.

\[
\text{mass flux} = \left[ \left( \frac{1}{PR} \right)^{\frac{k}{2}} \left( \frac{k}{k - 1} \right) \right] \left[ 1 - \left( \frac{1}{PR} \right)^{\frac{k-1}{k}} \right]^{\frac{1}{2}} \frac{P_{\text{atm}}}{\sqrt{R_{\text{SIH4}}} T_{\text{atm}}} \quad (2.2)[46]
\]

Figure 2.3: The silane injector nozzle designed for the ignition study tests.
injector in a layer of carbon dioxide. In the final two ignition study tests, the silane injector was relocated to the center of the reactor and welded to a 1/4” piece of Swagelok stainless steel tubing. This assembly rested concentrically inside a 5/8” piece of Swagelok tubing through which carbon dioxide then flowed.

![Image](image)

**Figure 2.4:** The second carbon dioxide injector design used in the ignition study.

### 2.1.2 Control and Instrumentation

Despite being relatively unsophisticated, the ignition study burner required an extensive support system, largely because of the pyrophoric nature of silane. Two initial developmental tests yielded results establishing a support system composed of a number of solenoid valves, check valves, tubing, and fittings as displayed in Figure 2.5. Essentially, the system supplied four different gases to the burner from either a gas cylinder (silane, carbon dioxide, and argon) or shop compressed air. The line associated with the silane, or Line 1 (denoted by a rectangle) in the schematic in Figure 2.5, contained a high pressure solenoid
valve manufactured by the Circle Seal Company which controlled silane supply to the system from the source cylinder. The regulator was located downstream of this valve; this order evolved from the need to connect an argon purge line directly to the CGA 350 fitting that coupled with the valve on the silane cylinder itself. Space requirements then prevented the regulator from coupling directly to the CGA 350 fitting, leading to its placement downstream of the first solenoid valve and the section of Line 1 operating at cylinder pressure.
Figure 2.5: The ignition study support system.
Also operating at cylinder pressure was the portion of Line 1 supplying argon to the previously mentioned purge line connected to the CGA 350 fitting. Here a hand operated Nupro needle valve controlled argon flow originating directly from the cylinder and providing a high pressure purge when necessary. Also a 50 psig purge could have been supplied to the silane line by way of an ASCO Red Hat II ¼” solenoid valve that was located downstream of the regulator. This valve, along with the hand operated needle valve used in the high pressure purge situations, were placed upstream of a 25 psi check valve (1/4” Swagelok) to prevent silane backflow into the argon cylinder. This section of Line 1 composed a portion of the system used solely for purge purposes.

Another portion of the system used solely for purging appears as Line 3 in Figure 2.5. When a purge was required, the solenoid valve labeled 3 in Figure 2.5 opened, allowing silane to flow to a vertically oriented piece of 6”, PVC pipe filled with 2’ of water. Here, the silane entered the bottom of the pipe and bubbled out the top to prevent it from emerging from the purge system as a high speed jet. If that did happen, the flame would have resembled a torch, which presented an unsafe set of circumstances. On the other hand, bubbling the silane through the water and allowing it to contact hot combustion products from a propane flame assured it would flare off in a controlled manner without harm to property or personnel. Of course, this did not purge the silane injector. This required keeping Valve 3 closed and opening Valve 5 which purged the injector.

The remainder of the system shown in Figure 2.5 delivered oxidants to the reactor vessel. Here, Line 3 provided carbon dioxide to the injector previously described, from a cylinder at a regulated pressure of 40 psig. The solenoid valve (ASCO Red Hat II) controlled the flow of carbon dioxide to the reactor vessel and a check valve adjacent to the reactor
vessel prevented backflow of reactant and product gases into the carbon dioxide supply. At the same time, Line 4 brought compressed shop air to the reactor vessel at 120 psig via a check valve also installed to prevent backflow. Valve 6 controlled this flow with a hand operated valve.

During a test, the reactor vessel and associated systems were housed within a concrete reinforced, masonry test cell and all valves were either remotely operated or placed outside the test cell to ensure safe operation. Remote operation of the solenoid valves occurred via a switch panel mounted on a cart while all hand operated valves were strategically located within the control area either as part of the existing infrastructure (compressed air) or on their respective cylinder (argon). Argon and all other cylinders, including silane and carbon dioxide, were located outside of the test cell for safety reasons.

To further maintain a safe environment and obtain experimental data, various instruments provided information about important process variables as well as a visual record of the tests. First, four K-type Omega thermocouples arranged in a rake as seen in Figures 2.2 and 2.5 monitored flame temperature. Second, three carefully placed Omegadyne PX5500L1-100A5T pressure transducers with a 100 psia pressure range indicated flow by change in pressure for both carbon dioxide and silane. Pressure Transducer 1 in Figure 2.5 showed silane flow to the injector while Pressure Transducer 2 monitored carbon dioxide flow to the reactor and Pressure Transducer 3 provided silane supply information. These instruments relayed information to a Hewlett-Packard 34920A data acquisition system that worked in concert with a Gateway laptop computer. At the same time, a Panasonic 5100 HS camera coupled to a television and a Toshiba RD-XS32 DVD recorder captured video of the individual test runs.
Additional equipment employed during the ignition study included variations of both ignitors and gas heaters to promote the reaction between silane and carbon dioxide. Initially, an aviation type model CH34492 Champion ignitor was used to assist in the ignition of the silane and carbon dioxide. By the third version of ignition study test rig, however, the previously mentioned nichrome wire ignitor replaced the aviation ignitor as shown in Figure 2.2. The carbon dioxide heater was initially an Omega model AHP-5052 electric process heater rated between 100 and 400 watts. This process heater continued service until the eighth test in the ignition study where a simple coil heated by a propane burner replaced it. Then, for the ninth test, an electric cylinder heater (Ogden Mighty Miser 3000 W, 220V) was used to heat the carbon dioxide. Finally, in the tenth test, a Harris oxy-acetylene torch was included in the test to observe the interaction among products from this and the silane/air oxidation reactions.

### 2.1.3 Burner Control Parameters

The primary control parameter for this test was silane flow rate. However, as indicated in the design section, this parameter was set at 1.68 gm/min by the nozzle diameter. Thus, under normal operating conditions, the silane flow rate did not change between consecutive test runs. A secondary control parameter involved the temperature of the carbon dioxide. This did change between consecutive test runs. It was typically determined by the performance of the carbon dioxide heater in use during that particular test.
2.1.4 Ignition Study Procedure

Overall the experimental procedure for the ignition study tests consisted of two main sections. The pretest procedure outlined the steps necessary to ensure that all valves were in good working order and that all fittings were free of leaks. Next, the main procedure consisted of a short preliminary procedure outlining start up activities as well as additional safety precautions. Then, the main procedure outlined the steps necessary to start the flows and light the flame. Finally, the post procedure contained steps to ensure a safe shut down and secured the system for either preparation for the next test or dismantling.

On a more detailed level, the pretest procedure involved pressurizing each of the lines displayed in Figure 2.5 in a specific sequence so as to inspect them. Inspection of the silane line, of course, was of utmost importance because of its potential to leak, producing a flame in the process. To carry out the inspection, the line was typically charged with argon at cylinder pressure. Then, Snoop was applied to fittings, allowing leaks to be observed because of its propensity to bubble when exposed to a slow leak. The line charging process would continue until the entire line was charged, verifying along the way the operating condition of the valves present along that line. A similar process confirmed the condition of the other lines carrying carbon dioxide and compressed air. Upon completing this process, the system was ready for the experiment, meaning that all valves were in the correct position and all lines were leak free.

After completing the pretest procedure, a preliminary procedure addressed other precautionary measures. First, all personnel involved in the test received a briefing on the hazards of silane, carbon dioxide, and the equipment in use. Then, the procedure concentrated on response to emergency situations so those present could react in a safe
manner and anticipate the order of action in the event of an emergency. After that, the actual test began with the opening of the silane cylinder valve and the securing of the test cell and surrounding areas. At the same time, ignition of the propane torch on the silane water purge system occurred. Finally, an alert to all ARL Steam Facility personnel of the test commencement sounded over the public address system, officially beginning the test.

At this point, the main portion of the procedure began, starting with the activation of both the data acquisition and video recording systems. Typically, directly following the beginning of data acquisition, the reactor was flushed for thirty seconds with compressed air. At that point, the ignitor was activated. Then, silane flowed from the silane injector producing a steady, turbulent flame. Once the flame was steady for a period of 5 seconds, carbon dioxide flow was started and the process heater began heating the carbon dioxide. After adequate observations had taken place, the process heater was shut down and the carbon dioxide flow was stopped. Silane flow continued as the main experimental procedure terminated.

The post procedure began with the reactivation of the ignitor and the termination of data acquisition. To completely clear line 1 of silane, the silane cylinder was manually closed allowing the line to be charged with argon at cylinder pressure. The argon forced the bulk of the silane in line 1 out through the silane water purge system. Then, the remainder flowed through the silane injector into the reactor. The purge continued until no flame was observed on either the injector or the water purge system. At this point argon flow was terminated and the system pressure was decreased to zero gauge pressure. After that, the propane torch on the silane purge system was extinguished and the silane injector was
cleaned in an ultrasonic bath. In the event of an emergency, this post experiment procedure also served as a safe shutdown method.

A step by step description of the entire procedure is located in Appendix A. A copy of the formal test announcement issued to ARL staff displays specific information about safety hazards and equipment along with vital personnel information. In developing this procedure and knowing about the equipment, two important themes emerged. First, and of utmost importance, safety was paramount because of the inherent risk for injury because of silane’s pyrophoric nature. Second, sound procedural development ensured safe observation of the interactions of silane and carbon dioxide while providing meaningful results. These themes combined created the foundation for the next series of tests.

