Title
Towards improved spinnability of chemical vapor deposition generated multi-walled carbon nanotubes

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Towards Improved Spinnability of Chemical Vapor Deposition Generated Multi-Walled Carbon Nanotubes

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

in

Materials Science and Engineering

by

Gregg Sturdivant Burke McKee

Committee in charge:
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Professor Sungho Jin
Professor John Kosmatka
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2008
The Dissertation of Gregg Sturdivant Burke McKee is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2008
Dedication

For Helen, whose faith and confidence in my ability to complete this dissertation remained strong even after my own failed.
# Table of Contents

Signature Page ................................................................................................................. iii  
Dedication ........................................................................................................................ iv  
Table of Contents ............................................................................................................. v  
List of Abbreviations ..................................................................................................... viii  
List of Figures ................................................................................................................... x  
List of Tables ................................................................................................................. xiv  
Acknowledgements ......................................................................................................... xv  
Vita ....................................................................................................................................... xvii  
Abstract of the Dissertation ......................................................................................... xviii  

1. Introduction ................................................................................................................. 1  
   1.1 The Forms of Carbon ........................................................................................ 3  
      1.1.1 Carbon Black ............................................................................................ 4  
      1.1.2 Glassy (Vitreous) Carbon ......................................................................... 5  
      1.1.3 Amorphous Carbon (a-C) ......................................................................... 6  
      1.1.4 Diamond ................................................................................................... 7  
      1.1.5 Graphite .................................................................................................... 7  
      1.1.6 Carbon Fibers ............................................................................................ 9  
      1.1.7 Graphite Whiskers .................................................................................. 13  
      1.1.8 Fullerenes ................................................................................................ 16  
      1.1.9 Carbon Nanotubes .................................................................................. 19  
         1.1.9.1 Carbon Nanotubes: General .............................................................. 19  
         1.1.9.2 Carbon Nanotubes: Properties and Applications ............................ 21  
         1.1.9.3 Carbon Nanotubes: Structure .......................................................... 25  
         1.1.9.4 Carbon Nanotubes: Growth Mechanisms ....................................... 31  
         1.1.9.5 Carbon Nanotubes: Synthesis Methods ........................................... 34  
            1.1.9.5.1 Arc Discharge .............................................................................. 35  
            1.1.9.5.2 Laser Ablation ............................................................................ 37  
            1.1.9.5.3 Chemical Vapor Deposition (CVD) .......................................... 38  
            1.1.9.5.4 High Pressure Carbon Monoxide (HiPCO) .............................. 39  
      1.2 References ....................................................................................................... 41  

2. Background ............................................................................................................... 49  
   2.1 Characterization .............................................................................................. 49  
      2.1.1 Microscopy ............................................................................................. 50  
      2.1.2 Thermo-Gravimetric Analysis/Temperature Programmed Oxidation ... 51  
      2.1.3 Raman Spectroscopy .............................................................................. 53  
      2.1.4 Other Characterization Techniques ........................................................ 55  
   2.2 Refinement ...................................................................................................... 55  
   2.3 Nanotube Reinforced Composites .................................................................. 56  
      2.3.1 Unaligned Composites ............................................................................ 58  
         2.3.1.1 Unaligned Polymer Matrix Composites ......................................... 58  
         2.3.1.2 Unaligned Metal Matrix Composites ............................................. 60  
         2.3.1.3 Unaligned Ceramic Matrix Composites ........................................... 60  
      2.3.2 Aligned Composites ................................................................................ 61  
      2.3.2.1 Aligned Polymer Matrix Composites ............................................... 62  
      2.3.2.2 Aligned Metal Matrix Composites .................................................... 64  
      2.3.2.3 Aligned Ceramic Matrix Composites ............................................... 64  

References ....................................................................................................................
# List of Abbreviations

<table>
<thead>
<tr>
<th>Letter</th>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>a-C</td>
<td>Amorphous Carbon</td>
</tr>
<tr>
<td>A</td>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>A</td>
<td>AFM</td>
<td>Atomic Force Microscope (or Microscopy)</td>
</tr>
<tr>
<td>C</td>
<td>CCVD</td>
<td>Catalytic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>C</td>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>C</td>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>D</td>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>D</td>
<td>DMF</td>
<td>Dimethyl Formamide ((CH$_3$)$_2$NC(O)H)</td>
</tr>
<tr>
<td>D</td>
<td>DWNT</td>
<td>Double Walled Nanotube</td>
</tr>
<tr>
<td>E</td>
<td>EDS/EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>E</td>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>E</td>
<td>ESR</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>F</td>
<td>FC-CVD</td>
<td>Floating Catalyst Chemical Vapor Deposition</td>
</tr>
<tr>
<td>F</td>
<td>FTIR</td>
<td>Fourier Transform Infrared (Spectroscopy)</td>
</tr>
<tr>
<td>H</td>
<td>HAp</td>
<td>Hydroxy-Apatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$)</td>
</tr>
<tr>
<td>H</td>
<td>HiPCO</td>
<td>High Pressure Carbon Monoxide</td>
</tr>
<tr>
<td>H</td>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>I</td>
<td>IBAD</td>
<td>Ion Beam Assisted Deposition</td>
</tr>
<tr>
<td>I</td>
<td>ICPS</td>
<td>Inductively Coupled Plasma Spectroscopy</td>
</tr>
<tr>
<td>I</td>
<td>ITO</td>
<td>Indium-Tin Oxide</td>
</tr>
<tr>
<td>I</td>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>L</td>
<td>LDS</td>
<td>Lithium Dodecyl Sulfate or Lithium Lauryl Sulfate</td>
</tr>
<tr>
<td>L</td>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>M</td>
<td>MeOH</td>
<td>Methanol (CH$_3$OH)</td>
</tr>
<tr>
<td>M</td>
<td>MWNT</td>
<td>Multi Walled Nanotube</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td><strong>P</strong></td>
<td><strong>R</strong></td>
</tr>
<tr>
<td>--------</td>
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</tr>
<tr>
<td>NMR</td>
<td>PAN</td>
<td>RMS</td>
</tr>
<tr>
<td>Nuclear Magnetic Resonance</td>
<td>Poly-AcryloNitrile</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td><strong>PMMA</strong></td>
<td><strong>PVA</strong></td>
<td></td>
</tr>
<tr>
<td>Poly(methyl methacrylate) or poly(methyl 2-methylpropenoate)</td>
<td>Poly(vinyl alcohol)</td>
<td></td>
</tr>
<tr>
<td><strong>S</strong></td>
<td><strong>T</strong></td>
<td><strong>V</strong></td>
</tr>
<tr>
<td>SCCM</td>
<td>TEM</td>
<td>VGCF</td>
</tr>
<tr>
<td>Standard cubic centimeters per minute</td>
<td>Transmission Electron Microscope (or Microscopy)</td>
<td>Vapor Grown Carbon Fiber</td>
</tr>
<tr>
<td>SDS</td>
<td>TGA</td>
<td></td>
</tr>
<tr>
<td>Sodium Dodecyl Sulfate or Sodium Lauryl Sulfate</td>
<td>Thermo-gravimetric Analysis</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>TG/DTA</td>
<td></td>
</tr>
<tr>
<td>Scanning Electron Microscope (or Microscopy)</td>
<td>Thermo-gravimetric/Differential Thermal Analyzer</td>
<td></td>
</tr>
<tr>
<td>SMSI</td>
<td>TPO</td>
<td></td>
</tr>
<tr>
<td>Strong Metal-Substrate Interaction(s)</td>
<td>Temperature Programmed Oxidation</td>
<td></td>
</tr>
<tr>
<td>STM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scanning Tunneling Microscope (or Microscopy)</td>
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<tr>
<td>SWNT</td>
<td></td>
<td></td>
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<tr>
<td>Single Walled Nanotube</td>
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<tr>
<td><strong>X</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XRD</td>
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<tr>
<td>X-ray Diffraction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### List of Figures

| Figure 1-1. | Sketches illustrating some of the general morphologies which carbon fibers may assume. | 11 |
| Figure 1-2. | SEM micrographs of varying graphene-sheet morphologies observed in carbon fibers. | 13 |
| Figure 1-3. | Concentrically arranged carbon fiber as grown and after heat treatment at 3000°C. | 14 |
| Figure 1-4. | Proposed model for the growth of vapor-grown carbon fibers. | 14 |
| Figure 1-5. | Proposed model of the scrolled structure present in a graphite whisker. | 15 |
| Figure 1-6. | Time-of-flight mass spectrum of carbon clusters produced through the laser vaporization of a graphite disk in an inert gas environment. | 17 |
| Figure 1-7. | Buckminsterfullerenes: (a) C$_{60}$, (b) C$_{70}$, (c) C$_{80}$. | 18 |
| Figure 1-8. | Experimental setup (a) and results (b) used by Frank et al. to demonstrate quantized conductivity in carbon nanotubes. | 22 |
| Figure 1-9. | Upon exposure to a photographic flash at close range, nanotubes can give a photoacoustic retort and may ignite. | 23 |
| Figure 1-10. | (a) The chiral vector OA, describing a (4,2) nanotube, overlaid on a graphene sheet as the vector addition of n$\hat{a}_1$ + m$\hat{a}_2$. The chiral angle, $\theta$, is measured between the zigzag direction, defined as $\theta = 0^\circ$, and the chiral vector. | 26 |
| Figure 1-11. | The three general nanotube structures: (a) an armchair nanotube, (b) a zigzag nanotube, (c) a chiral nanotube. | 27 |
| Figure 1-12. | (a) Pentagonal defects in a graphene sheet induce curvature towards the nanotube axis. (b) Heptagonal defects induce curvature of the graphene sheet away from the nanotube axis. | 28 |
| Figure 1-13. | An example of how pentagonal and heptagonal defects may alter the diameter of a nanotube. | 29 |
| Figure 1-14. | Through pairs of pentagons and heptagons, two nanotubes of differing chirality, but similar diameter may be joined, yielding a crooked or kinked nanotube. | 29 |
| Figure 1-15. | TEM micrograph showing the compartmentalization of a multi-walled nanotube, known as a bamboo structure. | 30 |
| Figure 1-16. | TEM images showing open multi-walled nanotube structures. | 33 |
| Figure 1-17. | Simplified model for base- and tip- based catalytic growth of carbon nanotubes. | 35 |
| Figure 1-18. | Schematic experimental setup for an arc-discharge synthesis apparatus. | 36 |
| Figure 1-19. | Schematic experimental setup for a laser-ablation synthesis apparatus. | 38 |
| Figure 1-20. | Schematic illustration of a typical CVD furnace. | 39 |
| Figure 1-21. | HiPCO reactor, with detail of the showerhead mixing and reactor region. | 40 |
| Figure 2-1. | Raman spectra of carbon nanotubes. | 54 |
Figure 2-2. Example of idealized load transfer between two adjacent fibers in a yarn.

Figure 2-3. Behavior of equation 2.2 with changing twist angle $\alpha$, with the component terms’ individual behaviors.

Figure 2-4. Proposed by Jiang et al., nanotubes pulled from a “superaligned” array remain stuck together near the surface and base of the array, allowing their drawing into long nanotube yarns.

Figure 2-5. Normalized carbon deposition rates of methane (solid line), ethylene and acetylene (dashed line), and benzene (dotted line) as a function of increasing residence time in the CVD furnace.

Figure 2-6. The geometry around a nanotube for consideration with equation (2.4).

Figure 2-7. The behavior of equation (2.4) for a van der Waals interaction distance ($2l$) of 1nm.

Figure 3-1. Schematic of complete CNT growth setup.

Figure 3-2. Scanning electron micrographs of CNT’s.

Figure 3-3. A pair of individual nanotubes, representative of size variations observed.

Figure 3-4. Mass loss profiles for graphite and graphite-catalyst mixtures (top) and graphite-catalyst oxide mixtures (bottom).

Figure 3-5. Oxidation rates derived from the mass-loss profiles shown in Figure 3-4.

Figure 3-6. Mass-loss profile and rate of oxidation of an amorphous carbon/nanotube sample.

Figure 3-7. Mass-loss profile and rate of oxidation of MWNT mixed with high purity graphite.

Figure 3-8. Effects of synthesis temperature upon mass-loss profile (top) and oxidation rate (bottom).

Figure 3-9. Catalyst effects upon oxidation of low-flow generated nanotubes: mass profile (top) and rate (bottom).

Figure 3-10. Catalyst effects upon oxidation of spray pyrolysis generated nanotubes: mass profile (top) and rate (bottom).

Figure 3-11. Raman Spectra for samples with varying synthesis temperature (top, using an iron catalyst) and varying catalyst type (bottom, using a synthesis temperature of 800°C).

Figure 3-12. Mass loss and rate of burn-off profiles for a given sample under varying temperature ramp rates.

Figure 3-13. Mass-loss profile and rate of oxidation of the biphenyl sludge byproduct.

Figure 4-1. TEM micrograph of an individual nanotube from Sample 6, but exhibiting the general structural form of all nanotubes tested.

Figure 4-2. SEM micrographs of CNT’s used in this examination.

Figure 4-3. The kinetic parameters (activation energy and frequency factor) measured for Samples 1 through 5.
Figure 4-4. Kinetic parameters for length sorted nanotube arrays, derived through the same methods as Samples 1-5. ............................................................. 138
Figure 4-5. TEM micrographs of Sample 1b after partial oxidation. ....................... 142
Figure 5-1. Retained iron content plotted as a function of the ferrocene to benzene ratio in the synthesis feedstock. ............................................................. 155
Figure 5-2. Deposition rate (yield) is plotted as a function of catalyst concentration. .............................................................................................................. 156
Figure 5-3. Nanotube diameter and standard deviation are plotted versus the retained iron content. ........................................................................................... 157
Figure 5-4. Raman studies of nanotube structure are summarized in terms of the (a) G:D and (b) G’:D peak ratios, plotted versus the retained iron content in the sample. ............................................................................................ 159
Figure 5-5. (a) An example SEM micrograph of a nanotube sample. The nanotubes examined appear free of impurities on the micron scale. (b) Samples synthesized using the higher catalyst concentrations analyzed were frequently observed to (contd) .............................................................................................................. 160
Figure 5-6. Thermo-gravimetric burn-off of nanotube samples is summarized and plotted versus the sample iron content. .............................................................................................................. 161
Figure 5-7. Nanotube array length (a) and deposition rate (b) are plotted as a function of growth time. .............................................................................................................. 163
Figure 5-8. Nanotube diameter and standard deviation are plotted versus the growth time during stage 1 growth. ........................................................................... 164
Figure 5-9. Nanoscale non-nanotube carbonaceous contamination was observed on larger tubes in several samples. ........................................................................... 167
Figure 6-1. Mean nanotube diameter and standard deviation are compared across several different deposition substrates. ............................................................. 173
Figure 6-2. TEM micrographs showing nanotube size and structure for FC-CVD nanotubes grown on (a) alumina (Al₂O₃) (b) silicon, and (c) quartz (SiO₂). ................................................................................................... 173
Figure 6-3. 5µm x 5µm AFM scans of (a) alumina, (b) silicon, and (c) quartz substrates. .............................................................................................................. 177
Figure 6-4. Thermodynamics of the reduction of silica and alumina by carbon, iron, and hydrogen gas (H₂) to Si or Al and CO, FeO, and H₂O, respectively. .............................................................................................................. 178
Figure 6-5. Free energy of the reduction of silica and alumina by atomic hydrogen, expected to be present during synthesis in small quantities. ..................... 180
Figure 6-6. The silica-wustite phase diagram. .............................................................................................................. 180
Figure 6-7. The alumina-wustite phase diagram. .............................................................................................................. 181
Figure 6-8. The phase diagrams for the NiO-SiO₂ and NiO-Al₂O₃ systems. ............ 184
Figure 6-9. 5µm x 5µm AFM scans of a 10nm layer of nickel on (a) silica and (b) alumina substrates, annealed in 10% H₂, 90% Ar for 10 minutes at 850°C. .............................................................................................................. 185
Figure 7-1. The experimental setup for measuring shear strength between nanotube arrays and substrates. .............................................................................................................. 191
Figure 7.2. Crusts were observed at the base (a) and top surface (b) of nanotube arrays.

Figure 7.3. Catalysts were frequently observed enclosed at the tips of nanotubes, suggesting the tip growth mechanism.

Figure 7.4. Nanotubes were also frequently observed without catalyst particles at their capped ends, suggesting a basal growth mechanism.

Figure 7.5. Dual-ended growth from a single catalyst particle.

Figure 7.6. TEM micrographs show distinct changes in the inner diameter of nanotubes from one side of a catalyst particle to another, suggesting dual-tube growth from the vapor phase.

Figure 7.7. Arrows and hemispheres mark sites where nanotubes are believed to have anchored or attached during floating catalyst synthesis, but broken off due to sonication forces during TEM sample preparation.

Figure 7.8. Carbon generated by auto-pyrolysis of the hydrocarbon may deposit onto the outside of existing nanotubes, forming additional graphene walls which may extend beyond the capping of the supporting nanotube.

Figure 7.9. (a) Nanotubes generated by the revised synthesis method show a significantly increased tendency to stick together when the mat is separated, compared to (b) nanotube arrays generated through FC-CVD methods used previously.

Figure 7.10. (a) Nanotubes generated at 750°C exhibit improved alignment of the array. (b) Nanotubes generated at 940°C show increased variability of the axial direction.

Figure 7.11. A basal crust was observed when nanotubes were generated with ethylene at 940°C, binding the nanotubes to the substrate and indicating auto-pyrolysis of the carbon source.

Figure 7.12. Nanotubes grown at 940°C exhibit a bamboo-like structure due to increased diffusion of carbon through the catalyst particle bulk.

Figure 7.13. Nanotubes grown at 750°C show continuous hollow structures with thin walls.

Figure 7.14. Raman spectra for samples grown by thin-film CVD at differing synthesis temperatures.

Figure 7.15. Arrays grown via the revised synthesis method show a strong propensity to cling and draw adjacent nanotubes, indicating their amenability towards spinning or drawing into threads.

Figure 7.16. A 100 µm thread drawn from a 20 µm long array of carbon nanotubes, showing the ability of nanotubes grown by the revised synthesis method to form thread structures.
List of Tables

Table 3-1: Summary of the synthesis conditions for all samples used in this chapter. ................................................................. 104
Table 4-1: The synthesis conditions for the samples examined in this chapter .... 132
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Finally, I would like to acknowledge my family, without whose love and encouragement this would never have been possible.

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Chapter 4, in part, is a reprint of the material as it appears in “Length and the Oxidation Kinetics of Chemical-Vapor-Deposition-Generated Multiwalled Carbon Nanotubes”, McKee G. S. B., Flowers J. S. and Vecchio K. S. J. Phys. Chem. C 112 10108-10113, 2008. The dissertation author was the primary investigator and author of this paper.
Chapters 5 and 6, in part, have been submitted for publication of the material as it may appear in Carbon, McKee, Gregg S. B., Deck Christian P. and Vecchio, Kenneth S., 2008. The dissertation author was the primary investigator and author of this paper.

Chapter 6, in part, is currently being prepared for submission for publication of the material. McKee, Gregg S. B., Deck, Christian P. and Vecchio, Kenneth S. The dissertation author was the primary investigator and author of this paper.
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2008   Doctor of Philosophy, University of California, San Diego

Publications


ABSTRACT OF THE DISSERTATION

Towards Improved Spinnability of Chemical Vapor Deposition Generated Multi-Walled Carbon Nanotubes

by

Gregg Sturdivant Burke McKee

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2008

Professor Kenneth S. Vecchio, Chair

While many research groups have successfully generated aligned arrays of single- and multi-walled nanotubes, a very limited number of these have been shown to be amenable to drawing into a thread without the use of a polymer matrix. The purpose of this research is to explore and develop enhancements to the structure and
arrangement of aligned arrays of carbon nanotubes in order to improve their ability to be drawn into such threads. This is accomplished through investigations into the relationship between synthesis conditions and resulting products. Characterization methods include scanning and transmission electron microscopy, Raman spectroscopy, thermo-gravimetric analyses, atomic-force microscopy, and other techniques. Criteria for drawing are proposed and examined and an in-depth understanding of the chemical-vapor-deposition synthesis of carbon nanotubes is developed. Factors important to the spinnability of nanotube arrays are found to include nanotube diameters, tube stiffness, amorphous carbon deposition, and the catalyst introduction method. Spinnable nanotube arrays are generated and discussed in terms of tube properties, limitations with regard to spinning and the potential for further improvements to the process.
1. Introduction

The purpose of this research is to explore and develop enhancements to the structure and arrangement of carbon nanotubes to improve their ability to be drawn into exclusively-nanotube threads for use in composite materials or as light weight conductors in weight-sensitive applications. The research will enhance the field of knowledge regarding the synthesis, purification, and manipulation of carbon nanotubes for their inclusion within composite structural materials.