2.1.5 Ignition Study Test Matrix

The ignition study consisted of ten tests. The first of these tests was intended to develop an understanding of silane and its pyrophoric behavior. At the same time, the aviation ignitor was tested to determine if it was a practical method to aid the ignition of silane in a carbon dioxide environment. The second test involved using a propane pilot flame to ignite the silane/carbon dioxide reaction after the ignitor failed to do so. This test, however, was canceled indefinitely due to safety concerns. Consequently, the third test addressed the use of a silane/air pilot flame while verifying a new procedure and test rig along with determining the applicability of a nichrome wire ignitor.

The fourth test continued testing of the nichrome ignitor, but also included heating the carbon dioxide before it entered the reactor through the Omega process heater. In
addition, this test was the first to use the carbon dioxide injector that was intended to flood the bottom of the reactor vessel through the use of four horizontal holes underneath a flat plate. After unsuccessfully completing the fourth test, test number five had the same purpose as test four. The sixth and seventh tests then continued testing of the heated carbon dioxide through use of the Omega process heater. Test number eight was the first with the carbon dioxide injector that was arranged concentrically with the silane injector and a propane heated coil to heat the carbon dioxide. The ninth test then introduced the electric cylinder heater in addition to the propane heated coil heating the carbon dioxide while continuing to test the concentric carbon dioxide injector. Finally, the tenth test introduced an oxy-acetylene torch to combine with the silane/air flame products for carbon production.

2.2 Laminar Burner

After completing the ignition study, it was clear that the prospects of advancing into the creation of silicon doped carbon nanotubes required a more reliable, robust, and practically predictable burner because of the complexity of the chemistry and the inherent safety issues. A laminar diffusion flame burner seemed a good fit. The selected design originated from a soot particle study conducted by Santoro et. al. in 1982 [47]. Its maturity and ease of applicability made it very attractive for the first in depth investigation into the synthesis of silicon doped carbon nanotubes. More specifically, it provided easy control of the fuel flows, which created a predictable, well-behaved flame. At the same time, it permitted a simple sampling system to successfully capture samples.
2.2.1 Burner Design

The design of this burner focused on information provided by Santoro et. al [47]. Essentially, they produced a burner consisting of two concentric tubes through which fuel and air flowed from the interior and exterior tubes, respectively. This burner then ran under a set of four different conditions burning either ethane or ethylene (ethene). Listing the specific operating conditions, Santoro et. al noted whether those specific conditions created visibly sooting flames or not. Since nanotubular structures were the goal in this research, soot would merely add difficulty to identifying them. Thus, a visibly nonsooting flame would help to prevent samples from becoming overrun with soot. This criterion and the fact that ethylene previously performed well in flame synthesis of carbon nanotubes, established the operating conditions best suited for the current application [18]. These conditions included an ethylene flow rate of 3.85 cm$^3$/s at a velocity of 3.98 cm/s and an air flow rate of 713.3 cm$^3$/s at a velocity of 8.90 cm/s [47]. This operating condition along with the two tube arrangement composed the foundation for the burner design.

After selection of the conceptual design of the burner, the main task was sizing the constituent tubes. In contrast to the original burner design, where the fuel flowed from the central tube and air flowed from the next tube, silane flowed from the central tube and ethylene from a concentric tube. This assembly was surrounded by a larger pipe which housed a compressed air flow to provide a shield for the laminar diffusion flame from the surrounding environment. At this point, sizing the tubes was a simple task since the volume flow rates and flow velocities were already specified by the flame characteristics.

To size the tubes, the integral form of the principle of continuity was applied to the control volume shown in Figure 2.6. For the flow conditions set forth by the desired flame
characteristics, a number of safe approximations could be used to simplify Equation 2.3, the integral form of the principle of continuity. First, the low gas velocity indicated that incompressibility would be a safe approximation. Second, given that the goal was to create a stable flame, the flow must be steady state. Third, the control volume employed in this calculation was stationary and nondeformable with a single inlet and outlet due to the geometry of the boundary. Finally, the velocity at both the inlet and the outlet were approximated as the average values at both locations. The result is the relationship shown in Equation 2.4, which is the balance of the mass flow rates entering and exiting the control volume. \( Q \) [length\(^3\)/time] is volume flow rate and the product of the cross sectional tube area [length\(^2\)] and the gas velocity [length/time]. Canceling the density, \( \rho \), in each term, Equation 2.4 relates the volume flow rate at the inlet and outlet directly.

\[
\left. \frac{dm}{dt} \right|_{sys} = 0 = \frac{d}{dt} \int_{CV} \rho dV + \int_{CS} (\hat{V} \cdot \hat{n}) dA \tag{2.3}
\]

\[
\dot{m} = \rho \vec{V}_{in} \cdot \vec{n}_{in} = \rho \vec{V}_{out} \cdot \vec{n}_{out} = \rho Q_{in} = \rho Q_{out} \tag{2.4}
\]
Using this principle, calculating the cross sectional flow area was straightforward since the gas velocity did not change appreciably between the inlet and outlet of the control volume. The total fuel flow rate used by Santoro et. al. of 3.85 cm\(^3\)/s was divided between the silane and ethylene flows for the new burner. As a result, the total volumetric flow rate for silane and ethylene (\(Q_{\text{SiH\textsubscript{4}}}\) and \(Q_{\text{C\textsubscript{2}H\textsubscript{4}}}\), respectively) became 1.925 cm\(^3\)/s to provide equal parts of both constituent gases. To maintain flow characteristics, the velocity remained equal to that used by Santoro et. al. at 3.98 cm/s.

Solving continuity for the required cross sectional flow area yielded a required value of 0.484 cm\(^2\) or 0.07497 in\(^2\) for both silane and ethylene. It turned out that a 3/8” diameter Swagelok 316 stainless steel tube with 0.035” wall thickness had a flow area of 0.4714 cm\(^2\) which, at a flow rate of 1.925 cm\(^3\)/s resulted in a new velocity of 4.08 cm/s. The next tube, through which ethylene flowed, also required 0.4714 cm\(^2\), but had to house the first tube within it, requiring a total cross sectional area of 1.197 cm\(^2\). As it turned out, a 5/8” Swagelok 316 stainless steel tube with 0.065” wall thickness provided a total ethylene flow area of 0.529 cm\(^2\), resulting in a gas velocity of 3.64 cm/s. Finally, the pipe through which air flowed required a cross sectional flow area of 80.15 cm\(^2\), while housing the other two concentric tubes, whose total cross sectional area totaled 1.979 cm\(^2\). After considering the materials and channel shapes obtainable, a 4.5” diameter 304 stainless steel pipe with an internal diameter of 4.026” (offered by McMaster-Carr) provided the required cross sectional area of 82.13 cm\(^2\). A layer of 1/8” glass beads (McMaster-Carr) installed inside the pipe ensured a uniform air flow. Two pieces of 304 stainless steel coarse mesh with 0.1” square holes and 0.025” diameter wire (McMaster-Carr) held these glass beads in place. The tubes and pipe were then tied together with a piece of stainless steel.
The required length of the constituent tubes was the next design parameter of interest. Even though the flow must not necessarily be fully developed for the previous calculation’s validity, a concept of the flow’s velocity profile was helpful for sampling considerations. As a result, the flow entry length became a desired quantity for each gas flow. Equation 2.5 shows the relationship to estimate the entrance length for laminar flows in ducts. In this relationship, Re represents the Reynolds number, d represents the internal diameter of the duct, and $L_e$ is the entrance length. Assuming the gases were at standard temperature and pressure, the Reynolds numbers became 38.5, 54.9, and 966.3 for silane, ethylene, and air, respectively. Correspondingly, the entrance lengths developed into 1.79 cm (0.704”), 4.06 cm (1.60”), and 5.93 cm (2.33”) for silane, ethylene, and air, respectively. Despite these values, the actual, required length of the burner assembly to guarantee fully developed flow was 6”.

\[
\frac{L_e}{d} = 0.06 \text{Re} \tag{2.5}
\]

Altogether, these components complete the laminar burner. Further details of the burner and base plate appear in Figures 2.7 and 2.8, respectively. Then, an image of the laminar burner itself is presented in Figure 2.9.
Figure 2.7: A schematic of the laminar burner.

Figure 2.8: A schematic of the laminar burner base plate.
2.2.2 Sampling System

The products of the flame in laminar burner required systematic sampling and characterization to find any nanotubes that were produced and determine their composition. To accomplish this task, a sampling system, seen in Figures 2.8 and 2.9, was developed around the concept of thermophoretic sampling [19]. In this process, solid particulate matter within a hot gas flows to a relatively cold solid substrate, upon which the solid particulate matter deposits due to the strong temperature gradient imposed by the relatively cold solid substrate [19]. In this work, 316 stainless steel mesh (McMaster Carr) composed of wire 0.001” (25.4 µm) in diameter and a rectangle size of 0.0015” (38.1 µm) cut into pieces ½” by 2” served as the solid substrate. Each piece then attached to a piece of slotted steel via alligator clips and the right hand corner facing the flame cut off to indicate the mesh’s
orientation in the flame. Knowing the orientation became important later in the characterization process.

Coupled to the slotted piece of steel was a 7/16” bore pneumatic cylinder (McMaster-Carr) that moved the stainless steel mesh in and out of the flame. Compressed air to the cylinder was controlled by a hand operated ¼” Whitey needle valve mounted to a control cart. Accompanying this valve was a ¼” Whitey ball valve, which released pressure from the system. Nylon ¼” tubing connected the valve manifold to the pneumatic cylinder. Figure 2.10 shows the sampling system while Figure 2.11 displays the control valves on the remote control cart. Prior to placing the stainless steel mesh pieces in the sample system, they were coated with a catalyst through a simple process involving ferric chloride. This involved submersing the individual pieces into ferric chloride while under a fume hood for safety, subsequently coating the mesh with a catalyst. After drying under a fume hood, iron and iron oxide deposits remained connected to the mesh and it was ready for use.
Figure 2.10: The sampling system viewed from above.

Figure 2.11: The sampling system control valves on the remote control cart.
2.2.3 Controls and Instrumentation

Although the burner itself is quite different from the ignition study burner, the support system shown in Figure 2.12 is quite similar, with only three main differences. First, the most apparent difference is the addition of the ethylene supply line and accompanying nitrogen supply line denoted as area A in Figure 2.12. Ethylene flowed at a regulated pressure of 25 psig through a remotely operated ASCO Red Hat II ¼” solenoid valve to a ¼” Swagelok metering valve equipped with a Vernier scale that metered the flow of ethylene to the burner itself. While traveling between these two valves, the ethylene passed through a ¼” inline filter with 40 micron passages that served as a flashback arrestor (McMaster-Carr) in case the flame did happen to propagate back up the supply line. Eventually, the ethylene passed through a check valve and finally reached the burner itself. The nitrogen supply line connected to the ethylene line originally served merely as a purge for the first five laminar burner tests. Finally, in the sixth laminar burner test, it served both as a purge and a diluent for the ethylene flame. Another Whitey ¼” needle valve served to initiate the diluent flow, while a ¼” Swagelok metering valve with a Vernier scale located downstream actually regulated the flow.

The second major difference (shown as area B in Figure 2.12) between this system and the ignition study system arises in the presence of metering valves on both the silane supply line and the compressed air supply line. Silane flowed from a cylinder in a similar fashion as in the ignition study, but to achieve the required flow velocity, it also passed through a Swagelok ¼” metering valve with a Vernier scale. In addition, another important component appearing on the silane supply line is the ¼” inline filter with 40 micron passages which served to alleviate some of the concerns of the pyrophoric nature of the silane by
preventing a flashback. At the same time, compressed air flow was regulated by a \( \frac{1}{4} \)" Whitey needle valve and no additional equipment.

The third and final major difference between this support system and the laminar burner support system is the placement of the instrumentation, which appears in region C in Figure 2.12. Instead of four thermocouples, only one monitored the temperature of the flame in the laminar burner. Primarily, it indicated when the flame ignited. Then, three pressure transducers still served to monitor flows in the laminar burner support system, however, the transducer that observed carbon dioxide flow in the ignition study system monitored ethylene flow in the laminar burner support system. Besides these differences, the support system was identical to that used in the ignition study including equipment placement and the data acquisition equipment. For better understanding of the overall support system, Figure 2.12 displays these changes and the overall organization relative to the laminar burner.
Figure 2.12: The laminar burner support system.
2.2.4 Burner Control Parameters

Despite the similarities of the laminar burner support system to that of the ignition study, the control of the laminar burner was markedly different. Here, two fuel flow rates served as the primary control parameters because they determined the flame behavior and composition. First, as in the ignition study, was the silane flow rate. In this burner, though, one of the ¼” Swagelok needle valves with a Vernier scale controlled the flow instead of a choked nozzle.

To calibrate this valve, a separate setup passed nitrogen through this needle valve and then through a rotameter (Cole Parmer N034-39G). Supplied with the rotameter was a calibration curve for air at standard temperature and pressure. Noting the scale readings for a given valve position on both the rotameter and the Vernier scale on the needle valve in the presence of a nitrogen flow provided a method to find the volume flow rate. This flow rate directly corresponded to that valve position for any gas via the rotameter calibration curve and Equation 2.6. Here, \( q_{\text{gas}} \) and \( q_{\text{air}} \) are the flow rates of the measured gas and air, respectively, while \( \rho_{\text{gas}} \) is the density in gm/ml of the measured gas. Upon completion of the calibration process the valve was ready to control the flow rate of the silane. Originally, the silane flow rate was 1.93 cm\(^3\)/s or 115.5 cm\(^3\)/min, but, after difficulties establishing a stable flame in the first two laminar burner tests, an increase in the silane flow rate became necessary. This increase resulted in a new flow rate of 3.85 cm\(^3\)/s or 231 cm\(^3\)/min.

\[
q_{\text{gas}} = q_{\text{air}} \sqrt{\frac{0.00120}{\rho_{\text{gas}}}} \quad (2.6)[48]
\]
The second fuel flow rate was the ethylene flow rate. A procedure similar to that used for the silane control valve calibrated the ¼” Swagelok needle valve to control the ethylene flow rate, which ultimately became 3.85 cm$^3$/s or 231 cm$^3$/min. In the sixth laminar burner test, a third flow consisting of nitrogen was introduced. A third ¼” Swagelok needle valve metered its flow after undergoing a similar procedure as the first two for calibration. The calibration curves produced for the three valves along with flow rates of each of the gases appear in Figure 2.13.

![Laminar Burner Flowmeter Curve](image)

Figure 2.13: The calibration curves produced for the ¼” Swagelok needle valves used to meter the gas flows in the laminar burner support system.

In addition to these primary control parameters, two secondary control parameters, including the placement height of the sampling mesh above the injector and the mesh dwell time served very important roles. The sample mesh placement height above the burner was vital to retrieving interesting structures and avoiding the capture of overwhelming amounts of amorphous carbon. The fifth laminar burner test investigated three heights above the injector (HAI) including ½”, ¾”, and 1”. After completing this brief investigation, ½”
seemed to provide the purest samples. Also investigated in this test was the sample dwell time. Trial times of 6, 10, and 20 seconds indicated that a dwell time of 6 seconds yielded the highest quality samples. As a result, samples taken in later tests were at a height above the injector of ½” and remained in the flame for 6 seconds. Together, these parameters controlled the flame synthesis process in the laminar burner.

### 2.2.5 Laminar Burner Procedures

The procedure employed in operating the laminar burner was essentially the same as that used in the ignition study as it contained two main parts. First, a lengthy pretest procedure prepared the burner and its support system by verifying the entire system was leak free. Just as in the ignition study, this involved pressurizing both the silane and ethylene supply lines with either argon or nitrogen along with verifying the operational status of all of the solenoid and hand operated valves within the support system. Next, the main portion of the procedure consisted of three different sections. A brief preliminary section addressed placement of safety equipment and informed others present for the test of the inherent dangers and emergency procedures. Also, this section included officially announcing the test to the ARL Steam Facility.

After the preliminary portion of the procedure, the test officially began. This portion of the procedure differs considerably from the ignition study. Typically, the test began with the establishment of an ethylene flame and the procurement of any required samples. In order to change the samples meshes, entry into the test cell was necessary, but was deemed safe under the operating conditions of the laminar burner because of the controlled release
and immediate oxidation of the fuels involved. Upon retrieval of the samples involving ethylene only, the silane was introduced to the flame while the ethylene continued to burn. The order of fuel introduction was important because the ethylene flame stabilized the flame at the tube end. In the absence of the ethylene flame, the silane burned down into the injector because of the presence of oxidant inside the tube. After a stable dual fuel flame was established, the required samples were collected. In the tests that required a diluted ethylene flame, the nitrogen supply in shown in Figure 2.11 provided the diluent. After the introduction of the nitrogen, the flame was sampled again.

After sampling was completed, a sequence to purge the fuel lines similar to that undertaken in the ignition study began. First, the silane cylinder valve was closed and the majority of the silane lines were purged with argon through the water purge system. After that, the argon flowed through the silane line and out of the injector until the visible silane flame disappeared from the core of the ethylene flame. Then, the ethylene line underwent a similar purge procedure using nitrogen in place of the argon as indicated in Figure 2.11. Once the data acquisition and video recording ceased, the test was complete. Typically, the tubing supplying silane to the burner was carefully disassembled shortly thereafter to ensure all the silane had been purged from the system. Appendix B contains the formal test announcement and procedure for the final test involving nitrogen dilution.

### 2.2.6 Laminar Burner Test Matrix

The laminar burner study included six main tests. The first of these tests involved proof of the potential of the new burner and attempting to synthesize and capture
nanotubular structures. Test number two introduced the wire mesh sampling system for capturing particulates from the flame gases. The third test explored the dwell time of the wire mesh in both the ethylene and dual fuel ethylene and silane flames by simply passing the mesh through the flame. Test number four continued this exploration of the dwell time by testing both flames with a mesh pass through and a 10 second dwell time. The fifth test continued along similar lines by testing both flames at 6, 10, and 20 second dwell times. Also, the affect of height above the injector was tested in the fifth test. Each of the six dwell time and flame conditions was sampled at ½”, ¾” and 1” above the injector outlet. Finally, the sixth test added the effect of nitrogen diluent in the ethylene flame. In this test, samples were retrieved at ½” above the injector and at a dwell time of 6 seconds in both flames for no diluent, 50% of ethylene flow diluent, and 75% of ethylene flow diluent.

2.3 Characterization Procedure

To determine the concentration of nanotubular structures on each sample mesh, a field emission scanning electron microscope was used to capture images of the samples. Once a test was complete, each sample acquired a label describing the flame conditions used and then was placed in a wood block containing slots for each sample. While in transit to the Materials Characterization Laboratory, this block provided protection for the samples against contamination and other damages. Imaging of the samples began with removal of approximately a square centimeter piece of mesh for each flame condition of interest occurred. This small piece of mesh was placed on a sample stub using carbon tape with the side which faced the flame attached to the carbon tape itself. The side facing up, away from
the stub was then usually coated with iridium to prevent charging while in the microscope. At this point, microscopy analysis of the specimens was done using a Jeol 6700F field emission scanning electron microscope. Usually, this involved searching the specimen at various magnifications to locate structures of interest with the intention of capturing images of these structures. The samples produced in each test underwent this type of characterization analysis, except the products of the third laminar burner test which were analyzed using Raman spectroscopy in addition to the microscopy. Appendix C expands on the details of this characterization.
Chapter 3

Results and Discussion

3.1 Ignition Study Results

The ten tests of the ignition study provided useful information about the combustion behavior of SiH$_4$ in air and CO$_2$ environments. The first three tests provided vital information for the design of a robust, safe test rig and development of accompanying procedures to create silicon doped carbon nanotubes (Si-CNTs). This series of three tests offered the opportunity to sample multiple test rig arrangements along with variations of procedures and documentation of the test events. The next six tests investigated the reactivity of SiH$_4$ in a CO$_2$ environment under a variety of conditions to determine if CO$_2$ was a viable carbon source. Throughout these six tests, various ignitors, injectors, and heaters were used in an attempt to overcome the activation energy of the SiH$_4$ and CO$_2$ oxidation reaction. The final test combined the SiH$_4$ and air flame with an oxy-acetylene torch. This test provided the opportunity to observe the behavior of an alternative carbon source in the presence of the SiH$_4$/air flame. Table 3.1 summarizes the important findings of this and each of the other tests in the ignition study.
3.1.1 Silane Combustion Behavior

The use of SiH₄ as a silicon dopant source in a combustion synthesis process presented a challenge because of its pyrophoric nature. In a practical sense, this behavior meant that it would oxidize instantly upon mixing with any available oxidant in a potentially violent manner if not controlled. Consequently, extra effort was required to ensure safety at

Table 3.1: Summary of ignition study.