While three independent research groups [1-3] have succeeded in spinning as-synthesized nanotube arrays into exclusively-nanotube threads, no work has yet been performed on the characteristics and differentiating properties of the nanotubes used. Aligned arrays of single-walled and multi-walled nanotubes of varying lengths have been synthesized by many different groups [4-16], using varying methods, but none outside these three initial groups have made note of unusual tackiness apparent in the nanotube arrays or any tendency of contact with the arrays to pull off isolated, let alone, self-sustaining strands. The question must be asked as to how the nanotube arrays used to make these threads differ from those widely generated over the past several years.

This work examines and attempts to optimize the catalytic chemical vapor deposition (CVD) synthesis of carbon nanotubes to improve length and quality with regards to spinnability and to identify exactly what properties are necessary for thread formation. Criteria for the spinnability of a nanotube array are proposed, discussed, and experiments for their validation undertaken.
Chapter 1 (this chapter) provides a brief discussion of the many forms of carbon and an introduction to the physics, properties, and synthesis methods of carbon nanotubes.

Chapter 2 discusses characterization and refinement of carbon nanotubes and then moves on to discuss the state of the art with respect to carbon nanotube-reinforced composite materials. The chapter finishes with a discussion of CVD synthesis considerations and proposed criteria for nanotube spinnability.

Chapter 3 reports on significant changes in thermo-gravimetric oxidation profiles brought about through variations in synthesis temperature, catalyst material, and other synthesis variables. The results show measureable impacts on nanotube stability with particular importance attributed to the synthesis catalyst used.

Chapter 4 reports kinetic parameters for the oxidation of nanotube arrays determined through isothermal analysis, demonstrating improved nanotube structure and oxidative stability with increasing array lengths as well as significantly increased reactivity at defect sites.

Chapter 5 reports an in-depth study of the relationship between synthesis variables and the resulting nanotube dimensions in order to improve the product specificity. The floating-catalyst CVD (FC-CVD) process for generating nanotubes is compared to the parent process for the generation of vapor-grown carbon fibers, from which it is derived.
In Chapter 6, the substrate-catalyst relationship is examined in detail, highlighting the importance of strong electro-chemical interactions in limiting catalyst agglomeration.

Finally, Chapter 7 discusses lessons and observations from the prior chapters not specifically discussed therein and reports on revised synthesis procedures utilizing these lessons. This revised process allows the production of aligned nanotube arrays amenable to spinning or drawing into threads. Limitations of the revised process are discussed along with potential opportunities for further improvement.

Before entering into a detailed examination of the experiments involved in this work, some understanding of the ubiquity of carbon and its many varieties is helpful on the part of the reader.

1.1 The Forms of Carbon

Carbon has shown itself to be a most versatile and useful element in all its many forms. It provides the basis for flora and fauna alike, the backbone for the coal, petroleum, and natural gas energy sources used to enable daily human life as well as the waste pollution, which increasingly presents such a challenge. The decay of $^{14}$C is frequently used to determine the time period in which organic-based artifacts originated. As a polymer, it insulates, helps keep comestibles fresh, corrects vision, forms inexpensive fabrics, and provides impact protection. Its ability to bond with itself and with other atoms in seemingly endless ways established the field of organic
chemistry. Carbon, in one form or another, is employed for everything from decoration to drug delivery to lightweight structural reinforcements.

No other element can take on so many different appearances, properties and morphologies. In its various forms, carbon exhibits the highest thermal conductivity and highest melting point of all materials. It is the only group IV element that can have sp$^1$, sp$^2$, or sp$^3$ electron orbital hybridization, largely accounting for its ubiquity and utility in so many areas [17]. Should mankind be able to unlock the potential held by this one element, who can say what the future might hold?

Elemental carbon presents itself in a large number of differing solid forms including carbon blacks, glassy carbons, amorphous carbon, diamond, graphite, fullerenes, graphite whiskers, carbon fibers, and carbon nanotubes, each with unique properties. Each has a differing structure and, as such, differing properties which lend themselves to a variety of applications. In the interest of developing a minimal familiarity with these various forms for the purposes of later discussions, the following summaries are offered.

1.1.1 Carbon Black

Carbon black is perhaps one of the most commonly observed forms of carbon encountered in daily life, particularly in the form of soot as a combustion byproduct. Blacks are generally small round particles of approximately 100nm [17, 18] or larger, but have been produced in laboratories with size ranges between approximately 20 and 50nm [19]. These spheroids are composed of small graphite-like layers arranged
around a sometimes-hollow core. Concentricity of the layers becomes apparent towards the outside edges of each particle, but the layers are not continuous, as is shown by the facetization of the particle upon annealing at ~2800°C [19].

These forms of carbon are usually produced on industrial scales through the dehydrogenation of various hydrocarbons, and are classified by the manner in which they are produced (e.g. thermal blacks, plasma blacks, acetylene blacks, etc.) [17]. The individual methods for production are outside the scope of this paper and will not be covered here. Carbon blacks are frequently used as fillers to modify the mechanical, electrical, or optical properties of the matrix to which they are added [17].

1.1.2 Glassy (Vitreous) Carbon

Glassy carbon is a form of non-graphitizing carbon which, due to its name, is sometimes confused with amorphous carbon. In fact, this form has little in common with silicate glass aside from its glassy surface appearance [20]. The structure of glassy carbon is thought to be made up of turbostratic graphene layers [17], but more recently has been suggested to contain a significant proportion of fullerene-related materials [21]. It is moderately hard, can be polished, thermally conducting, biocompatible, and extremely chemically inert, even at high temperatures. The material is gas-impermeable despite a relatively large proportion of pores.

Manufacture is generally accomplished through the slow degradation of various polymers in the temperature range of approximately 900 – 1000°C. In certain cases, depending upon heat treatments and the size of the piece in question, this
process may take three to four months [22]. Common applications include those where the material would be subjected to high temperature or highly reactive conditions such as in nuclear reactors, as electrolysis electrodes, and frequently as high temperature laboratory crucibles.

1.1.3 Amorphous Carbon (a-C)

According to the International Union of Pure and Applied Chemistry (IUPAC), amorphous carbon is defined as a form of carbon with no long range order. The term is restricted to those carbons with localized $\pi$-electrons where deviations in the inter-atomic bond distance of more than 5% of the ideal and variations in bond angles due to dangling bonds are observed [20]. Some short-range order (length scale of ~ 10Å) is frequently present as the sp$^2$ and sp$^3$ hybridized carbons tend to form clusters (there is typically almost no sp$^1$ hybridized carbon present). The nature of this short range order varies significantly with the synthesis method and is generally characterized by the ratio of sp$^2$ to sp$^3$ bonding (spectroscopically determined via NMR, EELS, etc.) and hydrogen content. Amorphous carbon may also be characterized in terms of its density relative to that of graphite. In general, as the sp$^3$-hybridized content of an amorphous carbon increases, the mechanical hardness and electronic band gap increase, and the conductivity decreases [17].

Hydrogen impurities in a-C act to stabilize the carbon by passivating dangling bonds [17]. Despite this, amorphous carbon is generally more reactive than other forms of carbon, allowing its preferential removal by thermally programmed
oxidation. Alternatively, inert-atmosphere heat treatment of amorphous carbon can be used to thicken carbon fibers [17].

1.1.4 Diamond

Diamond is a metastable, allotropic phase of carbon generally occurring with cubic space group Fd3m, but also existing as a hexagonal form under certain conditions [17, 20]. Society places a high value on diamonds as decorative gems, but they are also very utilile, used as thin film coatings for high wear applications such as cutting blades (due to high hardness, 10, on the Mohs scale). Ideal cubic crystals are made entirely of sp³-bonded carbon in a tetrahedral lattice and have an extraordinarily high atomic density (56% higher than that of graphite) meaning that very few chemical species may enter the lattice substitutionally [17]. As a result, naturally occurring high quality diamonds typically contain impurity levels of approximately 10ppm.

A metastable phase, diamond is formed at high temperatures and pressures and will revert to graphite at temperatures in excess of roughly 1700°C at atmospheric pressure [18]. Together with in-plane graphite sheets and nanotubes, it has the highest room temperature thermal conductivity of known materials [23, 24].

1.1.5 Graphite

Another allotropic carbon form, and perhaps the most well known, graphite, exists in both hexagonal and rhombohedral forms. The rhombohedral phase (space
group \( R\overline{3}m \) exhibits an ABCABC type stacking order and is thermodynamically unstable, tending to revert to the hexagonal phase on heating above 1600K [17, 20]. It may be considered a type of extended stacking fault in the hexagonal phase, which shows ABAB stacking and a P6\(_3\)/mmc space group. Carbon atoms are bonded in-plane through sp\(^2\) hybridization (the strongest bond occurring in nature [25], a\(_{c-c} \approx 1.421\)Å) and multiple planes are held together through weaker \( \pi \)-bonding [18]. As a result, the inter-atomic spacing is extremely small and the inter-planar spacing relatively large. Impurities are thus unlikely to enter the lattice substitutionally and occur most commonly at interstitial sites between the graphene planes [17, 26]. As quantities of interstitial atoms increase or other defects cause larger separations between graphene layers, registry between the atomic positions in adjacent planes of graphite decreases until a separation of approximately 3.44Å is reached. At this point, it is believed no registry between layers is retained and the material is referred to as turbostratic graphite [17, 26].

Due to the weak inter-plane bonding, graphene layers will slide with relative ease over each other (shear strength \( \sim 4.8 \times 10^5 \) Pa [27]), thus making powdered graphite a dry, inexpensive lubricant for various applications. The thermal stability, formability, and machinability of graphite make it ideal in many high temperature applications including furnace parts, electrodes, etc.

Graphite occurs naturally, but individual crystals are small (typically < 0.1mm thick) and contain a variety of structural defects and impurities that make it less desirable for most applications. “Kish” graphite is a synthetic single-crystal graphite
form harvested from the surface of high-carbon iron melts. These crystals are somewhat larger than naturally occurring graphite and are frequently used in scientific experiments. Highly Oriented Pyrolytic Graphite (HOPG) is a high purity synthetic polycrystalline form of graphite formed through the pyrolysis of hydrocarbons at temperatures in excess of 2000°C. The resultant carbon is frequently heat-treated further to improve the crystalline order, after which the HOPG exhibits mechanical and electrical properties very similar to single-crystal graphite [26].

1.1.6 Carbon Fibers

The first carbon fibers were prepared from Japanese Kyoto Bamboo filaments by Thomas A. Edison for use as incandescent filaments in early electric light bulbs [28]. These filaments were found to be fragile and were eventually replaced with the more resilient tungsten filaments in use today. Research in the field of carbon fibers continued at a slow pace through the early 20th century, but truly began in earnest in the 1950’s and 1960’s when stronger, stiffer, and lighter materials were sought for use in composite materials for the rapidly progressing aerospace industry. Vapor grown carbon fibers (VGCF’s) were identified in the 1960’s and early 70’s with much smaller diameters than traditional carbon fibers, paving the way for the later discovery and identification of fullerene forms of carbon.

Carbon fibers offer significant improvements in strength, stiffness, and density over traditional materials. For example, carbon fibers offer a weight-normalized
strength of seven to thirteen times that of steel [24], and their properties may be tailored towards specific applications.

Fiber diameters are typically in the range of ~7 – 20 microns and can usually be fabricated in continuous lengths. Vapor-grown carbon fibers may range in size from 1mm down to ~100nm [27] and have not yet been synthesized in continuous lengths. The lower bound of their diameter range and the distinction between multi-walled nanotubes and VGCF’s is somewhat fuzzy and depends upon the resource consulted. This fact might arise from observations of very small diameter (<10nm) structures in VGCF experiments prior to the identification of nanotube structures [29]. More precise definitions of nanotube and fiber will be examined in Section 1.1.9.

Carbon fibers are synthesized from a variety of sources including hydrocarbons, polymers such as rayon, nylon, and poly-acrylonitrile (PAN), and mesophase pitch. Synthesis methods may be generally classified as either extrusion or chemical vapor deposition (CVD), but are highly nuanced and play a significant role in the properties of the resulting fibers [26]. Morphologies are heavily dependent upon the fiber precursor and synthesis steps (e.g. the shape of the stirrer used to mix the pitch prior to extrusion [24]) and vary considerably. In general, fibers are made up of graphene sheets oriented within approximately 20° of the fiber axis, but these may be arranged radially, concentrically, randomly, any combination of these, or in still other orientations (see Figures 1-1, 1-2). Vapor-grown carbon fibers frequently exhibit a hollow core, further blurring the lines distinguishing them from multi-walled nanotubes. Heat treatment to ~3000°C causes further graphitization of the fiber
structure, inducing facetization in concentrically arranged fibers (see Figures 1-1b and 1-3).

Figure 1-1. Sketches illustrating some of the general morphologies which carbon fibers may assume. (a) Vapor-Grown carbon fibers as deposited frequently exhibit a hollow core, similar to a multi-walled carbon nanotube. (b) Upon annealing at ~3000°C, the carbon fibers will graphitize and become faceted. (c, d, e) Various arrangements of graphene planes observed in different types of carbon fibers [17, 24, 26].

In polymer and mesophase pitch fibers (also known as ex-polymer and ex-pitch fibers, respectively), synthesis starts with the extrusion of the precursor into a fine fiber form, typically at or near room temperature. These are heated in an oxygen-containing atmosphere to temperatures of 200-300°C in order to stabilize them for subsequent heat treatment steps. This step is known as conversion or stabilization.
The stabilized fibers are then carbonized at temperatures between 1000 and 1500°C (typically at the lower end of this range for commercial applications), causing the formation of well-defined graphene sheets and the removal of non-carbon impurities, such as nitrogen and hydrogen in PAN fibers. Depending upon the desired properties of the fiber and its eventual purpose, the carbonized fiber may be further heat treated or graphitized at very high temperatures. This step further anneals the graphene planes, removing structural defects and other impurities, and increases the fiber modulus at the cost of strength [17, 24, 26].

Vapor-grown carbon fibers are synthesized by catalytic chemical vapor deposition (CCVD). This process takes place at temperatures around 1000°C and a substrate may or may not be used. Catalyst particles, typically transition metals such as Fe, Ni, or Co, are introduced into a furnace either prior to or concurrently with a gaseous hydrocarbon. The gas is believed to decompose on the catalyst particle, saturating it with carbon. As the decomposition is generally exothermic, this causes a temperature and thus saturation gradient over the particle. At the far end from where the decomposition occurs, the particle is supersaturated with carbon, causing the precipitation of graphene planes into the carbon fiber. Subsequent to precipitation, the fiber may thicken through deposition of graphite directly onto the fiber’s length. Growth continues until the catalyst particle becomes “poisoned”, or coated in graphite, preventing the further decomposition of the hydrocarbon (see Figure 1-4) [24, 27, 30].

The high strengths of carbon fibers are related to the presence of structural defects, which prevent the slip of adjacent graphene sheets. Conversely, high moduli
are a result of significant structural perfection and c-axis alignment of these sheets. As a result, the two are somewhat mutually exclusive – a carbon fiber cannot have optimal modulus as well as optimal strength.

Figure 1-2. SEM micrographs of varying graphene-sheet morphologies observed in carbon fibers. The sheet orientations depend strongly upon the precursor material as well as the synthesis steps used to create the fiber [24].

1.1.7 Graphite Whiskers

Through research on the synthesis of carbon fibers in the 1960’s, a new form of carbon was uncovered. Roger Bacon produced a new fiber via condensation of carbon plasma from a DC arc under high pressure inert gas [31]. He named these new
forms “graphite whiskers”, despite the fact that they are not whiskers in the metallurgical sense, and was able to elaborate on their structure and properties. Bacon’s whiskers became of significant interest in carbon fiber research as they exhibited physical properties very similar to that of “ideal” graphite [24]. Until the identification of carbon nanotubes, they were the standard by which all other carbon fibers were judged [17].

Figure 1-3. Concentrically arranged carbon fiber as grown (a) and after heat treatment at 3000°C (b). Note facetization of graphene sheets upon heat treatment [26].

Figure 1-4. Proposed model for the growth of vapor-grown carbon fibers. (a) A catalyst particle is introduced into the CVD furnace either prior to or concurrently with a gaseous hydrocarbon which then decomposes on the catalyst (b). Graphitic carbon precipitates on the opposite side of the particle (c) causing the growth of the fiber. Growth continues until the catalyst particle is coated, preventing the further decomposition of the hydrocarbon [30].
Bacon noted the structure of the whiskers to be much more regular than carbon fibers derived from ex-polymer or even vapor grown carbon fibers. He was able to show that the whisker structure was similar to a scroll or rolled carpet and demonstrated this by unrolling one, forming graphite sheets with dimensions larger than the original whisker’s circumference [31] (see Figure 1-5).

![Figure 1-5. Proposed model of the scrolled structure present in a graphite whisker [31].](image)

Whiskers are considered distinctly different from multi-walled carbon nanotubes for this reason, but also because of the dimensional differences between the two types of carbon: these whiskers have diameters in the range of 1 – 5μm and lengths of up to ~3cm [17, 18, 24]. The temperature dependence of the electrical resistivity suggests structural perfection close to that of a single crystal and the sides show high reflectivity, consistent with that expected from the basal planes of graphite. The whiskers have a Young’s Modulus of approximately 800 GPa and a tensile strength of ~20 GPa or roughly 47 times that of steel when normalized for weight [18, 24, 27]. In many ways, Bacon’s whiskers were something of an intermediate step between carbon fibers and carbon nanotubes.

Synthesis of whiskers is performed in a DC arc apparatus at 75-80 V and 70-76 Amperes under an inert atmosphere near 92 bar [17, 24]. Literature agrees that the
positive electrode should be carbon, but differs on whether the negative electrode should be copper [24] or carbon [17]. Since the carbon plasma appears to originate from the positive electrode, the distinction may not be important.

1.1.8 Fullerenes

Carbon, like most elements examined by plasma condensation, exhibits a tendency to form clusters of atoms when condensing from vapor in an inert environment. However, it differs in its unique tendency to form clusters of even numbers of atoms when more than ~30 atoms condensed (see Figure 1-6) [32]. In particular, clusters of 60 atoms appear to be predominant and their proportion may be increased by varying synthesis conditions, suggesting a more stable morphology than other cluster sizes. For some time, there was a significant question of what arrangement of 60 atoms could be stable enough to account for the large cluster population and remain consistent with the bonding exhibited by carbon.

In 1985, Kroto et al. [33] suggested a truncated icosahedron, more commonly recognized as the shape of a soccer-ball, might satisfy the structural and energetic requirements for this cluster size. These structures were initially termed “Buckminsterfullerenes” in honor of Buckminster Fuller and his geodesic domes. Interestingly, Kroto et al. expressed some discomfort by the “number of letters and syllables in the rather fanciful but highly appropriate name” [33] they chose, and suggested it be shortened to some more concise and easily used name selected by consensus, eventually yielding the term “Fullerene”.
Graphene layers of finite size have a significant proportion of edge atoms with dangling bonds, creating a high energy structure. Even while increasing the strain energy, elimination of these dangling bonds through the wrapping of the layer into a ball structure creates a net reduction in the overall energy of the structure, leading to its remarkable stability [26, 34].

Figure 1-6. Time-of-flight mass spectrum of carbon clusters produced through the laser vaporization of a graphite disk in an inert gas environment [32].