<table>
<thead>
<tr>
<th>Test</th>
<th>Reaction Tested</th>
<th>Result</th>
<th>Course of Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X, SiH₄/air</td>
<td>SiH₄/air flame</td>
<td>Removal of reactor windows</td>
</tr>
<tr>
<td>2</td>
<td>X, SiH₄/CO₂</td>
<td>No flame</td>
<td>Safety concerns result in test rig and procedural revision</td>
</tr>
<tr>
<td>3</td>
<td>X, SiH₄/air</td>
<td>SiH₄/air flame proved test rig and procedure revisions</td>
<td>Change CO₂ injector design to flood SiH₄ injector, preheat CO₂</td>
</tr>
<tr>
<td>4</td>
<td>X, SiH₄/air</td>
<td>No flame</td>
<td>Revise procedure to include purge of SiH₄ injector</td>
</tr>
<tr>
<td>5</td>
<td>X, CO₂</td>
<td>CO₂ extinguished SiH₄/air flame, Ni-Cr ignitor proven</td>
<td>Rerun test with preheated CO₂ using electric process heater</td>
</tr>
<tr>
<td>6</td>
<td>X, SiH₄/air</td>
<td>SiH₄/air flame only</td>
<td>Rerun test with CO₂ aimed at SiH₄/air flame</td>
</tr>
<tr>
<td>7</td>
<td>X, CO₂</td>
<td>CO₂ extinguished SiH₄/air flame</td>
<td>Change to concentric CO₂ injector design</td>
</tr>
<tr>
<td>8</td>
<td>X, CO₂</td>
<td>CO₂ extinguished SiH₄/air flame</td>
<td>Change to propane and cylinder CO₂ heater</td>
</tr>
<tr>
<td>9</td>
<td>X, CO₂</td>
<td>CO₂ extinguished SiH₄/air flame</td>
<td>SiH₄/CO₂ reactivity test conclusion</td>
</tr>
<tr>
<td>10</td>
<td>X, SiH₄/air</td>
<td>Combination of oxy-acetylene and SiH₄/air flames yielded no interesting results</td>
<td>Ignition study conclusion</td>
</tr>
</tbody>
</table>
every instant of a test. This extra effort came in the form of additional equipment and procedures, whose form took shape after the completion of the first two tests in the ignition study. In the first test, a steady turbulent flame, involving SiH₄ and air, was established using the nozzle described in Figure 2.3. From this, it was evident that the SiH₄ did indeed burn immediately upon mixing with air while, at the same time, producing large quantities of particulate silicon dioxide (SiO₂) or sand. The presence of this sand made observation of the flame difficult because the environment inside the reactor quickly became cloudy. As a result, the plexiglass windows in the reactor were removed after the completion of this test.

Also, in the process of completing this test, the need for several procedural changes became apparent. First, it was clear that every line and fitting would have to be pressure checked with argon or N₂ and Snoop after assembly to prevent leakage of SiH₄ which nearly always resulted in a flame and subsequent equipment damage. Second, a specific purge procedure was required to ensure that the entire system was void of SiH₄. Third, along those same lines, a fitting to permit the purge of the CGA 350 fitting connected to the SiH₄ cylinder would both help to guarantee a more thorough purge of the entire system along with preventing SiH₄ from remaining in the cylinder valve and regulator. Lastly, a more thorough documentation of the emergency procedures and equipment would further aid in preventing any injury to personnel.

Despite the success in the first test of establishing an air oxidized SiH₄ flame and the resulting improvements in equipment and procedures, a similar flame was not produced in the second ignition study test. Instead, the test was suspended prematurely for safety concerns. These concerns prompted the redesign of the test rig and further revisions to the experimental procedures. The result was the creation of the test announcement and pretest
checklist contained in Appendix A along with the new test rig shown in Figure 3.1. The test announcement addressed personnel, safety, and operational issues to further minimize safety hazards and optimize the test productivity. In addition, the pretest checklist insured that the test rig and all accompanying equipment were functioning properly prior to the start of any test.

Meanwhile, the new test rig provided mobility for transport in and out of the test cell while keeping much of the reactor support system assembled to further mitigate potential safety hazards associated with routine disassembly. Also, the previously described water purge system was added to the overall support system to prevent injury by controlling the release of purged SiH₄ into the surrounding environment. Along with this new test rig and
water purge system, a cart holding the controls and instrumentation was constructed, to further aid in the mobility of the experimental setup as a whole. The effectiveness of these improvements was shown in test three with a stable and safe SiH<sub>4</sub>/air flames along with some brittle, solid deposits depicted in Figure 3.2.

![Figure 3.2: Deposits from a SiH<sub>4</sub>/air flame.](image)

### 3.1.2 Silane/CO<sub>2</sub> Reactivity

After establishing a safe, robust method of conducting SiH<sub>4</sub> ignition study tests, tests were conducted to determine if CO<sub>2</sub> could actually oxidize SiH<sub>4</sub> under any conditions and
serve as a carbon source for creating carbon nanotubes. In an attempt to ignite SiH$_4$ and CO$_2$, a Ni-Cr wire ignitor and a pilot flame were added along with heating the CO$_2$ prior to entering the reactor. The method of heating CO$_2$ progressed from an electric process heater to a coil heated by a propane burner followed finally by the combination of the propane heated coil and an electric cylinder heater. At the same time, the CO$_2$ injector configuration progressed from a curved tube to a horizontally directed series of jets and then finally to a tube concentrically placed surrounding the SiH$_4$ injector. The details of both of these progressions can be found in Chapter 2.

Despite the variation of the injector design and CO$_2$ temperature, a SiH$_4$ flame oxidized by CO$_2$ was never observed. As a matter of fact, as indicated by Table 4.1, in every instance, the SiH$_4$ flame oxidized with air was extinguished upon introduction of CO$_2$ into the reactor. As a result, it appeared that CO$_2$ could not serve as an oxidizer for SiH$_4$ under practical circumstances.

### 3.1.3 Ignition Study Summary

The ignition study provided information in two vital areas. The first three tests offered a foundation for the design of a safe, reliable, and robust test rig along with the appropriate procedures to accommodate the pyrophoric nature of SiH$_4$. The following five tests explored the reactivity of SiH$_4$ with CO$_2$ with no avail, indicating that CO$_2$ would not serve as a carbon source when employing SiH$_4$ as the silicon source. These two facts provided the appropriate foundation for a more controlled test that would offer better
opportunity to collect the solid products of the oxidation of SiH₄ and an alternative carbon source: ethylene (C₂H₄).

3.2 Laminar Burner Test Results

Overall, six laminar burner tests were conducted to explore the combustion synthesis of silicon doped carbon nanotubes and develop an understanding of the important parameters affecting the yield of the process. The first three of these six tests mostly entailed familiarization with the laminar burner itself, the sampling system, and the characterization processes used to identify the solid products synthesized. Not only were these tests necessary for familiarization with the equipment, but also familiarization with the new ethylene (C₂H₄) carbon source. The latter three tests then actually explored the parameters involved in using the laminar burner to produce silicon doped carbon nanotubes. In particular, the parameters explored included the sampling height above the injector, the sampling mesh dwell time in the flame, and the level of N₂ dilution within the flame. Each of the three latter tests yielded structures of interest as seen in Table 3.2, which summarizes all six of the laminar burner tests.
3.2.1 Equipment Familiarization Tests

As mentioned, the first three tests using the laminar burner pertained mostly for familiarization with the equipment and procedures. This developed primarily in four different areas, including the combustion behavior of C$_2$H$_4$, the operation of the laminar

<table>
<thead>
<tr>
<th>Test</th>
<th>Purpose</th>
<th>Result</th>
<th>Course of Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Test functionality of laminar burner</td>
<td>Successful operation of laminar burner equipment</td>
<td>Implementation of new mesh sampling system</td>
</tr>
<tr>
<td>2</td>
<td>Test the wire mesh sampling system</td>
<td>Retrieval of carbon covered wire mesh</td>
<td>Install guide system to control position of sample mesh in flame</td>
</tr>
<tr>
<td>3</td>
<td>Retrieve two samples by pass through method</td>
<td>Retrieval of sparsely carbon coated wire mesh</td>
<td>Run test with both pass through and finite dwell times using a FeCl$_3$ catalyzed mesh</td>
</tr>
<tr>
<td>4</td>
<td>Retrieve four samples by passing mesh through flame and a 10 second dwell time</td>
<td>First record of creation of carbon nanotube</td>
<td>Repeat this test but vary the sampling height above the injector as well as the dwell time</td>
</tr>
<tr>
<td>5</td>
<td>Retrieve eighteen samples at 6, 10, and 20 second dwell times at ½”, ¾”, and 1” above the burner</td>
<td>High concentration of iron nanoneedles in the 6 second dwell, ½” above injector sample</td>
<td>At a dwell time of 6 seconds and ½” above the injector, add in the effect of a N$_2$ flame diluent</td>
</tr>
<tr>
<td>6</td>
<td>Retrieve eighteen samples at a 6 second dwell time at ½” above the burner in an undiluted, 50% diluted, and 75% diluted flame*</td>
<td>Multiple types of tubular structures of varying size as well as square tubular structures</td>
<td>End of current research</td>
</tr>
</tbody>
</table>

*N$_2$ is used to dilute the flame based on the flow rate of C$_2$H$_4$
burner, the effectiveness of the sampling system, and the characterization techniques available. It was necessary to acquire experience operating the laminar burner to create conditions conducive to nanotube formation. For instance, after the third test, the flow rates of SiH₄ and C₂H₄ were increased from 1.93 cm³/s to 3.85 cm³/s to prevent the burner from being disturbed by the surrounding environment. In addition, important issues such as the purge procedures developed in the ignition study were investigated during this portion of the laminar burner tests. These changes resulted in the flame shown in Figure 3.3 and the procedures presented in Appendix B.