Fullerenes were initially synthesized through laser vaporization of a graphite target, cooled via a 10 atm. helium jet. Krätschmer et al. [35] developed a fullerene
synthesis technique using DC arc condensation in 1990, which has since become the preferred production method.

The term “fullerene” generally refers to closed-cage carbon structures with a finite number of atoms in the molecule. Larger fullerenes such as C\(_{70}\) and C\(_{80}\), while less common than C\(_{60}\), are not uncommon (ratio of C\(_{70}\) to C\(_{60}\) depends strongly on synthesis conditions) and have structures similar to that for C\(_{60}\). The larger molecules can by visualized by adding a row of hexagons at the equator of a C60 buckyball (see Figure 1-7). After the discovery of this class of molecule, it was rapidly theorized and experimentally found that atoms or molecules of different species could be contained within the carbon cages, leading to potentially interesting properties [36, 37].

![Buckminsterfullerenes: (a) C\(_{60}\), (b) C\(_{70}\), (c) C\(_{80}\). Progressive additions of 10 carbon atoms each add an equatorial ring of hexagons to the structure. Continuous addition in this fashion leads to the formation of a 1-dimensional nanotube [17].](image)
1.1.9 Carbon Nanotubes

If one continues the addition of carbon moieties to a fullerene, extending the soccer ball to a rugby ball, an elongated rugby ball, and so on, before long a new quasi-one-dimensional structure emerges, closely related to the C_{60} molecule and still considered a fullerene. Indeed, discussions at a carbon-carbon composites workshop in December of 1990 led Richard Smalley to speculate on the existence of carbon tubules related to fullerenes [27]. This was quickly followed by a presentation by Dresselhaus in August 1991 on the theoretical properties of such structures. While such structures had been observed in the study of vapor-grown carbon fibers [38], they were not recognized and identified as such until the work of Iijima [29], published in November of 1991.

1.1.9.1 Carbon Nanotubes: General

A carbon nanotube is made up of one or more cylindrically rolled graphene sheets that are continuous in the axial direction of the fiber, without migration between core and surface [27]. Nanotubes have a hollow core and may or may not have caps on one or both ends of the structure, depending on synthesis and processing methods applied.

Nanotubes may be made up of a single tubule (a single walled nanotube or SWNT) or multiple, concentrically arranged tubules (a multi-walled nanotube or MWNT). Separation between walls of a MWNT (3.35 – 3.44Å) can be similar to that
observed for turbostratic graphite (3.442Å), implying varying, but generally poor, registry between the atomic positions of adjacent tubes.

The physical dimensions for a given nanotube depend upon the indexing of the chiral vector (discussed in Section 1.1.9.3) and the number of shells making up the complete nanotube. Nanotubes have been reported with diameters as low as 0.4nm [39, 40], but more commonly are observed with diameters starting at 0.7nm. Many groups discuss synthesis and processing of multi-walled nanotubes with diameters between ~20 and ~100nm [10, 41, 42], but these would usually not meet the strict definition set forth above. For example, many include non-continuous graphene sheets that migrate from core to surface over some segment of the fiber’s length. Indeed, most multi-walled nanotubes contain structural defects of this type to some degree or another and could therefore, perhaps, better be termed “carbon nanofibers”. However, as the verification of a single, continuous graphene sheet over lengths of up to several microns (or even millimeters) is a realistic impossibility, most researchers in the field opt to deem the structures nanotubes. It is generally accepted that hollow-core, tubular carbon structures with diameters less than 100nm are considered nanotubes. For the work presented herein, the terms “nanotube”, “multi-walled nanotube”, or “MWNT” will be used with the caveat and knowledge that the structures are likely defected and may not be perfect nanotubes in the strictest sense of the word.
1.1.9.2 Carbon Nanotubes: Properties and Applications

The huge amount of interest directed towards nanotube structures is largely due to their many unusual or unique properties. Due to their unusual dimensions, nanotubes are considered to be quasi-one-dimensional with an extremely high aspect ratio and are highly anisotropic. They offer an increased specific surface area over other forms of carbon, making them of interest in gas (particularly hydrogen) storage applications [43-45]. The stiff graphene sheet structure provides a thermal conductivity comparable to or greater than that observed for diamond or the in-plane direction of graphite [46].

One significant reason for interest in nanotubes is their ideal positioning to succeed carbon fibers as lightweight structural reinforcement. In theory, nanotubes are extremely stiff (modulus of SWNT’s is calculated to be ~1054 GPa, MWNT’s ~1200 GPa) and incredibly strong (tensile strength of SWNT’s is ~300 GPa, MWNT’s ~150 GPa), while remaining very light (density of SWNT’s ~ 1.4 g/cm$^3$, MWNT’s ~2.6 g/cm$^3$) [24, 47, 48]. Normalizing for weight, these figures show a fiber between 300 (MWNT’s) and 1124 (SWNT’s) times stronger than an equivalent steel wire. However, these are theoretical calculations and thus realization of these values is the subject of much effort in the scientific world. As yet, the best experimental values for tensile strength are close to 50 GPa (MWNT’s), which, while a long way from the ideal, is still about an order of magnitude higher than that available with carbon fibers [48].
Another reason for the significant interest in nanotubes arises from the diversity of electrical properties that have been predicted and observed in nanotube structures. Single walled nanotubes may act as semiconductors or as conducting semimetals, depending upon the chiral (wrapping) vector. Semi-conducting nanotubes may be doped to alter their electrical properties in a fashion similar to that used in the electronics industry today.

Electrical transport in nanotubes is similar to that for a quantum wire, where conduction occurs in well separated, discrete electron states [18]. Transport may also be ballistic in nature, with no scattering resistance due to defects or phonons [49, 50]. These ideas were demonstrated by Frank et al. by dipping a multi-walled carbon nanotube into a liquid mercury bath, while measuring the current as a function of position [51] (see Figure 1-8). Additionally, both individual and ropes of single walled nanotubes have demonstrated superconducting behaviors at low temperatures (<20K and <0.55K, respectively) [52, 53].

![Figure 1-8](image)

Figure 1-8. Experimental setup (a) and results (b) used by Frank et al. to demonstrate quantized conductivity in carbon nanotubes [51].
Slight alterations to nanotube structure, such as bends, kinks, and branches, may modify the electrical behavior of a nanotube to function in the manner of various electrical devices, such as diodes, LED’s, and transistors [54-56]. This has obvious and immediate ramifications for the future of nano-scale electronics.

Another interesting, but as yet unutilized property of carbon nanotubes is a photoacoustic effect and ignition (Figure 1-9) when exposed to a low to moderate fluence of electromagnetic radiation in the visible wavelengths [57-64]. This effect requires that nanotube, catalyst particle and oxygen be in close contact with each other when exposure occurs. Photon absorption by the nanotube with thermal confinement in the nanostructure causes heating to the point of ignition, assisted by the presence of the catalyst particle.

Figure 1-9. Upon exposure to a photographic flash at close range, nanotubes can give a photoacoustic retort and may ignite. Time order of the above image progresses from left to right and top to bottom. Photo flash occurs in the second frame. This property of nanotubes appears to require close contact between the nanotube, a catalyst particle (e.g. a retained iron nanoparticle from synthesis), and an oxygen containing atmosphere.
Recently, superplasticity has been demonstrated in carbon nanotubes at high temperatures with elongations of up to ~270% of the initial length [65].

Their intrinsic properties make carbon nanotubes ideal for electronics applications, as discussed above, but they can also be used as circuit interconnects or electron guides to build circuits via more traditional, lithographic approaches. The size and shape of nanotubes makes them interesting for photovoltaic applications and other potential applications, including sensors [66, 67], nano-extruders [68], and drug delivery vessels [69, 70].

With such diverse and promising properties, and with more being discovered all the time, scientists and engineers foresee myriad potential applications for carbon nanotubes and their related structures. They have already been put to successful use in the field of nanometrology as fine, flexible, and resilient tips for atomic-force microscopes and electron-beam writers. Easton Sports, Inc. has augmented their carbon fiber composites for sports equipment with nanotubes to reinforce the resin matrix between carbon fibers and is actively marketing these products to customers [71]. Various other companies have begun using carbon nanotubes as field emitters for both low-voltage (field emission display) and high-voltage (electron microscopy) applications. A New Hampshire company called Nanocomp Technologies recently announced commercial production of 2 sq. yd. sheets of nanotube textiles, kilometer lengths of nanotube yarns, and is in the process of significant manufacturing scale-up [72].
1.1.9.3 Carbon Nanotubes: Structure

Carbon nanotubes are frequently classified in very general and not-particularly-informative ways, such as by their conductive behavior ("a metallic or semi-conducting nanotube"), their general structure (zigzag, armchair, or chiral), or by the number of walls present in the structure (SWNT or MWNT). These names do not provide necessary information to the scientist investigating nanotubes. It should also be kept in mind that, while frequently described as a “wrapped sheet of graphite”, nanotubes are in fact a crystalline form of carbon and are grown in tubular form, not fabricated from graphene sheets.

An individual nanotube can best be classified by a pair of indices \((n,m)\) used to specify the chiral, or wrapping, vector:

\[
\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2
\]  

(1.1)

The chiral vector connects two crystallographically equivalent sites on a two-dimensional graphene plane (line OA, Figure 1-10a), which are then overlaid to define the circumference of the nanotube. In Figure 1-10a, the nanotube axis would be parallel to lines OB or AB’. The nanotube diameter, \(d_t\), is thus defined as:

\[
d_t = \frac{a_{c-c}(m^2 + mn + n^2)^{0.5}}{\pi} \sqrt{3}\]

(1.2)

The chiral angle, \(\theta\), measured between the “zigzag” direction (defined as \(\theta = 0^\circ\)) and the chiral vector, may also be described by the indices, using the equation:

\[
\theta = \tan^{-1}\left[\frac{n\sqrt{3}}{(2m + n)}\right]
\]

(1.3)
Due to the symmetry of the 2-D graphene sheet, three types of chiral vectors, and thus nanotubes may be generated: the zigzag nanotube is defined as having indices \((n, 0)\), a chiral angle \(\theta = 0^\circ\), and is so named because of the zigzag appearance of the uncapped nanotube edge; the armchair nanotube, defined as having indices \((n, n)\), a chiral angle \(\theta = 30^\circ\), and so named because of the armchair-like appearance of the uncapped nanotube edge. All vectors that do not fall into either the zigzag or armchair classifications are referred to as “chiral” (Figure 1-11).

![Figure 1-10](image)

Figure 1-10. (a) The chiral vector \(OA\), describing a \((4,2)\) nanotube, overlaid on a graphene sheet as the vector addition of \(n\vec{a}_1 + m\vec{a}_2\). The chiral angle, \(\theta\), is measured between the zigzag direction, defined as \(\theta = 0^\circ\), and the chiral vector. (b) Example indices or chiral vectors describing potential nanotubes. When \(n-m = 3x\) (x is an integer), the resulting nanotube is considered conducting (heavy dots). The number below each pair of indices shows how many distinct caps may be joined to a nanotube having the indices given [73, 74].

The conductivity of a nanotube is also defined by the chiral indices, and thus the chiral vector. The nanotube is considered to be conducting if the condition \(n - m = 3x\) is met, where \(x\) is some integer. More accurately however, many chiral tubes
meeting this criterion are, in fact, low band-gap semiconductors, which exhibit a conducting behavior at all but the lowest temperatures. All indices not meeting this condition result in semi-conducting nanotubes (see Figure 1-10b). As an example, all armchair nanotubes are considered metallic (n=m, so n – m = 0 in all cases), while zigzag and chiral nanotubes may be either semi-conducting or metallic.

Figure 1-11. The three general nanotube structures: (a) an armchair nanotube, (b) a zigzag nanotube, (c) a chiral nanotube. Names derive from the edge morphology of the uncapped nanotube end [73].

The nanotubes have a periodic structure, which can be described through the use of a unit cell made up of the chiral vector in conjunction with the one dimensional translational vector $T$ (Figure 1-10a). Alternatively, the unit cell can be described through the use of a rotation, $\psi$, combined with a translation, $\tau$, as $R = (\psi|\tau)$. “Zigzag” or “Armchair” tubules have symmorphic symmetry groups, so $\tau$ and $\psi$ are executed independently. The symmetry groups for chiral nanotubes have a screw axis running
along the axis of the tubule and are therefore non-symmetric, so symmetry operations must combine operations of $\psi$ and $\tau$ [73].

As with all crystalline structures, there exist intrinsic defects in the nanotube structures. Perhaps the most significant, and thus frequently the most discussed, are pentagonal (5-sided) and heptagonal (7-sided) defects within the hexagonal graphene sheet. These types of defects cause a deflection of the graphene sheet by 60°. In the case of pentagonal defects, this deflection occurs towards the tube axis, narrowing the tube (Figure 1-12a). In the case of heptagonal defects, the deflection is in the opposite direction (Figure 1-12b). By Euler’s rule, a nanotube should contain at least six pentagonal defects at either end to complete a cap [75], however, this number may increase if heptagonal defects are also present in the cap structure. In other locations, these types of defects may act individually to cause a change in nanotube diameter (Figure 1-13), or in pairs to cause deflection of the axial direction and change the nanotube’s chirality (Figure 1-14) [76, 77].

Figure 1-12. (a) Pentagonal defects in a graphene sheet induce curvature towards the nanotube axis. (b) Heptagonal defects induce curvature of the graphene sheet away from the nanotube axis [78].
Figure 1-13. An example of how pentagonal and heptagonal defects may alter the diameter of a nanotube. A pentagonal defect at (A) causes the tube structure to begin narrowing like a cone, while a heptagonal defect at (B) counters the effect, restoring the cylindrical form of the tube [77].

Figure 1-14. Through pairs of pentagons [gray area and dots on right side, (a) and (b)] and heptagons [dark gray area and dots on left side, (a) and (b)], two nanotubes of differing chirality, but similar diameter may be joined, yielding a crooked or kinked nanotube. Here, a (5,5) armchair nanotube (top) connects to a (9,0) zigzag nanotube (bottom) [83].
Other types of intrinsic defects occur with some frequency as well. Vacancies and vacancy clusters have been observed as well as dislocations in the graphene sheets [79]. Substitutional defects are infrequent given the difficulty of entering the graphene lattice and are typically limited to elements such as boron [24]. Interstitial defects have been used to dope nanotubes to acquire desirable electrical properties [80].

Imperfect multi-walled nanotubes occur frequently, but are not typically distinguished from perfect tubules. These include tubes where the structure falls more under the realm of “carbon nano-fibers” than nanotubes, where graphene planes migrate from core to surface of the tube/fiber or where the graphene planes surrounding the structure’s core are not continuous. Bamboo-type structures can occur depending on synthesis conditions, and have been observed with some frequency (Figure 1-15).

Figure 1-15. TEM micrograph showing the compartmentalization of a multi-walled nanotube, known as a bamboo structure [18].

Zhou et al. [81] and Amelinckx et al. [82] put forward arguments for the scroll-like structure of nanotubes, arguing that a wrapped morphology is more likely
than the “Russian doll” arrangement of stacked tubes. Their arguments are based upon compressibility measurements of nanotubes and gaps observed between graphene layers (recorded perpendicular to the tube axis). However, the majority of evidence seems to suggest that the concentric cylinder model is more likely: the lack of the scroll structures observed in carbon nanoparticles; the fact that the vast majority of TEM micrographs show equal numbers of tube walls on either side of a tube axis; the presence of capped nanotube structures, such as those observed in bamboo-type nanotubes.

1.1.9.4 Carbon Nanotubes: Growth Mechanisms

While single walled nanotubes appear to require a catalyst for growth [18, 78], multi-walled nanotubes have been observed to form with [10, 84] or without [29, 85] the presence of a synthesis catalyst. This alone suggests the significant probability of multiple growth mechanisms [86]. Further, nanotubes have been observed to grow in capped and open-ended configurations. While the actual mechanism of nanotube formation is still poorly understood, a large number of models have been proposed. Here is covered a brief summary of some of the more popular ideas.

Single-walled nanotubes are primarily observed with closed ends and generally lack an enclosed catalyst particle. When a particle is observed, it is frequently reduced to a finite number of metal atoms. It has been suggested that SWNT’s nucleate from small carbon ring structures containing 10-40 C atoms with metal clusters acting to add carbon dimers to the rings [87]. Thess et al. proposed a model for the growth of
armchair nanotubes where a catalyst particle moves around the open end of a nanotube, assisting in the hexagonal arrangement of added carbon atoms [88]. However, this model only appears to work for armchair nanotubes and does not account for the formation of chiral or zigzag tube structures [18]. Another model describes the formation of single-shell nanotube structures off a graphite-coated catalyst particle through the addition of carbon at pentagonal defects near the tube tip and via “handle” addition near the tube’s base [89].

When considering the growth of multi-walled nanotubes, one must consider growth without a catalyst particle as well as growth in the presence of such a particle. Without a catalyst, one must further consider the cases of closed and open ended growth. There is evidence of nanotube formation in both cases (see Figures 1-13 & 1-15 for closed-ends and Figure 1-16 for open). If it is assumed that multi-walled nanotubes remain closed during synthesis, growth may occur through the addition of C₂ dimers at pentagonal defects in the tube caps [90]. Stone-Wales transformations could then maintain the hexagonal/pentagonal stability of the tube structure. A Stone-Wales transformation involves the conversion of two pentagons and two heptagons into four hexagons, or vice versa, through the 90° rotation of a carbon dimer. This does not, however, explain the formation of multiple layers of tubule walls.

Open nanotubes require some form of stabilization during growth or otherwise tend to close themselves. It is possible for electric fields, such as those present in arc-discharge synthesis, to partially stabilize an open nanotube end, however, it has been shown that they are insufficient for complete stabilization and would induce field
emission from a nascent nanotube before it could be fully stabilized [91, 92]. Charlier 
et al. proposed the formation of carbon bridges between adjacent shells of forming 
multi-walled nanotubes (lip-lip interactions) [93]. In molecular-dynamics simulations, 
the bonding network of these bridges fluctuates, allowing for the incorporation of new 
carbon moieties. Bernholc et al. later found that bridging bonds between nanotube 
walls alone are insufficient for complete stabilization of an open-tube growth model 
[86]. Double tube models were found to spontaneously close over a time period of 
hundreds of picoseconds. In conjunction with other stabilizing effects, the lip-lip 
interactions or electric fields may assist in achieving stabilization, but even the two 
together is still inadequate to completely stabilize the growth mode [86].
Growth of multi-walled nanotubes with a catalyst particle is thought to occur by a mechanism similar to that of vapor grown carbon fibers as shown in Figure 1-4. In the case of nanotubes, however, the scale tends to be smaller, graphene planes precipitate as continuous cylinders, and a hollow core is preserved in the structure [95, 96]. Depending upon catalyst-substrate interactions, the catalyst may remain attached to the substrate, precipitating the tubule upwards (base-growth, Figure 1-17, left), similar to the manner in which single-walled nanotubes may grow from the surface of a catalyst via “handle” addition. If the substrate-catalyst interactions are weak, the catalyst will lift off from the substrate and be carried at the tip of the nanotube as growth occurs (tip-growth, Figure 1-17, right). Carbon precursor decomposition occurs at the catalyst, whether it is at the tip or base of the growing nanotube, but free carbon moieties may add to the nanotube structure at pentagonal defects, as discussed above.

1.1.9.5 Carbon Nanotubes: Synthesis Methods

The area of synthesis has seen great steps of progress since the pioneering work of Iijima [29] and researchers may now use any of a number of methods to fabricate carbon nanotubes. The techniques attempted to synthesize carbon nanotubes in their short history are numerous and could easily fill an entire book. As most of these are not widely used and in the interest of brevity, this manuscript will provide a succinct summary of the most popular methods for nanotube synthesis at this time, with a more detailed focus on chemical vapor deposition.
1.1.9.5.1 Arc Discharge

This synthesis technique has proven very useful in the study of various forms of carbon. Arc discharge between carbon electrodes has been used to synthesize graphite whiskers [31], soot, fullerenes [35], and was the method by which Iijima first identified nanotube structures [29]. The type and pressure of the gas used appears to play a significant role in the carbon morphology developed [97].

At the simplest level, the physical apparatus consists of a pair of carbon electrodes (although a copper negative electrode may be used) attached to a power supply. An inert gas (usually He or Ar) flows through the chamber at relatively low pressure (~500 torr) and an arc is struck between the electrodes. Ebbesen reports that a typical run uses approximately 20V DC and ~150A/cm² [97]. AC electricity may be
used, but best results are generally obtained under DC current. As the positive electrode is consumed in the process, one of the electrodes is typically attached to a translation stage, allowing adjustment and maintenance of the gap between anode and cathode (Figure 1-18).

![Figure 1-18. Schematic experimental setup for an arc-discharge synthesis apparatus [18].](image)

Carbon is deposited on the negative electrode in a pattern directly matching the positive electrode. For example, if a hole is drilled in the center of the positive electrode, the deposit on the negative will also have a hole in the center [97]. A properly formed deposit will typically have a hard shell around the outside (fused nanotubes and nanoparticles) and a spongy core made up of nanotube bundles and carbon nanoparticles. Proper cooling of both electrodes assists in the formation of
ideal deposits. Current modulation is also essential for good yields. Too much current leads to a reduction in the size of the soft core with respect to the hardened shell [98], while lower currents provide improved nanotube yield [99]. Nanotubes are observed only in the electrode deposit and are not present in the fullerene soot deposited on the chamber walls.

The graphite cathode may be doped with transition metals to assist in single- or multi-walled nanotube formation, but this technique can also generate multi-walled nanotubes without catalysts. Deposited nanotubes are generally roughly aligned along the axis between the electrodes, but are not aligned in the traditional macroscopic sense.

1.1.9.5.2 Laser Ablation

Guo et al. originally developed this apparatus for the study of synthesis conditions for other metallofullerenes, but discovered high quality nanotubes in the resulting soot [100]. In this technique, intense laser pulses are used to vaporize a carbon target inside a furnace held at roughly 1200°C. The carbon vapor condenses as it is carried through the furnace on a flow of an inert gas such as Ar or He, forming fullerenes, carbon onions, and nanotubes, which are eventually collected on a water-cooled copper “cold finger” at the end of the reaction chamber (Figure 1-19). This technique was subsequently refined using a nickel-cobalt alloy catalyst for the high yield (~70-90%) production of high quality single-walled nanotubes of very narrow
diameter distribution [101]. The primary disadvantage to the technique is economic and arises from the cost of the high-powered laser.

![Figure 1-19. Schematic experimental setup for a laser-ablation synthesis apparatus][100].

1.1.9.5.3 Chemical Vapor Deposition (CVD)

CVD is perhaps the simplest and cheapest method for producing carbon nanotubes, but it also has several disadvantages, including a high defect density and an extreme sensitivity to impurity contamination. The technique is very similar (the same, in some cases) to that used for the fabrication of vapor-grown carbon fibers, described in Section 1.1.6.

A quartz tube in a furnace is commonly used as a reaction vessel and is heated to ~600-1100°C (Figure 1-20). Helium, Argon, Hydrogen and Ammonia are common carrier gases (reaction vessel atmospheres) used individually or in various ratios. Carrier gas flow rates vary widely, but are typically below 1000 sccm. The catalyst may be pre-deposited upon a substrate within the reaction chamber, or may be
introduced in conjunction with the carbon source (a gaseous hydrocarbon) in a technique known as “volume seeding”, “vapor phase CVD” [18], or “floating catalyst CVD” [102-105].

Figure 1-20. Schematic illustration of a typical CVD furnace. Carbon source, catalyst and an inert gas are introduced at one end and flow through a furnace held at ~1000°C where nanotubes are deposited.

1.1.9.5.4 High Pressure Carbon Monoxide (HiPCO)

The HiPCO process was introduced for the synthesis of single-walled nanotubes by Nikolaev et al. in 1999 [106], but had been used for the growth of conical vapor-grown carbon fibers before this time [107]. This process is capable of generating large quantities (up to 450 mg/h) of high purity (up to 97 mol %) SWNT’s [108].

By this approach, single-walled nanotubes grow from the disproportionation of carbon monoxide per the reaction: \( 2CO_{(g)} \Rightarrow CO_{2(g)} + C_{(s)} \). Preheated carbon monoxide is passed through a reaction chamber (Figure 1-21) held at high temperature
and pressure (900-1100°C, 30-50 atm). The preheated CO is mixed with room temperature Fe(CO)₅ in CO in a nozzle (referred to as a “showerhead” per its close resemblance to one, Figure 1-21, top) and released into a different section of the heated reaction chamber. The Fe(CO)₅ decomposes upon heating, forming catalytic iron clusters on which the disproportionation reaction takes place. The nanotubes and catalyst clusters flow out of the reaction chamber and are collected on a series of cold fingers and filters. The gasses then pass through a series of purification steps where reaction products (primarily CO₂, but also other trace gasses such as H₂) are removed. Remaining CO is compressed and re-circulated through the reaction chamber to the “showerhead” to be reintroduced into the process [108].

Figure 1-21. HiPCO reactor, with detail of the showerhead mixing and reactor region (top) [108].
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2. Background

In the years following their identification [1], carbon nanotubes have generated considerable interest in a variety of fields from electronics to hydrogen storage to high strength composites [2-5]. Modeling and experimental examinations have shown them to exhibit many novel and interesting properties as discussed in Chapter 1, including an extraordinarily high specific surface area, tunable electrical properties (semiconductor or conductor, depending upon chirality), and high specific strength and stiffness. However, in order to realize their full potential, a more complete understanding of synthesis, refinement, and processing is still required.

In this chapter, the present state of the art is discussed in terms of the characterization and refinement of carbon nanotubes relevant to the discussion of these subjects in subsequent chapters. Discussion will then shift to focus on the many attempts at creating carbon nanotube reinforcements and reinforced composite materials, the variety of techniques used, and their results. Finally, variables intrinsic to the CVD synthesis of nanotubes are examined with regard to trends in previous literature allowing for the growth of arrays conducive to the spinning of nanotube threads.

2.1 Characterization

Examination of carbon nanotubes through various methods allows for the characterization of their structures, properties, and interactions. Nanotube diameter and length are the most basic properties of interest, but are of particular significance
for nanotube-reinforced structural composites. For example, the diameter determines the limit to packing density and thus the stress capacity for a composite material, while length directly impacts the area over which load transfer between nanotube and matrix may occur.

2.1.1 Microscopy

These properties may be quantified to varying degrees through a number of methods including electron microscopy [e.g. transmission (TEM) and scanning (SEM)], scanning tunneling microscopy (STM) [6], and atomic force microscopy (AFM) [7]. Different microscopy techniques provide different types of information about nanotube structures. TEM allows direct observation of the nanotube’s cross-section, enabling confirmation of single- or multi-walled structure and detailed structural information such as the number of walls in multi-walled nanotubes and wall orientation. SEM is useful for examination of many nanotubes together, such as determining the degree of alignment in an array or obtaining a qualitative measure of the amount of micron scale impurities. AFM and STM can provide diameter and chirality information, but are less frequently used due to sample preparation requirements. To yield useful information with these techniques, individual nanotubes must be examined on an extremely flat surface, such as freshly cleaved graphite, mica, or a silicon wafer.

Structure and defect densities in nanotubes are also of great interest. Much of the initial interest in nanotubes derived from the theoretically calculated properties for
idealized nanotubes, meaning those exhibiting absolute crystalline perfection. However, all materials have some degree of intrinsic defection and carbon nanotubes are no exception. These defects cause deviation from the ideal, calculated properties which may be useful, such as altering electrical behaviors to allow use as diodes, LED’s, or transistors [8-10]. On the other hand, defects can cause extreme reductions in the tubes’ mechanical properties [11, 12].

Direct identification of such structural defects has been accomplished through the use of electron microscopes [13], but the small sample size and area of examination make it difficult to generalize these results to macroscopic or batch quantities of nanotubes. Other methods have proven more useful for the qualitative characterization of nanotube defect densities.

2.1.2 Thermo-Gravimetric Analysis/Temperature Programmed Oxidation

The oxidation of nanotubes has been used as a method for characterization and purification of raw nanotubes [14-19], cap removal with subsequent nanotube filling for nanowire fabrication [20-23], and removal of nanotube templates used in fabrication of other structures [24]. Various oxidation methods have been examined in previous studies, including oxidation by acids [22], other oxides [15, 19, 23], and air, gaseous oxygen, or ozone [15, 18, 25, 26], with the objective of modeling nanotube oxidation chemistry.

Thermo-gravimetric analysis (TGA) of nanotube oxidation or, more specifically, temperature programmed oxidation (TPO), where oxidation leads to a
mass change, has shown to be a particularly useful technique for the characterization of CNT’s [20, 26-28]. Thermo-gravimetric analysis of oxidation provides information regarding the carbonaceous impurity content, residual catalyst content, and the crystalline defect density of the nanotubes in question. Differences in the reactivity of the various forms of carbon cause preferential burn-off at different temperatures. Defects in nanotube walls increase the local reactivity, leading to a lower-temperature oxidation and gasification of the carbon, and manifesting itself in the TGA mass-loss profile. TGA and TPO are generally regarded as bulk techniques, providing information about a large number of carbon nanotubes rather than individual tubes, thus yielding less risk when generalizing results to a large sample.

Ajayan and Iijima [21] first noted the removal of nanotube caps and the subsequent filling of nanotubes when heated in the presence of air and molten lead. Ajayan et al. [20] later confirmed the reaction between the nanotubes and air and observed that the tubes were opened exclusively at the caps. This study suggested a oxidation model for multi-walled nanotubes, wherein the caps oxidized first, followed by the “layer by layer peeling of outer layers.” Via ab initio calculations, Mazzoni et al. [29] confirmed the preferential oxidation of carbon atoms in the cap of a (6,6) nanotube over the oxidation of those in the wall, releasing a larger amount of energy due to the increased retained strain energy in the cap. However, structures used in these calculations were again idealized single-walled nanotubes, free of included defects other than pentagons in the tube caps. Shimada et al. showed that these results were inadequate to describe the oxidation of nanotube structures, and that defects in
nanotube walls such as cracks, vacancies, and dislocations play a significant role. Structural defects of this type are more reactive than pentagonal defects in a graphene sheet, potentially leading to the initiation of oxidation in nanotube walls rather than end caps [30].

2.1.3 Raman Spectroscopy

Raman spectroscopy has been used for qualitative and quantitative examinations of single- and multi-walled nanotubes. It is typically regarded as a bulk technique, but has been performed successfully on individual nanotubes as well [31]. The Raman fingerprint of nanotube structures is somewhat characteristic and consists of several distinct peaks (Figure 2-1).

A radial breathing mode appears between approximately 100 and 300 cm\(^{-1}\), but is usually only observed for SWNT’s. MWNT’s display this peak only when the innermost tubes have very low diameter (<1nm) [32]. The position of the radial breathing mode in the Raman spectra is highly sensitive to the nanotube diameter [31].

The D-band, at approximately 1350 cm\(^{-1}\), is associated with sp\(^3\) hybridized carbon bonding and disordering in the nanotube [31], while the G-band is a result of sp\(^2\) hybridized carbon bonding (the in-plane stretching mode for graphene sheets) and appears at approximately 1580 cm\(^{-1}\). The G’ band (sometimes referred to as the G*, D*, or D’ band) is the second order harmonic of the D band and appears in the realm of 2700 cm\(^{-1}\). Other higher order peaks occur in the neighborhood of the G’ peak as well, but are generally not useful for nanotube characterization. Each of these peaks
appear slightly offset from those observed for diamond or graphite due to curvature induced Raman shifts. Certain peak positions (e.g. D- and G’-bands) have some dependency upon the excitation wavelength.

Figure 2-1. Raman spectra of carbon nanotubes show several distinct and characteristic peaks including the D and G bands, associated with sp$^3$- and sp$^2$- hybridized carbon bonding, various higher order peaks (e.g. G’), and a peak associated with the radial breathing mode (RBM) of single-walled nanotubes [32].

The D- and G- bands are frequently compared to establish the ratio of sp$^3$ to sp$^2$ hybridized carbon as a measure of the purity and degree of structural perfection in the nanotubes [33-36], but it has also been suggested that a more accurate quality characterization may be obtained through comparison of the D and G’ bands [37]. Spectra for ideal nanotubes would reflect high G:D or G’:D peak ratios.
2.1.4 Other Characterization Techniques

Many other approaches have been applied to the characterization of individual or bulk carbon nanotubes and provide varying types and amounts of information, such as x-ray diffraction (XRD) [28], Auger electron spectroscopy (AES) [38], energy dispersive x-ray spectroscopy (EDS or EDX) [39], fourier transform infra-red spectroscopy (FTIR) [40], Mössbauer spectroscopy [41, 42], UV/Vis spectroscopy [32, 43], inductively coupled plasma spectroscopy (ICPS) [44], x-ray photoelectron spectroscopy (XPS) [45], and electron spin resonance (ESR) [46], but the three discussed above are the most significant and frequently used.

2.2 Refinement

Refinement of nanotubes involving the removal of non-nanotube carbon impurities such as amorphous carbon, other fullerenes, and graphite is possible through partial oxidation. Of course, oxidation progresses simultaneously among the various forms in a competitive manner, so only those structures less stable than nanotubes may be effectively removed in this way and nanotubes will usually be damaged in the process.

According to prior work [18, 26, 27], amorphous carbon and fullerenes may be removed in this way, but there exists conflicting evidence with regards to graphite. Bom et al. [26] report the oxidative stability of graphite to be higher than that of MWNT’s tested, provided both are in the same state of annealing, but thermogravimetric analyses by Saxby et al. [47] and Pang et al. [27] suggest a decreased
stability relative to nanotube forms of carbon. Significant work has also been done on the catalytic effects of transition metals upon the oxidation of graphite [48], however, very little has been performed with respect to the helical forms of carbon.

2.3 Nanotube Reinforced Composites

Due to their extraordinary mechanical properties, carbon nanotubes are of great interest in the field of structural reinforcement. However, challenges presented by the nature of their structure and extremely small sizes, as well as difficulties in synthesizing consistent, high quality nanotubes in large quantities have prevented their immediate adoption.

As synthesis difficulties are addressed and nanotubes become commercially available, more attention has focused upon the incorporation of nanotubes directly into a variety of matrices and the challenges arising from those processes. Accomplishing an even distribution of nanotubes within a composite matrix and transferring load between the matrix and nanotube reinforcements have proven to be difficult. Due to van der Waals interactions, nanotubes tend to form ropes and clumps with other nanotubes, reducing their interactions with the matrix and preventing the utilization of all nanotubes for bearing load in the composite. Also, creating a bond between the two materials is very much akin to trying to bond a material to the flat plane of a graphene sheet. Each carbon atom is sp²-hybridized, bonded to neighboring carbon atoms, and thus has only weak π-bonding available for interactions outside of the
graphene plane. As such, the nanotube-matrix interface frequently forms the ‘weakest link’ in nanotube composites.

This is exemplified in a 1994 study by Ajayan et al., where CNT-epoxy composites were cut into very thin layers [49]. Nanotubes were observed to pull out of a matrix and align themselves to the direction of the cut when slice thickness was less than ~1μm, simultaneously revealing the extremely impressive mechanical properties of the nanotubes as well as the equally impressive, though perhaps less useful, poor bonding between the nanotube and the matrix.

Frankland et al. performed several molecular dynamics simulations to examine the relationship between a composite and it’s reinforcement by nanotubes, emphasizing load transfer between the nanotubes and surrounding matrix [50]. Nanotube reinforcements were found to initially strain with a polyethylene matrix, then rebound and relax with no permanent stress transfer. Critical shear yield strength was calculated between the nanotube and the matrix and estimated to be ~0.7 MPa. By incorporating the hydrogen atoms into the estimation of shear yield strength, a higher value of 5 MPa was estimated. The model was then altered to have two cross-links per 2.5nm of nanotube length, improving the shear yield strength to 70 MPa. However, the drop in the tensile strength of the nanotube due to the introduction of these defects was not reported.

An equation estimating the critical length (l_c) for maximum load transfer is provided [50] as:
\[ l_c = \frac{\sigma_f d}{2\tau_c} \]  

(2.1)

Where \( \sigma_f \) is the tensile strength of the fiber, \( d \) is the diameter of the fiber, and \( \tau_c \) is the fiber-matrix shear yield strength. It should be noted that the critical shear stress and critical length are inversely proportional, thus improved bonding between fiber and matrix results in improved load transfer and decreased critical length. Given the poor bonding normally observed between nanotubes and a matrix, the significance of long nanotubes becomes obvious. Fibers longer than the critical length will fracture before pulling out of the surrounding matrix, providing maximum load transfer to the matrix and maximum reinforcement of the composite.

2.3.1 Unaligned Composites

2.3.1.1 Unaligned Polymer Matrix Composites

Other work with various unaligned, nanotube-polymer composites has been performed by various groups with varying results. Qian et al. homogeneously dispersed nanotubes within a polystyrene matrix before performing mechanical testing. A 1 wt% nanotube addition resulted in 36%–42% increase in elastic modulus and a 25% increase in the break stress. The authors noted that fractures initiated in areas of low nanotube density and tended to propagate along nanotube-polystyrene interfaces and relatively low nanotube density areas [51].

Schadler et al. examined load transfer between 5 wt% multi-walled nanotubes and an epoxy-resin matrix in tension and compression. The compression modulus was
observed to be increased relative to the tensile modulus, suggesting a difference in the load transfer mechanisms based on the nanotube loading. The authors proposed that in tension, load is transferred only to the outermost shell of a MWNT, while in compression, kinking, buckling, and the geometrical constraints of outer tubes allow for load transfer to an increased number of nanotube shells [52].

The stiffness of poly-vinyl alcohol-MWNT composites with varying nanotube content (0 – 60 wt%) was measured at various temperatures by Shaffer et al. in a 1999 study [53]. Fracture surfaces showed pull-out lengths on the order of 100nm compared to an overall average nanotube length of ~1.1 μm, suggesting fracture of the nanotubes prior to complete pull-out. Composites were prepared through evaporation of an aqueous solution and densities followed a linear rule of mixtures. In some cases, the presence of nanotubes was observed to retard the onset of thermal degradation of the matrix.

Deng et al. created polyaniline, 0-10 wt% nanotube composites through the in-situ polymerization of an aniline-nanotube mixture [54]. The nanotubes appeared to inhibit the onset of thermal decomposition of the polymer and conductivity was improved. While the results indicated the formation of polyaniline bridges between nanotubes, mechanical testing was not performed.

Composites for photovoltaic applications were synthesized by Ago et al. [55]. In this case, catalytically generated MWNT were spin coated with poly(p-phenylene vinylene), yielding a quantum efficiency of about twice that of a comparable ITO substrate. Nanotube content of the composite was limited to 0.5 – 2 wt%.
Large numbers of other studies have examined nanotube-polymer composites, utilizing a variety of polymers, synthesis methods and additives with varying results [56, 57]. In these studies, nanotube content ranged from 0.5 – 1 wt%.

2.3.1.2 Unaligned Metal Matrix Composites

Metal-nanotube composites have also been explored, but to a much smaller degree. Dong et al. examined the friction and wear behavior of a 0-25 vol% nanotube reinforced copper composite [58]. Kuzumaki et al. synthesized a 5-10 vol% nanotube-aluminum composite using a hot-press and hot-extrusion method [59]. Contrary to traditional aluminum-carbon fiber systems, no carbide formation was observed at the nanotube-Al interfaces. Tensile strength and strain at failure were observed to be comparable with pure Al, but, unlike pure Al, did not change significantly when annealed at high temperature. Other groups have also examined aluminum-nanotube composites, but with little focus on mechanical testing of the resultant materials [60-62]. Nanotube contents of these composites range from 1-10 wt%.

2.3.1.3 Unaligned Ceramic Matrix Composites

Ceramic-nanotube composites have experienced many of the same problems as other types of nanotube composites. Here also, dispersion of the nanotubes within the matrix without significant agglomeration and load transfer between matrix and nanotube continue to present significant difficulties.
Kealley et al. attempted to incorporate multi-walled nanotubes into hydroxyapatite (HAp) based ceramics through in-situ precipitation of HAp onto nanotubes. Nanotubes were introduced into an aqueous calcium nitrate solution and co-precipitated with ammonium hydrogen phosphate. The mixture was then dried and hot-pressed to form a sample for mechanical evaluation (unpublished at the time of this writing) [63]. Nanotube content of the composite was 2 wt%.