Figure 3.3: A typical flame produced in the laminar flame burner.

The third important area in which experience was gained was the sampling system because it was a new addition to the experimental setup. Many important issues arose throughout these three tests that were vital to the quality of the samples collected. One such
issue pertained to the orientation of the sampling mesh when it entered the flame. The desired orientation was perpendicular to the flame and after the second test it was clear the guide shown in Figure 3.4 was necessary to maintain this orientation. At the same time, it became clear that the sampling system was not located close enough to the burner to pass the mesh through the flame, which, after repositioning, resulted in the sample system position shown in Figure 3.4. Finally, after the third test it was clear that some method of catalysis was necessary to develop nanotubular structures as the typical product retrieved up to that point was amorphous carbon as shown in Figure 3.5. The result was the development of the mesh catalysis technique involving ferric chloride presented in Chapter 2.

Figure 3.4: The guide used to maintain the orientation of the sampling mesh in the flame.
The final area in which experience was gained involved determining which of the different characterization techniques available were the most effective for identification of structures in the samples collected. Characterization involves both determination of the morphology of any nanostructures synthesized as well as their chemical composition. As far as morphology was concerned, both a regular scanning electron microscope (SEM) as well as a field emission scanning electron microscope (FESEM) were available. The image in Figure 3.5 was captured using the regular SEM, which was sufficient for nanostructures in the micron scale. However, after comparing this image in Figure 3.5 with those captured using the FESEM in the second laminar burner test, it was clear that the FESEM produced higher magnification.

Figure 3.5: Typical carbon product retrieved in the first three laminar burner tests shown at 12,000 times magnification.
quality high resolution images. On the other hand, the SEM provided quick, high quality images at lower resolutions. The SEM was also capable of energy dispersive x-ray spectroscopy (EDS) which quickly identified the elements present in any sample. After test three, however, it was discovered that both Raman and infrared spectroscopy were particularly useful in identifying the presence of nanotubes in any sample because of their characteristic excitation or ‘breathing’ modes which appear in those spectroscopy techniques. Appendix C contains additional information regarding Raman spectroscopy and its applications in identifying carbon nanotubes.

3.2.2 Si-CNT Production Tests

The last three tests in the laminar burner test series explored the parameters involved in the synthesis of Si-CNTs in a laminar diffusion flame. This exploration produced a wide variety of interesting structures. The first of these structures appeared in the fourth laminar burner test. Figures 3.6 and 3.7 display these interesting nanotubular structures formed after a 6 second dwell time in the combined C$_2$H$_4$ and SiH$_4$ flame. Their presence suggests a number of important observations. First, it confirms the potential of a laminar diffusion flame to create nanotubular structures. Second, this occurrence supports the notion that catalysts are necessary to support the synthesis of nanotubular structures [30]. Third, the nanotubular structures appeared to be on the order of tens of nanometers in diameter which corresponds to other observations of MWNTs [23]; however, this could not be confirmed during characterization. Their chemical composition could not be determined because of their low concentration in the overall sample, even though this grouping of nanotubular
structures was the highest local concentration on the entire sample. Other nanotubes were located, but in singular occurrences as seen in Figure 3.8.

Figure 3.6: Nanotubular structures synthesized in a SiH₄/C₂H₄ flame during a 6 second dwell time shown at 50,000 times magnification.
Figure 3.7: The same grouping of nanotubular structures as seen in Figure 3.6 at 100,000 times magnification.

Figure 3.8: Individual nanotubular structures synthesized in a SiH₄/C₂H₄ flame during a 6 second dwell time shown at 100,000 times magnification.
This lack of uniformity in the production of nanotubular structures may be a result of the structure of the diffusion flame. The chemical structure of the diffusion flame varies radially from the core out to the surrounding atmosphere because of the simultaneous diffusion of fuel species away from the flame core and oxidant species toward the flame core. As a result, there is a continuous variation of oxidant to fuel ratio leading to a variation in equivalence ratio, producing different concentrations of flame products depending on the radial location in the flame. This may prevent large scale nanotube production because of its dependence on the local flame chemistry. Also important is the catalyst concentration at any one position on the stainless steel mesh.

The next structure of interest appeared in laminar burner test five. As mentioned, laminar burner test five tested dwell times of 6, 10, and 20 seconds at heights above the injector of \(\frac{1}{2}\), \(\frac{3}{4}\), and 1” for both a \(\text{C}_2\text{H}_4\) and a \(\text{SiH}_4/\text{C}_2\text{H}_4\) flame. At \(\frac{1}{2}\)” above the injector for both a 6 and 10 second dwell time in the \(\text{SiH}_4/\text{C}_2\text{H}_4\) flame, iron nanoneedles appeared on the catalytic ferric chloride as shown in Figures 3.9 and Figure 3.10. Xu and Tse successfully synthesized these nanostructures in a flame environment in late 2006 so they are an interesting recent addition to the nanostructure community, but are not directly tied to this research [49].
Figure 3.9: Iron nanoneedles synthesized in a SiH₄/C₂H₄ flame at ½” above the injector over a 10 second dwell time magnified 25,000 times.

Figure 3.10: Iron nanoneedles synthesized in a SiH₄/C₂H₄ flame at ½” above the injector over a 10 second dwell time magnified 100,000 times.
The sixth laminar burner test, unlike the fifth, yielded many interesting tubular structures. As mentioned, this test involved the addition of an N₂ diluent to the C₂H₄ flow at volume flow rates equal to 50% and 75% of the C₂H₄ itself and then burning the C₂H₄ with the SiH₄. Also, a flame without diluent was investigated. Based on the findings of the previous tests, these flames were sampled at ½” above the injector over a dwell time of 6 seconds. The result included two distinct groups of tubular structures. First, a number of nanotubular structures were captured both in groups and single occurrences. Figure 3.11 displays an image of one of the singular nanotubular structures along with dimensions observed in a FESEM. Given these dimensions, this particular tube is most likely a MWNT; however, the exact chemical composition of the tubular structure is unknown since the issue of low concentration remains in this sample as it did in laminar burner test number four. The sample containing this tube just so happened to originate from a C₂H₄/SiH₄ flame with no diluent sampled in this series of tests where N₂ diluent was included. The same flame also created groups of nanotubular structures similar to those shown in Figure 3.11. Figure 3.12 shows one such grouping. Meanwhile, Figures 3.13 and 3.14 show another grouping of similar nanotubular structures that again appear to be MWNTs, but were still appearing in too low of a concentration to characterize on a chemical basis.
Figure 3.11: A single nanotubular structure captured in a FESEM at 120,000 times magnification formed in an undiluted C$_2$H$_4$/SiH$_4$ flame.

Figure 3.12: A group of nanotubular structures captured in a FESEM at 75,000 times magnification formed in an undiluted C$_2$H$_4$/SiH$_4$ flame.
Figure 3.13: Another group of nanotubular structures captured in a FESEM at 50,000 times magnification formed in an undiluted C$_2$H$_4$/SiH$_4$ flame.

Figure 3.14: The group of nanotubular structures in shown Figure 3.13 magnified 100,000 times.
The second group of structures created in the sixth laminar burner test consisted of rectangular shaped tubes. These structures appeared in two different sets of flame conditions. Those appearing in Figure 3.15 were produced in a flame diluted with N₂ flowing at half that of the C₂H₄, which was the only fuel present when this particular sample was retrieved. Figure 3.16 shows similar structures retrieved from a flame using both C₂H₄ and SiH₄ as fuels while being diluted at a rate equal to three quarters that of the C₂H₄ flow rate. The dwell time and sampling height above the injector remained 6 seconds and ½”, respectively, for both of these samples. As before, unfortunately, the concentration of these structures was also too low for chemical analysis of the bulk sample.

Figure 3.15: Rectangular tubular structures created in a C₂H₄ flame diluted with N₂ flowing at half the volume flow rate of the C₂H₄ shown at 2,200 times magnification.
3.2.3 Laminar Burner Tests Summary

Overall the laminar burner tests yielded two important results. First, the equipment familiarization tests demonstrated the ability of the laminar flame burner to create a controlled SiH₄/C₂H₄ flame that could be safely sampled in a manner that could later be characterized. Second, the Si-CNT production tests synthesized a variety of interesting structures both on the nanometer and micron scale in size. In most instances, these interesting structures appeared on samples taken over a 6 second dwell time at ½” above the injector in undiluted SiH₄/C₂H₄ flames. As a result, the potential of the laminar diffusion flame method of nanotubular synthesis was established. However, whether or not it has

Figure 3.16: Rectangular tubular structures created in a C₂H₄ and SiH₄ flame diluted with N₂ flowing at three quarters the volume flow rate of the C₂H₄ shown at 22,000 times magnification.
proven its potential to synthesize Si-CNTs has yet to be determined. Nonetheless, it has combined a silicon and carbon source in the same flame to produce nanotubular structures and has allowed the investigation of the interaction between these two reacting gases.
Chapter 4

Conclusions and Future Work Recommendations

4.1 Overall Summary and Conclusions

Two series of experimental tests were conducted to determine the reactivity of silane with carbon dioxide and to synthesize Si-CNTs through a flame synthesis procedure. The first series of tests, or the ignition study, consisted of ten tests conducted in three parts. The first three tests addressed the combustion behavior of silane gas. Throughout these tests, test rig configuration and procedures were varied to ensure safe combustion of the silane gas. The next six tests addressed the reactivity of carbon dioxide with silane. Here, different carbon dioxide injectors, ignitors, and heaters were used in an attempt to overcome the activation energy associated with a carbon dioxide oxidized silane flame. Finally, the last test combined a silane flame with that produced by an oxy-acetylene torch. Here, the solid products of the flame were observed but not characterized.