In many cases, nanotubes are dispersed in a surfactant solution before being mixed with a suspension of ceramic particles, then filtered, dried and pressed. Zhao et al. used this process to form HAp composites with up to a 61% improvement in compressive strength for 2 wt% nanotubes [64]. Fan et al. were able to improve the fracture toughness of a 12 vol% nanotube-Al₂O₃ composite by 80% by using an CNT-SDS solution, compared to only a 6% improvement when no surfactant was used [65]. Hwang et al. created SiO₂ rods with nanotube cores for reinforcement of ceramic composite discs (6 wt% nanotube), increasing hardness by 100% over a similar composite reinforced with SiO₂ rods without nanotube cores [66].

2.3.2 Aligned Composites

As nanotubes exhibit highly anisotropic properties, orientation of nanotubes within a matrix is of extreme importance. Given that composite matrices are typically the weakest link in a nanotube reinforced composite structure, increasing the nanotube content of a material should improve the mechanical properties as well.
The lack of results approaching the experimentally observed properties of carbon nanotubes and the lack of significant progress with the type of unaligned composites described above implies that other tactics utilizing larger proportions of nanotubes aligned in some fashion may be more fruitful.

A variety of experimental approaches has been attempted to create a macroscopic orientation of nanotubes within a composite matrix. Perhaps the most promising of these is the extrusion or spinning of such nanotube-matrix composites into fibers, wires, or threads.

### 2.3.2.1 A Brief History of Spinning

The spinning of fibers into threads and yarns is an ancient process, developed many thousands of years ago [67]. Early civilizations mastered the art and subsequently the weaving of threads into fabrics long before they began working with crude metals or using pottery wheels.

Early spinning was performed by hand, slowly and carefully, likely rolling the fibers along the thigh to bind them together. Tools and techniques were later developed to improve the quality of the yarn as well as the efficiency with which it was produced. An early innovation, spindles were simply the combination of a stick and a weight to carry angular momentum, easing the spinner’s work. Spinning wheels, the tools most people associate with spinning, were not developed until the middle ages (~1300 AD).
Spinning and textile industries were of great economic significance, and allowed countries that developed them to enter a significant international market. The beginning of the industrial revolution in America, for example, was due in large part to Eli Whitney’s development of the cotton gin [68], which allowed for the quick and easy separation of seeds from cotton bolls [69].

Cotton is only one of a large number of fibers used for spinning thread. Other common natural fibers used for textiles include wool, silk, nettle, and flax. Attempts have also been made to use spider silk due to its impressive mechanical properties [68], (abandoned due to spider cannibalism) and, more recently, synthetic fibers such as nylon, polyester, and carbon nanotubes.

2.3.2.2 Comparing Traditional Staple Fibers to Carbon Nanotubes

Cotton fibers derive from plants and have been used extensively in textile manufacture. The fibers are single cells and are shaped as flat, twisted ribbons (making them more conducive to spinning), frequently with a wax-like coating. Typical dimensions are ~20µm diameter by 25mm long, yielding an aspect ratio of ~1250 [67, 70].

Flax fibers, also botanically derived, have bamboo-like morphology, with filaments joined together by pectin. Typical dimensions for flax fibers are 50 – 500µm diameter by 300-900mm long: an aspect ratio range of roughly 600 – 18000 [67, 70].
Wool fibers are made up of keratin and are irregular, roughly cylindrical and multi-cellular. Cohesive quality of individual wool fibers is improved by the presence of 40-160 scales per millimeter of length, allowing mechanical interlocking. Typical dimensions are ~25µm by 25 – 75mm, yielding an aspect ratio of ~1000 – 3000 [70].

Silk fibers are smooth, solid and have a slightly irregular diameter. Two brin (fibers) are held together by fibroin and sericin to make up one bave (filament). The filaments are primarily protein and have dimensions on the order of 25 – 125µm by 350 – 1200m, giving them aspect ratios around $10^6$ [70]. This extreme aspect ratio may account for the fine texture for which silk fabrics are noted.

As these raw materials are usually obtained in tangled and intertwined clumps, they are usually “carded” or combed to align the individual fibers, making them more conducive to spinning.

Carbon nanotube dimensions vary significantly by tube type, purity, and synthesis methods. Very generally, CNT diameters vary from 0.4nm up to ~100nm (with larger diameters regarded as nano-fibers). Lengths range from several hundred nm up to many millimeters (at present), yielding potential aspect ratios from ~500 to more than $3.5 \times 10^6$. As such, the ratio of the physical dimensions and the mechanical properties of nanotubes appear to lend themselves to the manufacture of carbon-nanotube-staple threads of extraordinary strength and quality. At the same time, however, the physical dimensions prevent the application of the same techniques utilized for traditional staple fibers.
2.3.2.4 Mechanics of Yarns & Threads

Interest in yarns and threads is a direct result of the increased strength and durability observed in comparison with their component fibers. Load transfer between fibers accounts for most of these improvements. If a single fiber breaks under loading or when the end of an individual fiber is neared, the load carried by that fiber is transferred by frictional forces, chemical bonds, and/or mechanical interlocking to those fibers adjacent to it. The adjacent fibers experience increased local stresses over the distance required to transfer that excess load from and back to the separated portion of the original fiber or to the next fiber in the yarn before returning to a baseline distribution of local stresses (Figure 2-2).

Equation 2.1 may be used to describe the critical length for fibers in a yarn, if the surrounding fibers are considered to make up the matrix and load transfer occurs between adjacent fibers.

A general relation between the strength of individual fibers and the strength of a spun yarn made up of those fibers is provided in Equations 2.2 and 2.3:

\[
\frac{\sigma_y}{\sigma_f} \approx (\cos^2 \alpha)[1 - k \csc \alpha] \tag{2.2}
\]

where

\[
k = \frac{\left(\frac{dQ}{d} \right)^{\frac{1}{2}}}{3L_f} \tag{2.3}
\]

\(\sigma_y\) and \(\sigma_f\) are the yarn and fiber tensile strengths, respectively, \(\alpha\) is helix angle of fiber to yarn axis, \(\mu\) is the coefficient of friction between fibers, \(L_f\) is fiber length, \(d\) is fiber...
diameter, and Q is fiber migration length or the distance along the yarn over which the fiber migrates from the surface to the deep core area and back again [71]. This approach assumes that the yarn diameter and fiber packing density are held constant.

Figure 2-2. Example of idealized load transfer between two adjacent fibers in a yarn. Arrows represent relative loading on fiber segment. A) Initially, two fibers (fibers 1 & 2) in a yarn share an equally distributed local tensile pressure. B) Upon fracture of one fiber (fiber 2), excess load is transferred to adjacent fibers (e.g. fiber 1) which is subject to increased local stress and will undergo additional strain. The adjacent fibers are loaded only in the local proximity of the fractured fiber before load is equilibrated again. This mechanism also applies to the ends of individual fibers. Adapted from [71].
Equation 2.2 may be analyzed in two separate parts: in terms of the \((\cos^2 \alpha)\) portion, and in terms of the \([1 - k \csc \alpha]\) portion. Since both terms are multiplied to yield the final strength ratio, both define upper limits to the strength possible for a given fiber configuration.

The first term describes the decrease in the strength of the yarn with increasing angle of twist resulting from the off-axis loading of the component fibers comprising the yarn. The behavior of this term is plotted versus twist angle in Figure 2-3, as the dashed line.

However, as Zhang et al. point out, there is little strength in the case of short fibers without twist, as there are no transverse forces to bind the fibers together [72]. The second term, \([1 - k \csc \alpha]\), describes the creation of transverse forces, which bind the individual fibers together. In Figure 2-3, k is assumed to be constant and this second term is plotted as the dotted line. However, it should be noted that Q, and thus k, is not entirely independent of the twist angle \(\alpha\). The value of this second term approaches \((1 - k)\) as \(\alpha\) approaches 90°.

The value of k is primarily a result of the fibers used in the yarn whereas the twist angle is a result of the spinning process itself. With smaller values of k, the maximum strength ratio is approached at lower twist angles and as a result, will be larger, as is shown in Figure 2-3. For example, when \(k = 0.005\), the optimum yarn strength of 94.5% the fiber’s strength occurs at \(~7.1^\circ\) twist. When k is increased by an order of magnitude, the maximum strength ratio drops to 74.5% of the fiber’s strength and occurs at \(~17.5^\circ\) twist. Values of k vary inversely with fiber length and
proportionally with the square roots of both the fiber migration length \((Q)\) and the fiber diameter \((d)\). Hence, longer fibers and smaller migration lengths and fiber diameters will improve the maximum theoretical strength of the yarn.

Figure 2-3. Behavior of equation 2.2 with changing twist angle \(\alpha\), with the component terms’ individual behaviors. Dashed line represents the \((\cos^2 \alpha)\) term. Dotted lines represent the \([1 - k \csc \alpha]\) term with differing values for \(k\). With lower values for \(k\), the maximum theoretical strength is higher and occurs with a lower twist angle. Adapted from [71].
2.3.2.5 Wet-Spun Carbon Nanotube Fibers

Several research groups have attempted to create either exclusively-nanotube fibers or nanotube-reinforced fibers by several methods. In a 2000 paper, Haggenmueller et al. reported on the synthesis of a PMMA-SWNT composite fiber through melt-spinning and extrusion. PMMA and 1-8 wt% HiPCO-generated SWNT were sonicated in di-methyl-formamide (DMF) and dried in Teflon dishes to form composite films. The films were then broken apart and re-pressed together under elevated temperature and pressure. This process was repeated up to 30 times, yielding a homogeneous mixture, which was extruded through a 600 micron spinneret. The elastic modulus was found to increase with nanotube content and increased somewhat as the ratio of the spinneret size to the drawn fiber size increased [73].

Gommans et al. reported on an electrically-induced coagulation of SWNT’s dispersed in DMF to form pure nanotube fibers and performed extensive Raman analyses [74]. A carbon fiber suspended from an electrically-isolated pin vice was positively charged (~1-2V) relative to a platinum electrode and both were immersed in a low concentration (~0.01mg/mL) SWNT-DMF solution. After sitting for 10-30 minutes, a cylindrically symmetric cloud of nanotubes was observed to form around the positive electrode. As the fiber was withdrawn from the solution, an agglomeration of nanotubes formed spontaneously onto the end, held together by surface tensions and nanotube entanglement, similar to the way a tangled string of seaweed might be extracted from the surface of the ocean. Selected area electron
diffraction pattern analysis suggested the majority of the nanotube ropes lay within ~25° of the fiber axis.

Vigolo *et al.* created a relatively simple method for nanotube-fiber synthesis, which has been adopted by several other research groups with impressive results. As initially designed and performed by this group, the method involves the suspension of 0.35 wt% nanotubes in a 1 wt% aqueous sodium dodecyl sulfate (SDS) solution, which is then injected into a slowly spinning bath of 5 wt % polyvinyl alcohol (PVA) [75]. When dried, the fiber diameter collapses to a few microns and the overall anisotropy and alignment of the nanotubes relative to the fiber axis appeared to decrease somewhat, but still exhibited an overall preferential orientation. The Young’s modulus for these fibers varied between 9 and 15 GPa. Interestingly, nanotubes used in this report were from arc-discharge synthesis and not purified, meaning they contained a significant fraction of carbonaceous impurities. Upon drying, however, the nanotubes and impurities segregated themselves into different regions of the fiber: nanotubes concentrated in the core, while impurities tended to form a shell.

Dalton *et al.* reported improvements upon the process in 2003 [76], and Muñoz *et al.* elaborated upon them in 2004 [77]. High quality HiPCO nanotubes were used instead of the more impure arc-discharge SWNT’s and lithium dodecyl sulfate (LDS) replaced SDS. Further processing of the wet fibers was added to improve the drying process without extracting the PVA, including passing the wet fiber through acetone and drying baths. By this method, this group reported that the resultant 60 wt%
nanotube fibers could be drawn up to five times their original length. A modulus of 80 GPa and ultimate tensile strength of 1.8 GPa were reported, as well as an energy to break (toughness) of ~600 J/g.

Polymer free nanotube fibers were reported in 2005 by the same group using another modification of the Vigolo et al. method. Instead of a PVA coagulation bath, this report used a concentrated 37% HCl bath. The gel fibers were then washed in methanol to remove residual HCl and then dried under tension. The spun fibers exhibited a specific stress of 65 MPa/(g/cm$^3$), Young’s modulus of 12 GPa/(g/cm$^3$), and a strain to failure of ~1%, suggesting a low degree of mechanical coupling between the as-spun nanotubes [78]. Subsequent intercalation of PVA into the as-spun fibers increased their tensile strength and strain to failure significantly, but not to the extent of the fibers from [76, 77].

Polymer-free nanotube fibers were also synthesized by Steinmetz et al. in 2005, again using modifications on the Vigolo et al. method. Arc grown nanotubes were suspended in an aqueous-SDS solution then injected into a coagulation bath of ethanol and either glycerol or glycol using mix ratios chosen to maintain a consistent density between the nanotube suspension and the coagulation bath. The authors noted that while wet, the fibers remained flexible and the morphology could be altered. Upon drying, the fibers became brittle and shrank to approximately 20-30 μm in diameter. Nanotube alignment was rather poor, varying up to 60-70° from the fiber axis. Young’s modulus was measured on the order of 2 GPa and strain at fracture was 4.5% [79].
Utilizing a method for the dispersion of nanotubes through protonation in a super-acid [80], Ericson et al. reported on the spinning of polymer-free nanotube fibers from 102% H₂SO₄ (2% excess SO₃). Raw materials were combined in a nitrogen-purged dry box to create a homogeneous mixture, while preventing the introduction of any additional water. Mixing occurred through alternating pneumatic cylinders, which pushed the mix through a shear cell within an evacuated housing. Extrusion was performed into several different baths, including diethyl ether, water, and dilute sulfuric acid. Ericson et al. noted that the latter two baths resulted in better structures than the former and suggested the rate at which the sulfuric acid is extracted may play a significant role in the resulting fiber [81].

2.3.2.6 Direct-Spun Carbon Nanotube Fibers

Direct synthesis of nanotube fibers and strands, where fibers are drawn straight from the synthesis furnace, has been reported by Zhu et al. [82] and Li et al. [83] using two different techniques. The first, described in a series of papers in 2002 [82, 84, 85], uses self-assembly of SWNT’s in a vertical CVD furnace under certain synthesis conditions. Generally, n-hexane, ferrocene and thiophene are combined and flown through a furnace held at 1423 K with a hydrogen carrier gas (250 mL/min). The SWNT’s form and agglomerate naturally into ropes or bundles, which continue to agglomerate into macroscopic strands. The authors report typical dimensions of 0.3 – 0.5 mm diameter and an average of ~20cm length. The process may be performed continuously, synthesizing ~0.5g/hour of SWNT strand lengths [82]. Increased
thiophene content or rate of introduction of the feedstock into the furnace results in larger diameter strands (~1mm) [84]. Characterization of the strands indicates good alignment of the nanotube bundles within the strands over centimeter lengths [85]. Tensile yield stress and Young’s modulus were measured as approximately 700 – 900 MPa and between 49 and 77 GPa, respectively. However, because the structures contain roughly 50% open space, the true modulus may be higher by a factor of two.

The second method also utilizes a vertical furnace arrangement, but instead of exclusively single-walled nanotubes self-assembling, an aerogel of SWNT and MWNT is generated and extracted. CVD of an oxygen-containing hydrocarbon (e.g. ethanol, diethyl ether, polyethylene glycol, 1-propanol, acetone, etc), along with ferrocene and thiophene in a hydrogen carrier gas creates the aerogel, which increases density with decreasing temperature. This may be continuously drawn from the reaction zone by winding it onto a rod introduced into the hot zone (leading to spun fibers), or by winding it onto a spindle at the base of the reaction chamber (leading to aligned, but not spun fibers) [83]. Aromatic hydrocarbons were also examined for use as a carbon source, but were found to lead to carbon particles, thick fibers, or both, and did not enable the sustained spinning of fibers unless mixed with an oxygen-containing molecule. Once sustained spinning of the fiber was achieved, the hydrocarbon used as feedstock did not appear to have significant impact in determining the fiber properties [86]. Hydrogen content was also found to affect the precipitation of non-nanotube carbon impurities, with higher hydrogen concentrations
serving to prevent these formations. Fiber cross sections were non-uniform and varied between 10 – 100 μm.

Mechanical testing of the fibers revealed a low-modulus initial region in stress-strain curves [86]. The authors assume that this region corresponds to further orientation of the nanotubes in the fibers and is analogous to that observed in as-spun polymer fibers before drawing. A similar, but smaller feature is apparent in the stress-strain curves presented by Zhu et al., but is not noted in the paper’s text [82]. Mechanical analysis of the fibers indicated strengths in the range of 0.1 to 1.0 GPa with a strain to failure of up to 100% upon initial loading. Fiber strength versus iron concentration plots suggest lower catalyst concentrations led to stronger fibers, which is unusual as Bai et al. indicate that lower catalyst concentrations lead to larger diameter nanotubes [87]. It is possible that the improved strength is a result of an increased proportion of SWNT’s and DWNT’s in the fiber, but as the fiber properties do not yet approach the theoretically or experimentally observed properties of individual nanotubes, it is more likely that the differences arise from variations in the tube organization within the fibers, possibly having to do with the number or density of catalyst particles and impurities decorating the outsides of the individual nanotubes.

2.3.2.7 Dry Spun or Drawn Nanotube Fibers

At this time, three research groups have succeeded in drawing or spinning threads from aligned mats of carbon nanotubes after synthesis. The first report on this accomplishment, by Jiang et al., described the self-perpetuating drawing of nanotubes
off what was described as a “super-aligned” nanotube array [88]. The process was later described in more detail as remarkably similar to other catalytic CVD processes [89, 90]. The resulting nanotube arrays, however, were capable of being drawn off into fibers with minimal encouragement. The report did not describe any twisting of the fiber as it was drawn from the array, but as-drawn fibers were observed to be very sticky and would become permanently attached to anything they came into contact with. By passing the fiber through an ethanol droplet, the stickiness could be ameliorated, allowing the fiber to be wound onto a spool.

Zhang et al. created similar spun yarns in the way that one might spin cotton into thread [72]. Here, as well, aligned arrays of nanotubes were synthesized by catalytic CVD of acetylene over a silicon wafer substrate with a 5nm iron film to serve as a catalyst. The spinning process consisted of hand-winding part of the nanotubes around a toothpick, then mechanically spinning the toothpick at approximately 2,000 rpm with a rotary motor.

Li et al. reported the synthesis of ultra-long arrays of carbon nanotubes by catalytic CVD synthesis of ethylene over a 0.3 – 1.0nm iron thin film. The longest array length achieved was 4.7mm over a two hour growth, with a small amount of water vapor added to prevent amorphous carbon deposition, however arrays between 0.5 – 1.5mm in length were most favorable for spinning [91]. Perhaps the most interesting result in this report was that arrays grown without the addition of water vapor were more conducive to spinning than those grown with water. Threads formed from the arrays were not discussed in detail.
In the first two cases, the width of the array’s sidewall used to initiate the drawing or spinning process determined the number of nanotubes included within the yarn and thus the dimensions of the resulting fibers.

Using a process similar to that of Jiang et al. [88], Zhang et al. were able to create wide sheets of carbon nanotubes, drawn from aligned arrays [92]. Here, the entire edge of a nanotube array was pulled, leading to the formation of a semi-transparent, quasi-two-dimensional array.

The mechanism by which nanotubes continue to draw adjacent nanotubes off the array and into the fiber is the subject of some discussion. Zhang et al. suggest that intermittent bundling within the nanotube array is important and that disordered areas at the top and bottom of the arrays may assist in maintaining continuity of the threads [92]. Zhang et al. note, however, that while their arrays contained disordered regions at the tops, no disordering was present near the bottoms, so that while the disordered entanglement may assist in the formation of a yarn, it is not prerequisite [90]. Instead, nanotubes were observed to remain attached to those adjacent to them when the surface of the array was neared, causing the adjacent nanotubes to be pulled off, thereby continuing the yarn formation like stretching a piece of accordion-folded paper (Figure 2-4). Li et al. also report that nanotube arrays with curved, intertwined nanotubes are not conducive to spinning [91].