The second series of tests involved testing of a laminar burner, using acetylene as the carbon source, for Si-CNT synthesis. This series of tests can also be divided into two parts. The first three tests involved familiarization with the laminar burner itself as well as the required sampling techniques. Here, the ferric chloride catalysis, operation, and characterization techniques were developed. The following three tests composed the production phase of the laminar burner tests. Here, parameters such as flame sampling dwell time, sampling height above the injector, and fuel diluent levels were investigated. From these and the ignition study tests, conclusions can be drawn in two specific areas.
The first several conclusions pertain to the combustion chemistry observed throughout these two series of tests. First, it is clear that SiH₄ can be used in a safe manner as a combustible silicon source in spite of its hazardous pyrophoric nature. Second, the series of six tests indicate that SiH₄ does not react with CO₂ under practical conditions. As a result, it cannot serve as a carbon source for synthesis of Si-CNTs. Third, C₂H₄ in the presence of SiH₄ may have the potential to form Si-CNTs. Finally, synthesis does not appear to be possible without a transition metal catalyst such as iron, nickel, or cobalt to support the growth of nanotubular structures. Although the simple FeCl₃ deposition method did catalyze the growth of a limited number of nanotubes, it did not support the desired large scale growth.

The other important conclusions from this research pertain to the synthesis method. As demonstrated, a diffusion flame composed of equal proportions of SiH₄ and C₂H₄ can synthesize nanotubular structures. In the tests conducted, a sampling height of ½” above the injectors yielded the highest concentration of nanotubular structures using a 6 second dwell time. Other dwell times and sampling heights did not yield any interesting nanotubular structures. Likewise, the addition of a flame diluent did not promote the additional growth of nanotubular structures.

4.2 Implications

These conclusions present a number of implications to the future of related Si-CNT research. First, diffusion flames provide a solid platform for the investigation of the flame chemistry required to synthesize Si-CNTs because of the radially varying flame chemistry. At
the same time, though, their inherent structure may prevent large scale production of nanotubular structures because of the need for specific conditions to create the nanotubular structures. This fact also raises doubt about the diffusion flame’s potential to create chemically homogeneous Si-CNTs on a large scale. Second, the low nanotube yield prevents accurate characterization of the chemical structure of the nanotubes synthesized stemming from the need to locate and separate them from other materials simultaneously synthesized. Finally, this method involves the use of the dangerous, although manageable, silane gas which still poses a serious safety hazard.

4.3 Future Work Recommendations

The implications of the current research pose three distinct problems for the future Si-CNT synthesis research. First, the exact morphology and chemical structure of the products of the current research are unknown. Second, if the nanotubes already synthesized do not contain a silicon to carbon ratio of zero, methods of incorporating silicon into CNTs must be further investigated. Third, the nanotube yield is low for any given test, amplifying the difficulties associated with characterization. Each of these issues requires its own research plan.

Addressing the first issue, the products from the current research must be more fully characterized using a transmission electron microscope for a more thorough description of their morphology (i.e. single-walled or multi-walled). Then, they should undergo electron energy loss spectroscopy analysis to determine their chemical structure. If the characterization is successful, the outcome will aid in selecting the appropriate course for the
second issue of silicon to carbon ratio in the nanotubular structures. Most likely this course will follow one of two directions depending upon the ratio of silicon to carbon in the nanotubular structures.

If this ratio is equal to zero, the following direction for the research may be appropriate. As a first step, the current test rig and laminar burner should be employed for further exploration into the chemistry of nanotube formation. This exploration should begin with the construction of a shroud to protect the flame from environmental disturbances. Then, at a sampling height of ½”, over a 6 second dwell time, the flame should be sampled for a practical range of SiH₄ to C₂H₄ ratio. If this experiment produces more nanotubular structures with a silicon to carbon ratio of zero, the experiment should be repeated using an alternate silicon source such as tetramethylsilane or tetraphenylsilane. These silicon sources actually contain carbon/silicon bonds, which may promote the formation of nanotubes with a nonzero silicon to carbon ratio. At this point, if this ratio is still zero, it may be necessary to change to a premixed flame setup using tetramethylsilane or tetraphenylsilane as the silicon sources. The premixed structure will allow better control of the flame chemistry, which can then be explored by varying the equivalence ratio. Preferably, this flame would be at least shrouded as before from the surrounding environment if not operated in a vacuum to prevent surface reactions with the surrounding environment and preserve the nanotubular structures. Also, a means of separating any nanoparticles that remain in the product gas stream should be placed downstream of the flame. This device could range in complexity from a piece of filter paper to a magnetic field for use with ferromagnetic catalysts.

On the other hand if the nanotubular silicon to carbon ratio is nonzero at the outset or becomes nonzero at any time, a slightly different research direction may be appropriate.
In this case, a premixed flame may be the best next step. Of course, SiH\textsubscript{4} cannot be premixed; however, the premixed C\textsubscript{2}H\textsubscript{4} could be combined with the SiH\textsubscript{4} diffusion flame. This premixed flame could then be used to optimize the conditions for nanotube synthesis as well as to establish the practical limits of the silicon to carbon ratio within the nanotubular structures synthesized through variation of the equivalence ratio and SiH\textsubscript{4} to C\textsubscript{2}H\textsubscript{4} ratio, respectively. This method would also accomplish a similar goal with tetramethylsilane or tetraphenylsilane. At this point, careful characterization of the nanotubular structures formed and extensive investigation of the corresponding flame conditions would yield information about the Si-CNT nanotube synthesis process.

Such a progression from a diffusion flame to an optimized premixed flame could address the third issue of low nanotube yield. Changes in the catalysis method may also serve to further improve the nanotube yield. Two potential methods show promise for accomplishing such an improvement. First, sputtering the currently employed stainless steel mesh with a transition metal, such as iron, in a manner similar to Vander Wal et. al. [18] may serve better than the FeCl\textsubscript{3} currently in use. Special attention must be given to the fact that the surface of the substrate should not be completely covered with the catalyzing transition metal, but instead partially covered, preferably with particles on the order of 10 to 20 nm in diameter. This would provide the optimum catalyst particle for nanotube formation. A second method employs an aerosol or vapor catalyst introduced into the C\textsubscript{2}H\textsubscript{4} flow. Common metal compounds such as iron pentacarbonyl or nickel nitrate can either be flowed directly into the C\textsubscript{2}H\textsubscript{4} or nebulized from a liquid and injected into the flow [19]. These samples can then be collected from the flow using a filter paper and characterized. If the
catalyst metal is ferromagnetic, a magnetic field may serve as a means to extract the nanotubes from the product gas flow.
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Appendix A

Ignition Study Experimental Test Procedures

Title: Silane Ignition Study 7

Date: 7/26/06, 9:00 am

Location: ARL Steam Plant-Test Cell 2

Personnel:
1. Test Director: D. E. Marteeny
2. Supporting Engineers: T.J. Cawley, W. J. Holmberg
3. Mechanical: C. E. Plank
4. Instrumentation/Electrical: B.W. Foltz
5. Observers: C.E. Plank, B.W. Foltz, C.F. Ginter, or B.L. Sones

Objective: Determine if CO$_2$ will sustain a silane oxidation reaction using an air oxidized pilot flame and preheated CO2.

Procedure

Preliminary
1. Complete Ignition Study Pretest Checklist
2. Discuss experimental procedure with those present for test
3. Discuss emergency procedures
4. Conduct dry run with argon (valve 7) in place of silane.
5. Secure gate outside test cell
6. Announce test
7. Light propane torch
8. Close interior test cell doors
9. Open silane cylinder valve
10. Start data collection system

Main
1. Begin recording picture
2. Begin saving data
3. Turn ignitor on
4. Open valve 6 (compressed air) to flood chamber for 30 seconds
5. Close valve 6
6. Open valve 2 (silane!!)-verify by pressure that it is flowing
7. Open valve 5 (silane into reactor!!)
8. Observe to verify establishment of a flame-allow to burn for 5 seconds
9. Open valve 4 (CO2!!)-track pressure to verify CO₂ is flowing
10. Turn process heater on (be certain that CO₂ is flowing first!!)
11. Turn ignitor off
12. Observe temperatures after CO₂ has begun to flow, record results
13. Turn process heater off
14. Close valve 4 (CO2)
15. Repeat 1-14 (excluding 6, 10, 14, and 15 except when using process heater) as necessary
16. Complete post procedure (Keep valves 2 and 5 open!!)

Post
1. Turn ignitor on
2. Stop recording data
3. Open valve 1 (argon) to purge system
4. Manually close silane cylinder valve (wear proper safety equipment!)
5. Open valve 3 to purge under H₂O
6. Allow argon to purge until smoke disappears from H₂O scrubber and reactor (if necessary open valve 7).
7. Turn ignitor off
8. Close argon cylinder valve
9. Allow system to bleed off
10. Close all valves
11. Stop recording picture
12. Extinguish propane torch
13. Remove and clean nozzle

**Instrumentation**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Number</th>
<th>Position</th>
<th>Sample Rate</th>
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</thead>
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</tr>
<tr>
<td>Thermocouple</td>
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<td>2 1/16” above nozzle</td>
<td>0.5 samples/s</td>
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<tr>
<td>Pressure Transducer</td>
<td>3</td>
<td>Silane line pressure</td>
<td>0.5 samples/s</td>
</tr>
</tbody>
</table>
Safety Plan

Safety Issues:
1. Pyrophoric nature of silane
2. Unknown contents of product
3. Asphyxiation hazard (Ar, CO₂)
4. Electrocution hazard from nichrome ignitor

Safety Equipment
1. Latex Gloves (when handling product)
2. Welding Gloves (where necessary)
3. Lab Coat
4. Face Shield
5. Dust Mask (when handling product)

Emergency Procedure (assuming silane is flowing)
1. Turn ignitor on
2. Open valve 1 (argon) to purge system
3. Manually close silane cylinder valve (wear proper safety equipment!)
4. Open valve 3 to purge under H₂O
5. Allow argon to purge until smoke disappears from H₂O scrubber and reactor (if necessary open valve 7).
6. Turn ignitor off
7. Close argon cylinder valve
8. Allow system to bleed off
9. Close all valves

Injury Threat Minimization
1. Electrical: Ignitor and reactor will be grounded so as to prevent electric shock. Also, all personnel will not be in the vicinity of the reactor when ignitor is in operation.
2. Thermal/Chemical: Silane will not be introduced to test rig until after all connections are assured to be tight. Then, all personnel will be kept away from the test rig while silane is contained within it. If the situation should arise that the Test Director feels someone should enter the test cell, all silane will be flared off and the Roto-clone system will be used to ventilate the test cell. The personnel will also employ the protective equipment listed above.
**Ignition Study Pre-test Checklist**

___ 1. With valves 1, 2, 3, 5, and 7 shut, open argon cylinder and set regulator to 500 psi.

___ 2. Open valve 1 to assure it is working properly.

___ 3. Open valve 2 to assure it is working properly.


___ 5. Loosen nut on argon cylinder and allow pressure to drain to zero.

___ 6. Check pressure on high side of silane regulator, is it still 500 psi?

___ 7. Reconnect argon cylinder, close regulator and valve 1, open valve 7.

___ 8. Adjust silane regulator to 100 psig.

___ 9. Snoop this section of line 1 up to valves 3 and 5 to check for leaks.

___ 10. Open valve 5 to assure it is working properly.

___ 11. Snoop remainder of line 1 to check for leaks.


___ 13. Open valve 3 to assure it is working properly.

___ 14. Snoop line 2 to check for leaks and verify that water purge system is working properly.

___ 15. Readjust silane regulator to 40 psig.


___ 17. Be sure silane cylinder is closed and loosen nut to release pressure.

___ 18. Retighten silane nut.

___ 19. Open valve 1 and snoop silane nut once more.

___ 20. Open valves 2 and 3, readjust argon regulator to 50 psig.

___ 21. Close valves 1, 2, and 3.
22. Open CO2 cylinder valve.
23. Set CO2 pressure to 40 psig.
24. Open valve 4 to verify it is working properly.
25. Snoop line 3 fittings to check for leaks.
26. Open valve 6 to ensure it is working properly.
27. Close all valves.

Initialed: ____________  Date: ____________  Time: ____________
Appendix B

Laminar Burner Experimental Test Procedure

Title: Si-C NT Laminar Burner 6

Date: Thursday, November 9, 2007 9am (tentative)

Location: ARL Steam Plant-Turbine Test Cell

Personnel:
1. Test Director: D. E. Marteeny
2. Supporting Engineers: T.J. Cawley, W. J. Holmberg, T. A. Litzinger
3. Mechanical: C. E. Plank
4. Instrumentation/Electrical: B.W. Foltz
5. Observers: C.E. Plank, B.W. Foltz, C.F. Ginter, B.L. Sones, or W.L. Witherite

Objective: Retrieve 18 samples using iron catalyzed stainless steel mesh:
1. Ethylene alone, 6 sec., ½” (3 samples)
2. Ethylene alone, 6 sec., 50% (fuel) diluent flow rate (3 samples)
3. Ethylene alone, 6 sec. 100% (fuel) diluent flow rate (3 samples)
4. Ethylene and Silane, 6 sec., ½” (3 samples)
5. Ethylene and Silane, 6 sec. 50% (fuel) diluent flow rate (3 samples)
6. Ethylene and Silane, 6 sec. 100% (fuel) diluent flow rate (3 samples)

Procedure

Preliminary
1. Complete Laminar Burner Pretest Checklist
2. Discuss experimental procedure with those present for test
3. Discuss emergency procedures
4. Secure gate outside test cell
5. Announce test
6. Light propane torch
7. Open ethylene and silane cylinder valves
8. Close interior test cell doors
9. Start data collection system

Main
1. Begin recording picture
2. Begin saving data
3. Open valve 13 (overhead compressed air) to start air flow
4. Insert and switch on ignitor
5. Open valve 7 (ethylene)-verify by pressure that it is flowing
6. Upon establishing flame, turn off ignitor
7. Retract ignitor
8. Once stable flame is established, retrieve sample
9. Change sample mesh
10. Repeat for 2 additional samples
11. Open valve 17 (have valve 15 adjusted for 50% flow rate)
12. Once stable flame is established, retrieve sample
13. Change sample mesh
14. Repeat for 2 additional samples
15. Adjust valve 15 for 100% flow rate
16. Once stable flame is established, retrieve sample
17. Change sample mesh
18. Repeat for 2 additional samples
19. Close valve 16
20. Open valves 3 and 5 (silane!!!), and verify flow by pressure increase
21. Once stable flame is established, retrieve sample
22. Repeat for 2 additional samples
23. Adjust valve 15 for 50% flow rate
24. Once stable flame is established, retrieve sample
25. Change sample mesh
26. Repeat for 2 additional samples
27. Adjust valve 15 for 100% flow rate
28. Once stable flame is established, retrieve sample
29. Change sample mesh
30. Repeat for 2 additional samples
31. Close valve 16
32. Open valve 1
33. Close silane cylinder valve (Wear proper protective equipment!!)
34. Open valve 4
35. Purge until flame has extinguished over H2O scrubber
36. Close valve 4
37. Close valve 7
38. Purge until silane flame has extinguished, but ethylene flame remains.
39. Change sampling system position from pass through to dwell
40. Repeat 8-19 for additional dwell time samples
41. Repeat 8-20 for ¾”, and 1” positions above injector
42. Close all valves
43. Complete post procedure

Post
1. Turn ignitor on
2. Stop recording data
3. Manually close silane cylinder valve (if not already closed)
4. Open valve 2 (argon) to purge system
5. Open valve 4 to purge under $\text{H}_2\text{O}$
6. Allow argon to purge until smoke disappears from $\text{H}_2\text{O}$ scrubber and reactor.
7. Close valve 4
8. Open valve 5
9. Open valve 7
10. Allow system to bleed off
11. Close all valves
12. Stop recording picture
13. Close Nitrogen cylinder valve
14. Extinguish propane torch

**Instrumentation**

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<td>0.5 samples/s</td>
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<tr>
<td>Pressure Transducer</td>
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<tr>
<td>Pressure Transducer</td>
<td>3</td>
<td>Silane line pressure</td>
<td>0.5 samples/s</td>
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</tbody>
</table>

**Safety Plan**

**Safety Issues:**
1. Pyrophoric nature of silane
2. Unknown contents of product
3. Asphyxiation hazard ($\text{Ar,N}_2$)
4. Electrocution/burn hazard from aviation ignitor
5. Explosion/Burn risk from presence of ethylene flame

**Safety Equipment**
1. Latex Gloves (when handling product)
2. Welding Gloves (where necessary)
3. Lab Coat
4. Face Shield
5. Dust Mask (when handling product)

**Emergency Procedure (assuming silane is flowing)**
1. Close all valves
2. Turn ignitor on (reinsert into flame if not already there)
3. Manually close silane cylinder valve (wear proper safety equipment!)
4. Open valve 2 (argon) to purge system
5. Open valve 4 to purge under $\text{H}_2\text{O}$
6. Allow argon to purge until smoke disappears from $\text{H}_2\text{O}$ scrubber and reactor
(if necessary open valve 7).
7. Close valve 4
8. Open valve 5
9. Open argon cylinder to purge ethylene line
10. Open valve 7
11. Purge until flame is extinguished
96

12. Close valve 2
13. Close valve 7
14. Allow system to bleed off
15. Close all valves

Injury Threat Minimization
1. **Electrical:** Ignitor and reactor will be grounded so as to prevent electric shock. Also, all personnel will not be in the vicinity of the reactor when ignitor is in operation.
2. **Thermal/Chemical:** Silane or ethylene will not be introduced to test rig until after all connections are assured to be tight. Then, all personnel will be kept away from the test rig while silane is flowing. If the situation should arise that the Test Director feels someone should enter the test cell, silane flow will cease and the Roto-clone system will be used to ventilate the test cell. The personnel will also employ the protective equipment listed above.
3. **Asphyxiation:** Roto-clone system will be used to evacuate the test cell before any person is allowed to enter it.
Laminar Burner Pre-test Checklist

____ 1. With all valves and silane cylinder valve shut as well as the burner capped, open argon cylinder attached to silane supply.

____ 2. Open valve 2.

____ 3. Open valve 3 to ensure it is working properly.

____ 4. Snoop this section of line 1 up to valves 4 and 5 to check for leaks.

____ 5. Open valve 5 to assure it is working properly.

____ 6. Snoop remainder of line 1 to check for leaks.

____ 7. Close valve 5.

____ 8. Set valve 6 to ensure the correct flow rate.

____ 9. Open valve 4 to assure it is working properly.

____ 10. Snoop line 5 to check for leaks and verify that water purge system is working properly.

____ 11. Adjust silane regulator to 25 psig.

____ 12. Close valve 2 allowing pressure to decrease to 0 psig.

____ 13. Open valve 1 to assure it is working properly.

____ 14. Set argon regulator to 50 psig.

____ 15. Close valves 1, 3, and 4.

____ 16. Check to make sure valve 11 is closed and open argon cylinder valve.

____ 17. Set nitrogen for ethylene purge to 50 psig.

____ 18. Set valve 8 to ensure the correct flow rate.

____ 19. Snoop line 2 fittings to check for leaks.

____ 20. Close nitrogen cylinder valve and open valve 11.
21. Open valve 14 (over head shop air) to ensure it is working properly and set regulator to 100 psig.