Mechanical testing by Zhang et al. yielded maximum strengths of spun yarns in excess of 460 MPa [72]. Annealing (in air) by passing an electric current through a fiber caused a slight decrease in the observed tensile strength (attributed to partial
oxidation) and an increase in the Young’s modulus by a factor of two [90]. Under vacuum, the same electrical annealing was observed to increase the tensile strength ~6.4 times [88].

Figure 2-4. Proposed by Jiang et al., nanotubes pulled from a “superaligned” array remain stuck together near the surface and base of the array, allowing their drawing into long nanotube yarns [88].

2.4 CVD Synthesis Considerations for Nanotube Spinnability

While CVD synthesis of carbon nanotubes is probably the simplest of nanotube growth methods in terms of equipment and setup, there is considerable complexity when it comes to establishing control over nanotube products. As noted earlier, only three groups have created aligned arrays of nanotubes conducive to spinning, indicating the difficulty of the task. This section examines identified controlling variables of the CVD process, then examines the synthesis conditions used by those three groups.
2.4.1 Process variables

2.4.1.1 Synthesis Temperature

The CVD furnace temperature used for synthesis varies considerably from one research group and synthesis process to another. Synthesis is typically accomplished from ~600°C up to ~1200°C [93-96], but exceptions occur outside this range as well [97-100]. Nanotubes grown at different temperatures show vastly differing structure and quality. However, very few of the multitudes of synthesis groups actually produce carbon nanotubes conducive to spinning.

2.4.1.2 Synthesis atmosphere

The atmosphere within the furnace during nanotube growth is quite possibly the most important factor as well as the most difficult to control precisely. It is a combination of factors, including the choice of carbon source, the choice of carrier gas(es), the ratio of the carbon source to the carrier gas, the pressure at which growth occurs, the total flow rate through or residence time within the growth zone, and the potential addition of purifying components. That many reactions can and will occur between each of these components only complicates the question further.

2.4.1.2.1 Carbon source

A large variety of carbon sources have been used in the CVD synthesis of carbon nanotubes. Common carbon sources include ethanol [99, 101], methanol [101], methane [93, 102-106], ethylene [91, 104, 107-109], acetylene [93, 110-114],...
cyclo-hexane and n-hexane [82, 99, 115], benzene [87, 95, 96, 116, 117], toluene [116, 118, 119], and xylenes [116, 120-122]. Other sources are sometimes used as well [116, 123].

Each carbon source has its own characteristics in the furnace. Fortunately, there has been some research into the topic of hydrocarbon behavior at high temperature due to their extensive use in petroleum refining. For example, the homogeneous gas phase reaction of methane to ethane, ethylene, acetylene, benzene, and larger polyaromatic hydrocarbons is documented [124].

Of particular interest for nanotube synthesis is the rate at which each hydrocarbon deposits carbon during growth. Tesner [125] cataloged pyrolytic carbon deposition rates for a number of hydrocarbons over relevant temperature ranges for the scientist performing nanotube growth.

### 2.4.1.2.2 Carrier gas(es)

Carrier gases in CVD synthesis of carbon nanotubes are usually noble, non-reactive species, which serve to dilute the carbon source to acceptable levels, thereby controlling the amount of hydrocarbon present in the furnace at any given time. Typical carrier gases include argon or helium. Nitrogen has been used, but may become reactive at higher synthesis temperatures.

Hydrogen is frequently used, but should not be considered a carrier gas as it plays a role in controlling hydrocarbon decomposition reactions. Hydrogen is discussed further in Section 2.4.1.2.5.
2.4.1.2.3 Furnace Pressure

Due to the additional challenges associated with operating a high temperature furnace at high or low pressures, CVD synthesis is typically performed at atmospheric pressure. Altering the operating pressure allows some control over the partial pressure of the synthesis hydrocarbon, and thus the carbon deposition rates.

2.4.1.2.4 Total Flow Rate or Residence Time

As discussed in Section 2.4.1.2.1, the choice of carbon source has significant influence on the rate at which carbon is deposited in the furnace. However, the rate at which the carbon source is introduced into the furnace is also significant. This is determined by the mix ratio of the carbon source and carrier gas as well as the total flow of the mixture into the furnace. The total flow also determines the residence time of the carbon source in the furnace.

Benzinger et al. have shown that methane, ethylene, acetylene, and benzene have significantly different carbon deposition behaviors as a function of residence time within a furnace (Figure 2-5) [124]. Methane was found not to form carbon directly, instead reforming into ethane, ethylene, or acetylene (referred to as C$_2$ hydrocarbons) as described previously (solid line, Figure 2-5). While the C$_2$ hydrocarbons can deposit carbon directly, they also will undergo reforming reactions (dashed line, Figure 2-5), yielding benzene, which will form significant amounts of carbon directly and was found to be the primary carbon contributing species (dotted line, Figure 2-5). As such, methane and the C$_2$ hydrocarbons show an increase in
carbon deposition rate with increasing residence time until a peak rate is reached, after which the deposition rate will drop off. Benzene, on the other hand, will begin depositing carbon at its highest rate immediately, dropping off as the benzene is consumed. Thus, the residence time of the carbon source must be matched carefully with the carbon source selection.

![Figure 2-5](image.png)

**Figure 2-5.** Normalized carbon deposition rates of methane (solid line), ethylene and acetylene (dashed line), and benzene (dotted line) as a function of increasing residence time in the CVD furnace [124].

2.4.1.2.5 Reactive Gases

In addition to hydrocarbon and carrier gases, other gases are frequently added to the furnace environment for various purposes. Hydrogen is noted to prevent or limit carbon deposition [125-127], although whether by inhibition of decomposition or by blocking deposition sites is unclear, and may also serve to limit oxidative activity of water vapor. Water vapor has been utilized as a weak oxidizer at synthesis
temperatures for the in-situ removal of non-nanotube carbon or to prevent poisoning of the catalyst [91, 128]. Ammonia has also been used as an etching gas during chemical vapor deposition of nanotubes [38, 114], but has found more use in the pre-synthesis treatment of catalysts [113, 129].

2.4.1.3 Catalyst

The selection of the catalyst species is typically limited to cobalt, nickel, or iron [91, 93, 103, 109, 112-114], but binary alloys, particularly combining one of the above with molybdenum, have been seeing increased usage in recent years [93, 104]. During synthesis, the carbon source is thought to decompose on the catalyst, diffuse across the surface or be absorbed into the catalyst particle, then precipitate as a nanotube structure. Catalyst introduction for CVD synthesis is usually done in one of two ways.

In the first, a thin film (typically up to ~5nm) of the catalyst is deposited onto a substrate through sputtering, electron beam evaporation, or another method. The thickness of the catalyst film influences the final catalyst particle size, which, in turn, is understood to correlate to the diameter of nanotubes growing therefrom. In combination with lithographic patterning, the deposition arrangement of the nanotube arrays may be controlled, making the method very useful for applications requiring such precision [130].

The second method, floating-catalyst CVD, introduces the catalyst into the furnace as a vapor, frequently simultaneously with the carbon source [87, 99, 108,
Ferrocene is the most common catalyst source when using this method, likely due to the significant price difference between it and other organometallics and its relatively high solubility in aromatic hydrocarbons. The ferrocene is frequently dissolved into the carbon source and the two co-evaporated into the growth zone. The concentration of the catalyst precursor in the carbon source is thought to play a role in the resulting size of catalyst particles and therefore nanotube diameters.

2.4.1.4 Substrates

The substrate can be anything that the nanotubes deposit upon in the CVD furnace. In some cases (FC-CVD), the entire inside of the furnace acts as a deposition substrate. Typical substrate materials include silica, either thermally oxidized [93, 132] or bulk (quartz) [111, 117, 131], silicon wafers [112, 114, 133], and alumina [91, 104, 111], usually as a thin film on silicon, although others have been examined for various purposes [108, 111].

It has been noted that nickel and iron catalysts deposited directly onto silicon wafers will form silicides (FeSi$_x$ or NiSi$_x$) at synthesis temperatures [103, 112, 113]. For this reason, the use of barrier layers has been widely adopted when a silicon wafer is the primary substrate (frequently favored due to its smooth surface and amenability to lithographic techniques) [38, 91, 104, 107-109, 112, 114, 132].

Beyond being a support for catalysts and nanotubes, interaction between substrate and catalyst plays a significant role in synthesis. Whether catalyst is
introduced as a thin film or in the vapor phase, there is typically interaction between the catalyst particle and the substrate prior to formation of nanotube structures. These interactions have been the topic of several investigations [108, 109, 111, 113], and alumina has been noted as a promising substrate candidate in varying synthesis conditions [104, 108], but the relationship remains poorly understood.

Several mechanisms have been proposed, which might affect catalyst mobility on the substrate, including substrate surface roughness [93], catalyst oxidation, either by atmospheric exposure, thermal oxidation [110], or reduction of the substrate [109], or direct chemical interaction between catalyst and substrate [109, 111-113].

Surface roughness is thought to act as a physical barrier to surface diffusion, causing collection of catalyst material in valleys. Formation of catalyst oxides has been observed in nanotube synthesis [108], and is thought to act as a pinning mechanism, preventing agglomeration of the catalyst into large particles [102, 110, 134].

Strong interactions between catalyst and substrate have been suggested to both inhibit and promote proper catalyst particle formation. Seidel et al. suggest strong interactions prevent the catalyst particles from forming shapes appropriate for CNT growth [93]. On the other hand, Vander Wal et al. suggest that strong catalyst-substrate interactions promote electron transfer between the substrate and catalyst through catalyst interactions with cationic sites on the substrate (referred to as SMSI, or Strong-Metal Support Interaction) or with oxygen anions, acting as Lewis base sites [111].
2.4.1.5 Growth Time

The growth time is simply the time over which the reaction is allowed to progress. Generally, nanotube lengths increase with increasing growth times until catalyst poisoning occurs for a variety of reasons. Because of catalytic poisoning, growth times, and thus nanotube lengths, remain relatively short.

2.4.2 Known Spinnable Nanotubes

2.4.2.1 Jiang et al. and “Super-aligned Nanotube Arrays” [88-90]

From images presented in these reports, nanotubes generated by these processes appear to be 10-15 nm in diameter and form arrays up to 500µm long.

The CVD process used by this group was performed at atmospheric pressures and at low pressures (~260 Pa) with similar results. The temperature, gas composition and gas introduction rate differ slightly for the two processes. In both cases, CVD was performed using acetylene gas. Iron films, from 3.5 – 5.5nm thick, were e-beam deposited at very low deposition rates (typically 0.1Å/s) in order to achieve a high density film. Arrays were successfully grown on silicon, thermally oxidized silicon, and quartz substrates. Porous silica was noted to provide poor arrays. Several carrier gasses were used, including argon, helium, nitrogen, and hydrogen, though mixing of the carrier gasses is not noted.

In order to limit the amount of carbon being deposited in the furnace, the partial pressure of acetylene was kept very low. For example, in a 25mm tube furnace used at atmospheric pressure, 425 sccm argon was combined with 12 sccm acetylene.
Temperatures for atmospheric pressure synthesis were between 620 and 700°C. With low pressure CVD, low partial pressures are assured, so the proportion of acetylene in the gas flow may be increased. In this case, a 100mm tube furnace was used with a gas mixture of 500 sccm acetylene and 50 sccm hydrogen. Low pressure synthesis was carried out between 680 and 720°C.

2.4.2.2 Zhang et al. [72, 92, 135]

Nanotubes presented in these reports are arranged in well-aligned arrays, show diameters between 8 and 15 nm, and lengths (array heights) of approximately 100 - 200 µm.

Synthesis was carried out in a 45mm diameter quartz furnace tube held at 680°C. Acetylene served as the carbon source, and was mixed with helium in a 5% mole ratio. This gas mixture was introduced into the furnace at approximately 580 sccm (thus, approximately 30 sccm acetylene and 550 sccm He) over a 10 minute growth period. A 5nm iron thin film, e-beam deposited on a silicon wafer, served as a catalyst source. No barrier layer is mentioned in the articles.

2.4.2.3 Li et al. [91]

Nanotubes generated by this group are reported as multi-walled, with less than 8 walls, averaging 10nm in diameter, and in well aligned arrays up to 4.7mm in length. However, it is noted that only nanotubes grown without water vapor are favorable to spinning, and then only when lengths range from 0.5 – 1.5 mm.
CVD synthesis of the arrays was carried out in a 25mm diameter tube furnace at temperatures less than or equal to 750°C. Ethylene, as the carbon source, was introduced at 100 sccm. A mixture of 94% argon and 6% hydrogen was introduced as a carrier or “forming” gas at 100 sccm for a total flow rate of 200 sccm. Growth of arrays conducive to spinning occurred over 10-15 minute periods. Longer arrays could be grown using longer growth periods, but these did not lend themselves to spinning. Iron catalysts are sputter deposited as a thin film (0.3-1.0nm thick) onto a 10nm IBAD (ion beam assisted deposition) deposited alumina layer on a silicon substrate.

2.4.3 Theoretical Criteria for Spinning

Throughout Section 2.4.2, certain synthesis variables appear to remain relatively consistent: synthesis temperatures appear to have a limited range around 700°C; ultra-smooth substrates are utilized in each case; and carbonaceous impurities are detrimental to spinning. As such, certain criteria appear to be necessary in order for arrays of nanotubes to be spun in the manner these groups have pioneered [72, 88, 91].

Perhaps of greatest importance is the maximization of van der Waals interactions between adjacent nanotubes through elimination of all impurities. Nanotubes must be clean and smooth. Van der Waals forces act over very small distances and are inversely proportional in strength to the distance over which they act, falling off very rapidly.
Any impurities adhering to the sides of the nanotubes will cause an increase in the separation distance between nanotube walls. This applies to carbonaceous impurities, such as amorphous carbon or fullerenes as well as any other particulate matter that may be present, such as catalyst nanoparticles. Ideally, clean tubes will lack these particles and allow for contact between adjacent tubes for maximum van der Waals attractions.

Nanoscale smoothness in sidewalls follows similar reasoning. Surface roughness prevents lamination of nanotube surfaces, creating voids and spaces between adjacent nanotube walls. If the walls are perfectly smooth, the nanotubes may lie in contact with each other along the entire length, maximizing the surface area involved in bonding. It may be argued that nanoscale roughness could serve as a mechanism for load transfer between tubes, allowing for interlocking of peaks and valleys under stress. While this may be the case (but has not been verified), it will still inhibit the ideal packing of nanotubes and thus the formation of a nanotube thread.

Nanotube diameters should be in the low to moderate range. Each report of spinnable nanotubes describes diameters of less than 15nm. Thinner nanotubes are expected to exhibit improved flexibility due to fewer walls and a commensurately lower modulus, allowing more migration of the individual fiber through the thread and an increase in overall toughness. Also, a larger proportion of the nanotube structure should engage in van der Waals bonding compared to larger diameter tubes.

Consider the geometry in Figure 2-6, where \( r \) is the radius of a nanotube and \( \ell \) is half the maximum distance over which van der Waals interactions may be expected
to create a relevant attractive force (the half-distance of separation between two adjacent, equivalent nanotubes), the angle of the wall arc, $2\theta$, within $2\ell$ of an adjacent nanotube may be calculated using Equation (2.4). If $\ell$ is specified, the percentage of the wall angle ($2\theta/360$) available for interaction as a function of the tube radius, $r$, may be easily observed. The percentage of the total arc within the van der Waals interaction half distance $\ell$ drops precipitously with increasing nanotube radius (Figure 2-7, dashed line).

$$\theta = \cos^{-1}\left(\frac{(r - \ell)}{r}\right)$$  \hspace{1cm} (2.4)

Figure 2-6. The geometry around a nanotube for consideration with Equation (2.4). Where $r$ is the nanotube radius and $\theta$ is the half angle of the wall arc within the half distance $\ell$ of an adjacent nanotube.

Given the smallest normally observed single walled nanotube diameter of 0.7 nm, it is calculated that 64.1% of the overall nanotube arc is within 1nm of an adjacent, equivalent nanotube. If the nanotube diameter is doubled to 1.4nm, 40.8%
of the overall arc is within the same distance of an adjacent, equivalent nanotube. When a 10nm multi-walled nanotube is considered, only 14.4% of the overall arc is within 1nm of an adjacent, equivalent nanotube.

Ideally, a single tubule would be surrounded on all sides in a 2-D hexagonally close-packed array of nanotubes. Thus, the arc portion with sufficient proximity to an adjacent nanotube may be increased by a factor of six, yielding a much higher total percentage and less precipitous decrease with increasing diameter (Figure 2-7, solid line).

The last criterion is that nothing should bind the array together aside from the van der Waals forces between individual tubes. If each nanotube is to pull a second from the array, maintaining the continuity of the spun thread, the subsequent nanotube must not be held in place with greater strength than the strength of the forces attaching it to the pulling tube. If this is the case, the tube being pulled will be separated from the array without drawing adjacent tubules from the array.

Other carbonaceous deposits may serve to pin the tips of the nanotubes, preventing their easy removal and thus impairing their spinnability. Any such mechanism or impurity anchoring the array to the growth substrate or conjoining the surface of the array would severely impair sequential nanotube removal and the spinnability of the nanotube array.
Figure 2-7. The behavior of Equation (2.4) for a van der Waals interaction distance ($2\ell$) of 1nm: variation of the percentage of nanotube wall arc within a set distance of a single, adjacent nanotube (dashed line) and within the same set distance in a hexagonally close packed array (solid line) of adjacent, equivalent nanotubes given the radius of the nanotubes in question.

These requirements serve to reduce the distance between adjacent tubules over which the forces act, increase the relative area which may be included in interactions, and eliminate anything that could prevent the continuous drawing of nanotubes from the array.
2.5 Summary of Research Objectives

This research aims to develop enhancements to the structure and arrangement of carbon nanotubes to improve their ability to be drawn into threads or yarns, and to improve the quality of those yarns once formed. The research objectives are to:

- Retain aligned arrays of nanotubes,
- Improve nanotube stability,
- Increase nanotube lengths,
- Reduce nanotube diameters,
- Eliminate amorphous carbon deposits on the nanotubes,
- Eliminate or prevent crust formation on nanotube arrays,
- Demonstrate synthesis of nanotubes capable of being spun.

By accomplishing these objectives and understanding how they were achieved, the field of knowledge regarding the synthesis, purification and manipulation of carbon nanotubes for spinning into threads or yarns will be significantly advanced.

2.6 References


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3. **Thermo-Gravimetric Analysis of Synthesis Variation Effects on CVD Generated Multi-Walled Carbon Nanotubes**

3.1 **Summary**

Changes in the thermo-gravimetrically determined oxidation behaviors of CVD-grown multi-walled carbon nanotubes with varying synthesis conditions are examined. Catalyst type and synthesis temperature are found to have a measurable impact upon nanotube stability, suggesting differing levels of crystalline perfection in the resulting nanotubes. The results provide evidence showing the catalytic effects of nanotube catalyst particles and their oxides upon the oxidation of nanotube carbon and graphite. The significance of thermo-gravimetric analysis as a characterization tool for carbon nanotubes is discussed.

In this set of experiments, the thermo-gravimetric oxidation profiles of various forms of carbon and nanotube synthesis byproducts are compared to those of CNT’s grown via Chemical Vapor Deposition (CVD) with varying synthesis conditions in an attempt to further illuminate and optimize the generation of nanotubes and clarify the characteristics of their oxidation. The profiles are further compared with those obtained by several other research groups and reasons are suggested for the differences. The effects of catalyst type on the temperatures and rates of oxidation are compared and comparisons drawn between their effects on graphite versus that on CNT’s.
3.2 Experimental

The carbon nanotubes examined in this study were prepared through the pyrolytic decomposition of benzene with an organo-metallic or metal chloride catalyst precursor in a CVD furnace as shown in Figure 3-1. Nanotube growth temperatures, catalyst precursors (ferrocene, nickelocene, cobaltocene, NiCl₂, CoCl₂), and carrier gas flow rate (low and high rates of flow) were varied during synthesis, as described in Table 3-1, to elucidate oxidative differences in the resulting nanotubes.

Figure 3-1. Schematic of complete CNT growth setup.

In the case of the low carrier gas flow rate experiments (herein referred to as “low-flow samples”), CNT synthesis began with the initiation of the argon carrier gas through the reaction chamber at the rate of approximately 90 to 280 sccm while the furnace heated to the set temperature. Once at temperature, a mixture of the carbon source and catalyst precursor was introduced. The solution was collected in a crucible inside a quartz furnace tube and vaporized by the heat of the furnace. The vapor then entered the furnace where nanotubes deposited onto a quartz substrate. Upon
exhaustion of the feedstock solution or after a designated period of time elapsed, the feedstock supply was halted, the furnace shut down, and argon flow maintained until the chamber had completely cooled.

Table 3-1. Summary of the synthesis conditions for samples used in this chapter. *In the case of samples 8 & 9, the metal chlorides were dissolved in 5.0mL methanol and then combined with benzene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis temperature (°C)</th>
<th>Purge gas flow rate</th>
<th>Benzene volume (mL)</th>
<th>Catalyst</th>
<th>Where used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>800</td>
<td>88.9 sccm 99.5% Ar</td>
<td>excess</td>
<td>1.5g ferrocene</td>
<td>Fig. 3-6</td>
</tr>
<tr>
<td>2</td>
<td>760</td>
<td>200 sccm 99.5% Ar</td>
<td>10.0</td>
<td>0.75g ferrocene</td>
<td>Fig. 3-8, 3-11</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>95 sccm 99.999% Ar</td>
<td>10.0</td>
<td>0.76g ferrocene</td>
<td>Fig. 3-8, 3-9, 3-11</td>
</tr>
<tr>
<td>4</td>
<td>850</td>
<td>280 sccm 99.5% Ar</td>
<td>20.2</td>
<td>1.5g ferrocene</td>
<td>Fig. 3-7, 3-8, 3-11</td>
</tr>
<tr>
<td>5</td>
<td>900</td>
<td>200 sccm 99.5% Ar</td>
<td>20.0</td>
<td>1.5g ferrocene</td>
<td>Fig. 3-8, 3-11</td>
</tr>
<tr>
<td>6</td>
<td>800</td>
<td>88.9 sccm 99.5% Ar</td>
<td>10.0</td>
<td>0.75g nickelocene</td>
<td>Fig. 3-9, 3-11</td>
</tr>
<tr>
<td>7</td>
<td>800</td>
<td>91.2 sccm 99.5% Ar</td>
<td>9.9</td>
<td>0.74g cobaltocene</td>
<td>Fig. 3-9, 3-11</td>
</tr>
<tr>
<td>8</td>
<td>850</td>
<td>70,000 sccm 99.5% Ar</td>
<td>10.0</td>
<td>0.55g NiCl₂*</td>
<td>Fig. 3-10</td>
</tr>
<tr>
<td>9</td>
<td>850</td>
<td>64,000 sccm 99.5% Ar</td>
<td>5.0</td>
<td>0.55g CoCl₂*</td>
<td>Fig. 3-10</td>
</tr>
<tr>
<td>10</td>
<td>850</td>
<td>72,000 sccm 99.5% Ar</td>
<td>10.0</td>
<td>0.75g ferrocene</td>
<td>Fig. 3-10</td>
</tr>
</tbody>
</table>
One variation on this method occurred in the generation of the amorphous carbon and nanotube combination sample (Sample 1): instead of being mixed prior to introduction into the furnace, ferrocene was placed into the crucible inside the furnace and benzene dripped onto it. Similar to the process described previously, the evaporating vapors were then carried into the furnace. As this sample is used only to elucidate the difference in reactivity between amorphous and nanotube carbon and not to structurally characterize the nanotubes, the significance of this variation should be negligible.

For high carrier gas flow rate experiments (“spray-pyrolysis” samples), argon was again used as the carrier gas, but at a much higher flow rate (64,000 – 72,000 sccm ±5%). The furnace was brought to temperature and argon flow initiated. A mixture of catalyst and carbon source was introduced into the high velocity argon stream, rapidly atomized, and carried into the furnace where nanotubes deposited. On completion of the run, the furnace was shut down and the argon flow lowered to rates used in the low flow experiments while the furnace cooled to room temperature.

Upon conclusion of the growth process, mats of vertically aligned CNT were scraped from the quartz substrate and broken up into small chunks. Transmission (Philips EM420, 120kV accelerating voltage) and scanning electron microscopy (Philips XL20, 15kV accelerating voltage) were used to confirm the presence and alignment of multi-walled nanotubes (MWNT), determine their diameter and length, and to gauge the relative purity of the samples. Raman spectroscopy (Renishaw Raman) was performed at room temperature using approximately 0.347mW (as
measured at the sample) of 514.5nm laser light from an Ar ion laser. X-ray diffraction (Rigaku D/Max b, Cu x-ray source), and transmission Mössbauer spectroscopy ($^{57}$Co in Rh source, iron metal calibration) were performed on several samples as well.

Mass-loss profiles were obtained by individually placing small (<10 mg) samples in open top alumina sample pans in a Perkin-Elmer Diamond TG/DTA under a purge gas of 2% O$_2$, balance He. The temperature was raised to 200°C and allowed to equilibrate for a period of 10 minutes before ramping to 1000°C at the rate of 1 °C/min. The 1°C/min heating rate was chosen to approximate the reaction equilibrium state and allow direct comparison between this data and that found in other works [1-3].

In order to obtain a baseline for the comparison of the oxidation of nanotubes, a 99.9995% graphite sample (Alfa Aesar, 325 mesh) was examined. Similarly, mixtures of graphite and fine powders (200 – 325 mesh) of common nanotube catalysts such as iron (19.7 wt%, 200 mesh), cobalt (21.0 wt%, 270 mesh), nickel (19.9 wt%, 325 mesh by 0.37µm thick), and their oxides (generated through oxidation of the powders), iron oxide (Fe$_2$O$_3$, 19.0wt%), cobalt oxide (CoO and Co$_3$O$_4$, 20.0 wt%), and nickel oxide (NiO, 20.0 wt%) were prepared and analyzed. To enhance our capability to differentiate between forms of carbon, as well as other materials present, a homogeneous combination of amorphous and nanotube carbon (sample #1) and a heterogeneous mixture of graphite (1.44mg) and nanotubes (0.78mg, sample #4) were each profiled. In all cases, efforts were made to use samples with similar form, consisting of multiple small segments (the exact number depending upon sample size)
of broken-up nanotube mats instead of larger macroscopic chunks of well aligned nanotubes.

3.3 Results

As synthesized, the nanotubes ranged in diameter from ~15 to ~100 nm within any given sample and in length from several tens of microns to a few millimeters across all the samples. Sample purification was not undertaken as examination through electron microscopy showed most nanotube samples to be almost entirely nanotubes with little to no contamination with respect to other forms of carbon (Figures 3-2 & 3-3). In those cases where carbonaceous or metallic impurities were present, they were frequently detected through the TGA profile, as will be shown. Successive iterations with a given set of synthesis conditions resulted in similar quality nanotubes in terms of physical dimensions, morphology, and thermogravimetric oxidation mass-loss profile, so the results presented should be generally representative.

Graphite burn-off profiles, as measured, appear in Figure 3-4, and their corresponding burn-off rates in Figure 3-5. The high purity graphite burns off completely with a maximum rate of burn-off occurring at approximately 850°C, while the 20 wt% catalyst/graphite mixtures exhibited maximum rates at lower temperatures. The iron mixture exhibited the highest temperature of peak burn-off rate at 830°C, followed by nickel at 800°C, and cobalt at approximately 775°C. Nickel oxide/graphite and cobalt oxide/graphite mixtures showed peak rates at approximately
805 and 785°C, respectively, while iron oxide/graphite exhibited maximum rate of oxidation just below 800°C. In successive iterations, some variation was observed in the temperatures of peak oxidation rate, but the figures shown and temperatures quoted are indicative of the general trends observed.

Figure 3-2. Scanning electron micrographs of CNT’s: (top) Most nanotubes examined in this study were synthesized in preferentially aligned mats and appeared similar in form to those shown here. Scale bar = 10 µm. (bottom) higher magnification image showing individual nanotubes. Scale bar = 2 µm.

The first sample of mixed carbon forms was initially thought to be solely amorphous carbon, caked onto the sides of the furnace tube. In Figure 3-6, however,
there is a distinct two stage burn-off, with one peak rate occurring at approximately 500°C and a second at 581°C, suggesting a dual composition, later to be determined through comparison with other TGA results as well as XRD and transmission electron microscopy as amorphous carbon mixed with CNT’s.

Figure 3-3. A pair of individual nanotubes, representative of size variations observed. Catalyst particles are evident at center and right side of large nanotube and at the lower right end of the smaller nanotube. Scale bar = 200nm.

The profile for nanotubes mixed with high purity graphite appears in Figure 3-7. Similar to Figure 3-6, a distinct two stage burn-off is exhibited, with approximately 35% of the initial mass being lost in the first phase and the remainder in the second, corresponding very closely to the initial mix ratio. The points of peak burn-off rate occur at approximately 570°C and 760°C.
Figure 3-4. Mass loss profiles for graphite and graphite-catalyst mixtures (top) and graphite-catalyst oxide mixtures (bottom). Cobalt, its oxide, and iron oxide show a marked impact upon the oxidative stability of graphite.

Burn-off profiles and rates were recorded (Figure 3-8) for four nanotube samples (samples 2-5), where only the furnace temperature was varied significantly during synthesis: 760°C, 800°C, 850°C, and 900°C. Low-flow, ferrocene-catalyzed nanotubes were used for this examination as this combination of synthesis conditions resulted in relatively high yields of nanotubes. The oxidation of the lower synthesis
temperature nanotubes begins slightly earlier than those synthesized at higher temperatures, but oxidation completes at approximately the same temperature in all cases. This trend is evident in the oxidation rate results as well. All except the 900°C sample appear to have a maximum rate at 590°C, but for CNT’s synthesized at 850°C, initial oxidation is delayed in comparison to the other samples. Also, the nanotubes
synthesized at 850°C and 900°C tend to have a more acute and rapid oxidation than those of lower synthesis temperatures. The rate chart also exhibits two peaks for most synthesis temperatures. A burn-off peak at approximately 560°C is present, but secondary to the peak at 595°C in the curves corresponding to 760°C and 800°C synthesis temperatures, resulting in a broadened burn-off peak. At 850°C, the 560°C burn-off peak is almost nonexistent. At 900°C, however, the 595°C peak is significantly diminished and burn-off is dominated by the lower temperature peak.

Figure 3-6. Mass-loss profile and rate of oxidation of an amorphous carbon/nanotube sample. Two oxidation rate peaks are observed at 500°C and 581°C, corresponding to amorphous carbon (approximately 55% by mass) and carbon nanotubes (45% mass).

Burn-off profiles and rates for nanotubes generated by the low-flow method with varying catalyst types are shown in Figure 3-9 and those for nanotubes generated by the spray pyrolysis method, again with varying catalyst types, in Figure 3-10. In general, nanotubes grown using the low-flow method show a higher carbon fraction.
than those grown through spray pyrolysis, resulting in lower residual mass fraction at completion of burn-off. Catalyst particles are generally similar in size across the samples. A TEM survey of approximately 275 individual catalyst particles showed them to be generally cylindrical in shape with average dimensions: Co, 19nm dia. x 38nm long; Ni, 21nm dia. x 32.1nm long; and Fe, 15nm dia x 22.0nm long. Catalyst particle lengths varied widely, from approximately 7 to 458 nm long. Profiles and rates for the cobalt generated nanotubes are similar in both cases, showing peak oxidation rate in the vicinity of 480°C, as well as a lesser peak at approximately 860°C (Figure 3-9, bottom, and Figure 3-10, bottom). Nickel generated nanotubes show a slightly higher temperature associated with the maximum oxidation rate when synthesized using the spray pyrolysis method and a NiCl₂ catalyst precursor (maximum rate at 579°C) than when synthesized using the low-flow method and a
nickelocene precursor (maximum rate at 562°C). A very small peak is observed at approximately 860°C for the nickel spray pyrolysis sample as well. The case of

![Graph](image)

**Figure 3-8.** Effects of synthesis temperature upon mass-loss profile (top) and oxidation rate (bottom). Peak stability versus oxidation is observed at 850°C synthesis temperature, above and below which increased amounts of less stable forms of carbon are present.

ferrocene generated nanotubes is more significantly different for the two synthesis methods. In the low-flow synthesis case, the maximum rate of oxidation occurs at
approximately 590°C, whereas the spray pyrolysis sample exhibits maximum burn-off at roughly 537°C. Possible reasons behind this observation will be discussed later.

Figure 3-9. Catalyst effects upon oxidation of low-flow generated nanotubes: mass profile (top) and rate (bottom). Cobalt generated nanotubes showed the lowest stability, followed by nickel and iron catalysts. A small oxidation rate peak associated with graphite was noted when cobalt catalysts were used.
Figure 3-10. Catalyst effects upon oxidation of spray pyrolysis generated nanotubes: mass profile (top) and rate (bottom). Cobalt generated nanotubes again showed the lowest stability, followed by iron, then nickel catalysts. Graphite-related oxidation peaks were more pronounced with cobalt catalysts, but were also observed with nickel generated CNT.

Finally, Raman spectroscopy was performed on samples with varied synthesis temperatures and varied catalyst types in order to ascertain whether the observed burn-off curve changes were a result of structural defects in the nanotubes; these results appear in Figure 3-11. Multiple spectra were recorded at several different locations on
the nanotube samples, D-band normalized, and averaged in order to have a more accurate representation of the sample bulk.

Figure 3-11. Raman Spectra for samples with varying synthesis temperature (top, using an iron catalyst) and varying catalyst type (bottom, using a synthesis temperature of 800°C). Spectra have been offset for ease of viewing features.
3.4 Discussion

The first signs of mass loss in the graphite/catalyst mixture profiles occur in all samples at approximately the same point, close to 615°C, below which all samples appear to be relatively stable. From 615°C upward, however, the curves separate and follow different paths. Some variation in the temperature of maximum oxidation rate was observed, as noted previously, perhaps due to varying amounts of catalyst particles present or to distribution differences occurring through the imperfect mixing of the graphite and catalyst. In the samples tested, the remnant mass ranged from approximately 15wt% to 30wt% of the original sample size. The curves shown in Figures 3-4 and 3-5 are generally representative and reflect approximately equal amounts of metal catalyst.

The presence of transition metals is known to catalyze the gasification of carbon [4-6], but the mechanism by which the transition metal catalysts act is not fully understood. One theory [4] suggests that the metal particles form an intermediate, non-stoichiometric oxide and are then reduced through the oxidation of surrounding carbon particles. In this case, the catalytic effect of the metal particle would be partially dependent upon the thermodynamics of oxidation and would thus vary from one element to another, suggesting a possible reason for the differences between the observed catalytic effects of each metal on the nanotubes. A detailed investigation of the actual mechanism of the catalytic effect is outside the scope of these experiments and is not covered here.
In the cases of elemental nickel, iron, and nickel oxide, however, little change in the oxidation profile is observed. The burn-off profiles for these mixtures follow that of pure graphite before leveling off at a mass roughly corresponding to their initial mix ratios. The temperature of peak oxidation rate in each shows only minor variation from that of pure graphite, suggesting that they have minimal catalytic effect in the reaction. With such a small change between the profiles for pure graphite and these mixtures, it is reasonable to argue that no catalytic effect is observed, and that the temperature shift corresponding to peak burn-off reflects only the earlier slowing of the reaction due to the smaller relative amount of carbon.

In all cases where an elemental metal catalyst is present, a slight mass gain is apparent, arising from the initial oxidation of those metals. In each case, the oxidation of the metal begins before the oxidation of the carbon. Cobalt oxidation begins first, with mass gain beginning at 325°C, followed by nickel and iron at 400°C. Nickel oxidation appears to progress more quickly than iron, showing a more rapid mass gain apparent in Figure 3-4. While these mass increases may be attributed to the partial oxidation of exposed catalyst particles, they are not large enough to reflect the complete oxidation of all catalyst particles in the sample. The end result of the oxidation are black cobalt oxides, green nickel oxide, or reddish-brown iron oxide powder, confirmed by XRD to be CoO and \( \text{Co}_3\text{O}_4 \), NiO, or Fe\(_2\)O\(_3\), respectively, suggesting the remaining catalyst particles oxidize simultaneously with the graphite, and are thus not distinct in the mass loss curve.
The catalytic effects of iron oxide, cobalt and its oxides are quite evident in both the burn-off profiles and their corresponding rate curves. Of particular note is the difference in burn-off profiles between graphite with elemental iron and graphite with Fe₂O₃. The strong catalytic effect of Fe₂O₃ compared to the nearly negligible one of elemental iron contradicts the behaviors predicted by the intermediate composition catalytic mechanism theory, which implies that both would have equivalent catalytic activity. If iron and its oxide differ in catalytic activity, the data suggests that the elemental iron does not form an oxide early enough in the process to significantly impact the graphite gasification, but completes its transition to Fe₂O₃ once the graphite oxidation reaction has reached an active state.

Figures 3-6 and 3-7 clearly show the separation by reactivities of differing forms of carbon. Amorphous, nanotube, and graphitic carbon show peak oxidation rates at increasing temperatures. The distinct burn-off peaks confirm the potential for oxidative separation of the carbon forms and allow for the visual separation of nanotubes from other forms of carbon in TGA profiles. Biphenyl, a synthesis byproduct, was also analyzed by TGA (see Section 3.6) and was found to burn off at a low enough temperature (peak oxidation rate at 222°C) that it did not impact the profiles observed for other forms of carbon.

The nanotubes used in this study show a decreased stability with respect to graphite, as has been observed previously [1], but contrary to observations elsewhere [2, 3]. The catalytic effect of Fe₂O₃ (from the nanotube synthesis catalyst) upon graphite is also observed in Figure 3-7, reducing the peak oxidation rate temperature
from that of pure graphite. The synthesis catalyst particles are encapsulated within the nanotubes and are thus shielded from oxygen and oxidation until the tubes are opened or consumed. As such, one would expect a slight delay in the profile before the catalytic effects could be observed. Mössbauer analysis determines their forms as elemental iron (32%), Fe$_3$C (37%), austenite (28%), and a small amount of Fe$^{3+}$ (2%).

As the nanotubes are consumed, these forms of iron are oxidized to Fe$_2$O$_3$, which may then catalyze the oxidation of the remaining nanotubes as well as the graphite. This in turn lowers the temperature of the maximum graphite burn-off rate from 850°C to approximately 760°C, an even more pronounced effect than that observed by mixing Fe$_2$O$_3$ and graphite directly (peak rate at 800°C, Figure 3-5). Despite any delay due to the carbon encapsulation of the growth catalyzing iron, this is to be expected given the much smaller size of the resultant oxidized nanoparticles, which possess a greater specific surface area, allowing for increased surface interactions and a faster overall reaction.

CNT samples synthesized with differing furnace temperatures show increasing stability with respect to thermal oxidation as synthesis temperature increases to 850°C, after which stability appears to decrease. Hornyak et al. showed that CVD nanotube synthesis will not proceed above a certain temperature [7], so a temperature of maximum stability for a set of synthesis conditions is expected, above which stability will decrease as amorphous carbon deposits and nanotube defect sites increase. The 900°C synthesis sample confirms this, showing a decrease in temperature of maximum burn-off rate. Examination of Figure 3-8 reveals dual peaks in the rate curve at
approximately 560°C and 595°C. As the synthesis temperature increases up to an optimum point, the majority of burn-off shifts into the higher temperature peak, indicating increased formation of more stable or less defected nanotubes. The 900°C curve surpasses this point and a rapid return to formation of structures associated with the lower peak is observed. In each case, the reaction appears to terminate at approximately the same point.