22. Set valve 9 to 1.5 turns to ensure the correct flow rate.

23. Close all valves, except valves 11, 12 and metering valves 6, 8, and 9.

24. Open argon and nitrogen cylinder valves.

25. Remove cap from burner.

Initialed: ____________  Date: ____________  Time: ____________
Appendix C

Raman Spectroscopy Analysis Investigation

C.1 Introduction

Since the purpose of this entire experimental exercise was to create silicon doped carbon nanotubes, it was necessary to not only visually confirm the presence of the nanotube phase in the combustion products, but also required was information about the chemical makeup of the nanotubes. Two particular characteristics of the combustion product specimens made this task a particularly difficult one. First, as seen in the images produced in the microscopy analysis, the typical structure size in any single image ranged from 10 nm to 10 μm. Then, to further complicate matters, the structures of interest (nanotubes) always appeared with other structures or solid phases of unknown chemical composition. Consequently, isolating a single tube for chemical characterization became a challenge at best. Fortunately, though, Raman spectroscopy, a nondestructive spectroscopy technique, can detect nanotube presence in a specimen despite impurities within the specimen.

Raman spectroscopy uses electromagnetic radiation to gather information about a material’s chemical composition. Usually, a laser producing electromagnetic radiation near the visible portion of the spectrum impacts a Raman active specimen [C.1]. For a material to be Raman active, its molecules must possess the ability to polarize under electromagnetic radiation [C.1]. Fortunately, for the purposes of this investigation, carbon possesses this ability producing first order Raman shifts at wavenumbers of 1360 cm$^{-1}$ (D peak) and 1580
cm\(^{-1}\) (G peak) and second order Raman shifts at 2730 cm\(^{-1}\) (G' peak) according to DiLeo et. al. [C.2]. This polarizability produces a higher energy vibratory mode within the molecule known as a phonon [C.1]. This phonon then alters the wavelength and frequency of the photon which induces it because it requires energy from the photon to sustain itself. The term for this phenomenon is inelastic or Raman scattering of light and it produces a Raman shift [C.1]. By intercepting the light that reflects from the sample and filtering out the elastically scattered light (from the known laser source), detection of the inelastically scattered photons is possible as their frequency and wavelength is different from the source laser light [C.1]. This process typically involves an optical microscope to focus the laser beam on the specimen, a monochromator to eliminate outside light, and a CCD camera to intercept the scattered light and change it to an electronic signal [C.1].

As it turns out, Raman spectroscopy is particularly useful in this exercise because of its special ability to identify tubular nanostructures. Depending on the type, single or multi-wall, and the grouping, single or bundled, nanotubes produce a characteristic Raman shift that is unique only to them, say Rao et. al. [C.3]. This phenomenon is due to resonance in the tubular structure itself, which produces both a tangential and a radial vibrational mode [C.3]. With an incident light wavelength of 514.5 nm, the radial excitation band appears at a wavenumber of 195 cm\(^{-1}\) for a single, single-walled carbon nanotube and 186 cm\(^{-1}\) for a bundled, single walled carbon nanotube [C.3]. At the same time, the tangential excitations appear at 1600 cm\(^{-1}\) for both single and bundled, single-walled carbon nanotubes [C.3] Using these facts, it may be possible to detect nanotube presence within a specimen, their concentration, and possibly their chemical composition.
C.2 Experimental

To better understand Raman spectroscopy with respect to this particular application, it was necessary to analyze a portion of the substances thought to exist within the combustion products by themselves as well as in solid solution to find out if it could actually detect carbon nanotubes and indicate their relative concentration. Of course, this required acquisition of some of the constituent substances in their pure form. Fortunately, high purity multi-walled carbon nanotubes (MWNTs) were commercially available from Sigma-Aldrich as were graphite and silicon dioxide. Specimens of each of these substances were prepared along with a specimen of a 9.09 wt% solid solution of MWNTs in graphite.

After preparation, analysis of each specimen occurred. A WiTec CRM200 system completed the analysis using a 100 times magnification lens and a 514 nm wavelength Melles-Griot laser to produce a 325 nm spot. Reflected light passed through a diffraction filter with 600 lines per millimeter and then struck a 1024 pixel, 1 dimensional CCD camera. Each gathered spectrum was an average of 10 individual spectra resulting from 10 second integrations producing a 100 second sampling time for each spectra. Each specimen experienced this 10 times. Then, using the concept of peak ratio comparison developed by DiLeo et. al., a prediction of the purity of the MWNT/graphite solution was calculated and compared to a correlation set forth by DiLeo et. al. Specifically, this purity prediction compared the intensity of the second order G’ peak to the first order D peak [C.2]. Using this ratio, Equation C.1 predicted the purity. This equation corresponds to the correlation published by DiLeo et. al. [C.2]. In addition to this calculation, acquisition of the average, observed peak ratio for graphite and MWNTs took place.
\[ \text{Purity} = \left( \frac{1}{0.021} \right) \ln \left( \frac{G'/D}{0.31} \right) \]  

(C.1)

**C.3 Results and Discussion**

In completing this investigation, the first results were, of course, the spectra for each of the substances analyzed. Figure C.1 shows the Raman shift spectrum of graphite. Here, it is important to note the presence of four peaks, starting on the left with the Rayleigh scattering peak and then progressing to the right through the D, G, and G’ peaks. This situation of a large G to D peak intensity ratio is typical of graphite. As the data in Table C.1 indicates, the average graphite G to D peak ratio for the samples collected was 5.66. In future studies of the laminar burner products, this information will be extremely helpful in sensing the presence of the graphite solid carbon phase. A similar study of the MWNTs produced the spectrum in Figure C.2 along with the data presented in Table C.2. As seen in Figure C.2, the G to D peak intensity ratio is less than one producing an average of 0.851 over the ten samples. Although this ratio is much closer to unity, it is still useful in identifying the presence of MWNTs in the laminar burner products. Finally, Figure C.3 displays the silicon dioxide spectrum. Given the peaks present in this spectrum, a peak ratio study was not completed as the spectrum itself provided enough information to sense the presence of silicon dioxide in a laminar burner products specimen.
Table C.1. The graphite G to D peak ratio data.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Peak</th>
<th>Wavenumber (1/cm)</th>
<th>Intensity (CCD cts.)</th>
<th>Ratio</th>
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<td>1</td>
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<td>1361.2</td>
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<td>G</td>
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<td>G</td>
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<td>1041</td>
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Figure C.1. A sample graphite Raman shift spectrum.
Figure C.2. A sample carbon nanotube Raman shift spectrum.

Table C.2. The carbon nanotube G to D peak ratio data.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Peak</th>
<th>Wavenumber (1/cm)</th>
<th>Intensity (CCD cts.)</th>
<th>Ratio</th>
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<td>D</td>
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<td>1.01</td>
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<td>364.3</td>
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<td>0.866</td>
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<td></td>
<td>G</td>
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<td>335.7</td>
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</table>
Finally, the last result of this investigation was that of the 9.09 wt% MWNT/graphite mixture and Raman’s ability to detect carbon nanotubes in solid solution. In this instance, based on the carbon nanotube spectra and the findings of DiLeo et al., the ratio of the second order peak G’ to the first order D peak provided a more pronounced and accurate sensing of carbon nanotube presence in a solid solution. Much of this is thanks to the more pronounced difference in peak intensity between the G’ and D peaks in the carbon nanotube spectrum as seen in Figure C.2. Table C.3 shows the peak ratios and predicted purity calculated using Equation C.1 for the MWNT/graphite solid solution spectra captured. Then, Figure C.4 displays these results along with a continuous plot of Equation C.1 for comparison.
Table C.3. Data produced in the 9.09 wt% graphite/MWNT solid solution purity test.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>D</th>
<th>G</th>
<th>G'</th>
<th>G'/D</th>
<th>Predicted Purity</th>
</tr>
</thead>
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<td>1</td>
<td>211.7</td>
<td>755.2</td>
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<td>1.774</td>
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<td>2</td>
<td>190.7</td>
<td>584.8</td>
<td>201.7</td>
<td>1.058</td>
<td>58.44</td>
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<tr>
<td>3</td>
<td>86.7</td>
<td>627.4</td>
<td>180.9</td>
<td>2.087</td>
<td>90.79</td>
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<tr>
<td>4</td>
<td>25.1</td>
<td>113</td>
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<td>1.375</td>
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<td>5</td>
<td>30.3</td>
<td>120.6</td>
<td>36.2</td>
<td>1.195</td>
<td>64.24</td>
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<td>8</td>
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<td>852.1</td>
<td>301.8</td>
<td>1.463</td>
<td>73.89</td>
</tr>
</tbody>
</table>

Figure C.4 The results of the purity test conducted on a 9.09 wt% graphite/MWNT solid solution using Raman spectroscopy and the correlation in Equation C.1.

Of course, the experimental data lie on the continuous plot of the DiLeo et al. correlation (Equation C.1), but there is considerable spread in the data. This most likely indicates that the Raman spectroscopy technique focuses on a local concentration and that local concentration changes from one portion to another within the sample. However, the average measured purity was 76.03% as opposed to the actual 9.09 wt% for the bulk measurement. This produced a 736% difference, which is totally unacceptable, however, because the length scales of an individual nanotube are several orders of magnitude less than
the bulk mixture and even the laser spot size; this may be an inaccurate comparison. If that is indeed the case, Raman spectroscopy could still serve to sense the presence of nanotubes and detect a local concentration.

C.4 Conclusion

Overall, this investigation proved that Raman spectroscopy senses the presence of carbon nanotubes in a carbon solid solution. However, it brought to light the limitations of Raman spectroscopy in situations where it is required to determine the bulk purity of a mixture containing nanotubular structures. In these particular situations, Raman most likely indicates the local nanotube concentration but with an unknown accuracy. Therefore, caution must be exercised in using Raman spectroscopy in this application. In addition, this investigation produced an average G to D peak intensity ratio for graphite of 5.66 and for multi-walled carbon nanotubes, a G to D peak intensity ratio of 0.851. As important as these values are the spectra from which they originated for these materials along with that of silicon dioxide are equally as important. These spectra along with the additional observations will aid using Raman spectroscopy in identifying structures in the laminar burner combustion products.

Works Cited