The Raman spectra shown in the top of Figure 3-11 support this idea of an optimal synthesis temperature. For the temperatures examined, both G:D and G’:D peak ratios increase with temperature up to 850°C, showing a decrease in structural defects, then decrease again at 900°C. G:D ratios for synthesis temperatures of 760°C, 800°C, 850°C, and 900°C were measured as 2.21, 2.89, 3.60, and 2.76, respectively. G’:D ratios for the same samples were measured as 1.99, 3.08, 3.61, and 2.91, respectively.

When comparing Figures 3-5 and 3-7, it becomes apparent that the behavior of the iron and graphite in each system differs. In Figure 3-5, it appears that the iron does not noticeably catalyze the oxidation of the graphite. In Figure 3-7, however, a large shift in the burn-off temperature of graphite is observed. It appears that the oxidation of the nanotube structures may catalyze the oxidation of the contained iron or iron carbide nanoparticles, thereby bringing the catalytic role of Fe₂O₃ into the reaction earlier and at a lower temperature than was observed in Figure 5. It is also possible that the presence of iron carbides changes the reaction sufficiently to either
catalyze the oxidation itself or to generate the Fe$_2$O$_3$ at a lower temperature, allowing the catalyzed oxidation of graphite.

When varying catalyst types, it was found that the mass-loss and oxidation rate curves were largely insensitive to catalyst precursor composition, but depended primarily upon the actual catalyst metal used. For example, little variation in burn-off profile was observed between nanotubes generated with nickelocene and NiCl$_2$ catalysts, but large variations were observed between those generated with NiCl$_2$ and CoCl$_2$ catalysts.

Synthesis method appeared to play a role in the stability of some nanotubes investigated. When using a cobalt catalyst, no significant change was noted between the low-flow and spray pyrolysis conditions. However, when either a nickel or ferrocene catalyst was used, a shift was observed. Nickel catalysts showed an increase in the temperature of maximum oxidation rate (approximately 17°C) for the spray pyrolysis method where the iron catalysts showed a decrease of approximately 53°C. While a 17 degree change is inconclusive, the 53°C shift present in the iron catalyzed nanotubes suggests a non-trivial change in their defect density. Since the primary difference between the two methods is the reagents’ dwell time within the furnace, it is possible that nascent nanotubes formation occurs at a lower temperature due to their higher velocity through the furnace and slower heating rate and thus results in a higher defect density. That this effect is not observed when other catalysts are used suggests that their optimal synthesis temperatures may be lower than that for iron catalysts.
Of the samples tested, cobalt generated nanotubes consistently burned off most quickly, matching the behavior demonstrated in the catalyst-graphite mixtures. In both the low-flow and spray pyrolysis generated cobalt tubes, the profiles show the primary burn-off of the nanotubes, but also reflect a secondary burn-off peak at approximately 860°C. A similar, but much smaller oxidation peak is observed at the same temperature for the nickel-catalyzed spray-pyrolysis nanotubes. This peak corresponds to the temperature at which pure graphite was observed to oxidize, suggesting these catalysts may also assist the formation of graphite particles under the given synthesis conditions. Should these graphite particles remain free or isolated from the catalyst particles, they could account for these burn-off peaks. No signs of graphite were found in other nanotube samples, except for those where graphite was manually (intentionally) introduced.

With the exception of the ferrocene catalyzed spray-pyrolysis nanotubes, as noted above, oxidation of the various catalyst-grown nanotubes follows the trends observed in the graphite/catalyst mixtures. Cobalt catalyzed carbon nanotubes show the lowest stability relative to oxidation, followed by nickel and iron grown nanotubes with comparable stability. By comparison with Saxby et al., it is evident that each of the nanotubes tested exhibit an increased oxidative stability relative to amorphous carbon and C_{60}, but decreased relative to that of diamond [3].

Raman analyses of these samples show that the change in burn-off temperature is not a consequence of structural defects in the nanotubes. G:D ratios are comparable for all three catalyst types: 2.89 for Iron, 2.78 for Nickel, and 2.79 for Cobalt (Figure
suggesting the observed phenomena must be a result of the included catalyst type. However, G':D ratios show more variation: Fe: 3.08, Ni: 2.57, Co: 2.75. This latter set of results suggests that the differences between the nickel and iron curves may be a result of structural defects, but that the mass-loss curve associated with the cobalt catalyst definitely reflects a strong catalytic effect.

As a direct result of the differences in oxidation resistance discussed above, the specific circumstances of application of the nanotubes should be considered when determining what catalyst to use in their synthesis. In applications subjecting nanotubes to high temperatures or oxidizing environments, or where nanotubes are utilized in critical ways, an engineer should determine whether the degree of oxidation susceptibility corresponding to the use of a catalyst will compromise the nanotube over the life of the application.

As reported elsewhere [8], the nanotubes show a high resistance to oxidation until a critical temperature is reached, which appears to depend, in part, upon the catalyst used in the nanotube synthesis and, at least in the case of CVD grown CNT, the synthesis temperature. Nickel and iron generated nanotubes showed relative stability until approximately 450°C, while cobalt generated nanotubes appeared stable to approximately 400°C. Of course, oxidation commences at a lower temperature, but at rates slow enough that it was not measurable in the time scale of these scans. Competitive oxidation always takes place among different types of carbon, but will proceed at different rates, as has been demonstrated.
The mass loss profile shown for low-flow, ferrocene generated nanotubes is similar to that for the raw multi-walled nanotubes examined by Bom et al. [1]. The maximum mass loss for the present sample occurs at approximately 595°C, compared to approximately 575°C for xylene/ferrocene tubes in Bom et al. Notably different is the nanotube mass loss profile given by Pang et al. [2], which shows a maximum rate of mass loss at approximately 695°C, a full 100°C higher, with no catalyst used.

Different oxidation behaviors between laser-ablation generated and arc-discharge generated nanotubes have been reported previously [9]. The current nanotubes, as well as those used by Bom et al. [1], were fabricated through chemical vapor deposition, whereas those analyzed by Pang et al. [2] were produced through arc-discharge synthesis. The presence of an electric field during synthesis, such as that present in the arc-discharge method and generally lacking in standard chemical vapor deposition, has been shown to help stabilize the formation of carbon nanotubes [10, 11]. Similarly, higher temperatures present during synthesis allow the annealing out of defects as the nanotubes are formed. Given the comparatively low temperatures used in CVD synthesis (versus those present in laser ablation or arc-deposition methods) and lack of electric fields to assist formation, nanotubes created in this manner will exhibit a higher defect density, thereby resulting in lower burn-off temperatures [1]. Further, the present work demonstrates the potential for catalyzed oxidation by the growth catalyst, which could result in even lower burn-off temperatures. With these considerations in mind, the large temperature difference
observed between the CNT’s of Pang et al., Bom et al., and the present study may be understood.

3.5 Conclusions

Synthesis conditions and their resulting effects upon CNT structure and stability have been examined, and synthesis and analysis of each sample has been replicated with little variation, except as noted. Carbon nanotubes of comparable crystalline defect density have been synthesized with each of the catalysts examined utilizing the low-flow method. Iron oxide, cobalt oxide, and cobalt catalysts have been shown to have a significant depressing effect upon the oxidative stability of the nanotubes tested, while iron, nickel, and nickel oxide do not appear to significantly reduce the stability of nanotubes in their presence with the noted exception of iron in spray pyrolysis generated nanotubes. Carrier gas flow rates were compared and found to produce nanotubes of generally comparable stability with nickel and cobalt catalysts, but significant variation was observed when using iron. Nanotube synthesis temperature was found to have a small but measurable effect on structure, with an optimal temperature found to be in the region of 850°C for ferrocene catalyzed tubes. This analysis provides an upper limit to the window for the oxidative purification of CVD generated nanotubes and exhibits the significant impact a catalyst may have on the oxidative stability.
3.6 Supplemental information

3.6.1 TGA Ramp rate:

The impact of increasing the temperature ramp rate on a given sample in the thermo-gravimetric analyzer is shown in Figure 3-12. Increasing the rate of heating caused a shift in the mass loss profile of approximately 50°C, an increase in the maximum rate of burn-off, from just under 2%/minute to approximately 9%/minute, and a positive shift of roughly 60°C in the corresponding temperature.

![Figure 3-12. Mass loss and rate of burn-off profiles for a given sample under varying temperature ramp rates.](image)

3.6.2 Biphenyl:

Biphenyl, as identified through XRD, was a common byproduct of the nanotube synthesis process, and typically deposited in crystalline form near the furnace exhaust. A sample was taken directly from the furnace and run through the
same temperature program as the carbon samples, with results as shown in Figure 3-13. This sample was taken from a different location of the same run as Sample 1, shown in Figure 3-6. The majority of sample burn-off was completed at much lower temperatures than for other samples examined, with peak burn-off rates occurring at approximately 132°C, 222°C (roughly corresponding to its boiling point), 490°C, and 525°C.

Figure 3-13. Mass-loss profile and rate of oxidation of the biphenyl sludge byproduct.

Chapter 3, in part, is a reprint of the material as it appears in “Thermogravimetric Analysis of Synthesis Variation Effects on CVD Generated Multiwalled Carbon Nanotubes”, McKee G. S. B. and Vecchio K. S. *J. Phys. Chem. B* 110 1179-1186, 2006. The dissertation author was the primary investigator and author of this paper.
3.7 References


4. **On length and the oxidation kinetics for CVD generated MWNT**

4.1 **Summary**

Oxidation rates are measured and kinetic parameters determined by isothermal analysis for several length ranges of as-grown and processed chemical vapor deposition generated multi-walled carbon nanotubes within a range of 700 K to 900 K. The activation energy barrier is found to be within the range calculated by others previously and follows comparable progression patterns for similar length arrays. Activation energy and frequency factor are not observed to change with synthesis method, but increase gradually as oxidation progresses in longer nanotube arrays or peak and decline in shorter arrays. The results also confirm that the oxidation of carbon nanotubes need not originate in the nanotube caps, but may originate in other areas of increased reactivity, such as wall defects. The behavior of the kinetic parameters as oxidation progresses is commensurate of the consumption of defected structures followed by the coalescence of etched holes, suggesting lower defect densities in longer carbon nanotubes.

In the present study, measurement of the kinetic parameters for oxidation of CVD synthesized multi-walled carbon nanotube arrays is presented and discussed in terms of synthesis conditions, processing, and nanotube length. Practical limitations encountered in this method are examined and oxidative etching is observed on nanotube side-walls. Through these experiments, a more complete understanding of nanotube growth and oxidation reactions involving carbon nanotubes can be gleaned.
4.2 Experimental

Carbon nanotubes were synthesized through the pyrolytic decomposition of a benzene-ferrocene feedstock solution in a CVD furnace as described in Chapter 3 and shown in Figure 3-1. As the general methods behind “low-flow” and “spray pyrolysis” have already been explained, the relevant details and variations of sample synthesis are provided in Table 4-1.

Table 4-1: The synthesis conditions for the samples examined in this chapter, by sample number. All except Sample 5 were created using the “low-flow” synthesis technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Ferrocene : Benzene Ratio (g/L)</th>
<th>Carrier gas flow rate (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1123</td>
<td>75</td>
<td>280</td>
</tr>
<tr>
<td>2</td>
<td>1073</td>
<td>33</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>1073</td>
<td>62.5</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>1123</td>
<td>75</td>
<td>240</td>
</tr>
<tr>
<td>5</td>
<td>1123</td>
<td>74</td>
<td>60,000</td>
</tr>
<tr>
<td>6</td>
<td>1123</td>
<td>75</td>
<td>118</td>
</tr>
</tbody>
</table>

Upon conclusion of the growth process, tubes were removed from the quartz substrate as aligned mats or bundles and broken up into small chunks. Transmission (Philips EM420, 120kV accelerating voltage) and scanning electron microscopy (Philips XL20, 15kV accelerating voltage) were used to confirm the presence and alignment of multi-walled nanotubes, make diameter and length measurements, and gauge the relative purity of the samples.

Kinetic parameters were determined through isothermal analysis using a Perkin Elmer Diamond TG/DTA. Samples were placed in open-topped alumina pans under a purge gas of 2% O₂, balance He. The thermal program initiated the purge gas and
held the sample at 323 K for one minute before ramping to the target temperature where the sample soaked as oxidation progressed. Rate measurements and sample temperatures were collected as the sample’s relative mass passed specified reference points (95% mass, 93%, 91%, etc… every 2%). In all cases, efforts were made to use samples of similar form, consisting of multiple small segments of broken-up nanotube mats instead of larger, macroscopic chunks of well-aligned nanotubes in order to limit the impact of sample morphology.

Sample 1b was created by treating nanotubes from Sample 1 to remove the included catalyst synthesis particles. This treatment consisted of heating the sample in air for six hours at 725K, followed by stirring in dilute (3 molar) hydrochloric acid for 120 hours. The resulting products were filtered from suspension, washed three times with deionized water, rinsed with methanol and air dried. To remove adsorbed moisture, the sample was subsequently heated to 475 K for 30 minutes in air. FTIR was performed upon this sample to identify any attached functional groups using a Nicolet Magna-IR spectrometer 550 (HeNe laser with an excitation wavelength of 632.8 nm).

All other samples were tested as raw, untreated products.

4.3 Results

As synthesized, the nanotubes showed a mean diameter of approximately 45nm (Figure 4-1). Array length varied by sample: Samples 1 – 3 varied from one to three millimeters, with the majority at the upper end of this range; Sample 4 lengths
varied from 20 to 80 μm, with an average length of approximately 50 μm. Sample 5 lengths varied from 10 to 60 μm with an average length of approximately 40 μm. Nanotubes in all samples formed in preferentially aligned bundles or mats (Figure 4-2).

Figure 4-1. TEM micrograph of an individual nanotube from Sample 6, but exhibiting the general structural form of all nanotubes tested. Nanotube diameters ranged from ~15nm to ~100nm with an average of approximately 45nm. Scale bar = 100nm.

Successive iterations with a given set of synthesis conditions resulted in similar quality nanotubes in terms of physical dimensions, morphology, and thermogravimetric oxidation mass-loss profile. Repetition of the activation energy analysis yielded results commensurate with the initially determined data, so the results presented may be considered generally representative.
Figure 4-2. SEM micrographs of CNT’s used in this examination: (a) Sample 1 nanotube clump prior to testing, also representative of Samples 2, 3, and 6. Length range ~1-3 mm, Scale bar = 500 μm; (b) close-up of clump shown in (a), Scale bar = 2 μm; (c) Sample 4 image, length range ~20-80 μm, Scale bar = 20 μm; (d) Sample 5 image, length range ~10-60 μm, Scale bar = 50 μm.

Mass loss rates and temperature data collected from the experiments were fitted to a linearized form of the general Arrhenius type equation:

\[
\ln(Rate) = -\frac{E_{\text{act}}}{R} \left(\frac{1}{T}\right) + \ln A
\]  

(4.1)

where \((Rate)\) is the reaction rate, \(E_{\text{act}}\) is the activation energy barrier, \(R\) is the gas constant, \(T\) is the temperature in Kelvin, and \(A\) is a pre-exponential frequency factor dependent upon kinetic variables such as the reaction surface area, density of active sites, and the catalyst contact efficiency. Data collection occurred at reaction
coordinates \( x = 0.03 + 0.02n \), where \( n \) is an integer (e.g. when \( n = 1 \), the remaining mass is 95%). Linear regression was used to find appropriate values for the activation energy and the frequency factor. Figure 4-3 represents all data points where the coefficient of determination \( (R^2) \) was greater than 0.85. Error bars indicate the variation in the results when a mass variation of \( \pm 5\mu g \) (the approximate accuracy of the instrument) is introduced.

The initial results led to a follow-up investigation of the impact of length on kinetic parameters. In a single synthesis batch (Sample 6), nanotube arrays were manually sorted by approximate length; Sample 6a: 0.75 – 1.25 mm; 6b: 1.25 – 1.75mm; 6c: 1.75 – 2.25mm; 6d: 2.25 – 2.75mm; 6e: 2.75 – 3.25mm. Data collection and analysis was performed as before. Results with a coefficient of determination greater than 0.85 appear in Figure 4-4; the approximate error is \( \pm 3\% \).

4.4 Discussion

At points of equivalent relative mass, the rate data closely follow an Arrhenius relationship for temperature dependence.

Faster rates of oxidation were observed in Sample 1b and may be attributed to damage induced through the treatment to remove iron particles. Most of the nanotubes in this sample were opened in various locations (Figure 4-5) prior to thermal analysis, resulting in exposed edges of graphene sheets and significantly increased reactivity compared to an undamaged nanotube.
Figure 4-3. The kinetic parameters (activation energy and frequency factor) measured for Samples 1 through 5, derived through linear regression of rate of mass loss and temperature data, obtained through isothermal thermo-gravimetric analysis. In each chart, ▲ denotes the activation energy and ■ denotes the frequency factor. Error bars indicate the variation in the results when a mass variation of ±5 μg (the approximate accuracy of the instrument) is introduced.
Figure 4-4. Kinetic parameters for length sorted nanotube arrays, derived through the same methods as Samples 1-5. Part (a) shows activation energy, (b) shows the natural log of the frequency factor. The activation energy and frequency factor do not exhibit any significant dependence upon the length of the nanotube array in the range examined.

In each sample, it is noted that activation energy and frequency factor start relatively low and rise quickly. After the initial increase, in each of the long nanotube samples (1, 2, and 6) the parameters continue to rise, or, in the case of Sample 3, remain relatively constant. In the short length samples (4 & 5), the activation energy and frequency factor appear to peak in the neighborhood of $x \approx 0.4$ before declining significantly. The lower initial activation energy may be due to the presence of small amounts of more reactive, non-nanotube carbon (activation energies: ~144-176 kJ/mol for amorphous carbon and graphite [1-3]) or, as graphite oxidation requires the adsorption of oxygen molecules to the graphite layer prior to their reaction with the carbon [1], may also be a result of the reaction of the nanotube with pre-adsorbed oxygen molecules, not needing to adsorb from the atmosphere before reacting. The gradual rise observed in the kinetic parameters after the sharp initial increase reflects
the increasing purity and refinement of the nanotube arrays as the more reactive sites and structures (defects) are consumed.

The behavior of the kinetic parameters in Samples 4 and 5 strongly suggests the oxidation of two phases with differing reactivities. The more stable phase is consumed first, during which time the kinetic parameters gradually increase. At approximately 60% mass remaining, a less stable phase begins reacting, decreasing the observed kinetic parameters. The unusual behavior of the less-stable phase reacting second suggests that it is not available for oxidation during the early part of the reaction and is either exposed or created by the consumption of the more stable phase.

Given the nature of FC-CVD synthesis, it is unlikely that Samples 1-3 and 6 are made up of individual nanotubes running the entire length of the array. Instead, nanotube length is likely limited by catalyst poisoning during synthesis, with nanotubes constantly nucleating, growing, and terminating throughout the length of the array. In the case of a short array, such as Samples 4 and 5, the array length is short enough such that individual nanotubes likely run the entire array thickness and are limited by the growth time (array thickness) rather than catalyst poisoning. Thus, it is expected that, despite the constant re-nucleation of nanotubes, thicker arrays are made up of individual nanotubes with lengths greater than those making up the short array sample.

Given the observed differences between short and long arrays, it may also be argued that the short arrays have a higher defect density than long arrays. A higher proportion of defects may be created during the initial stages of growth, after which
the lattice growth proceeds in a steady state fashion through the extension of the wrapped graphene sheet. If it is assumed that long nanotubes have the same wall defect density as short nanotubes and that wall defect density is lower than is present in tube end-caps (which necessarily have at least six pentagonal defects in a comparatively small area), short nanotubes will necessarily have a higher overall defect density due to their lower ratio of wall atoms to end-cap atoms. If long nanotubes have a lower wall defect density than short nanotubes (which appears reasonable, given the results presented) this will only widen the gap. Thus, increasing the overall length of a nanotube may increase its overall chemical stability through a reduction in the average density of reactive sites.

Each defect serves as a nucleation site for oxidation. The sites grow into holes as carbon is consumed, with the edges serving as sites of increased reactivity compared to the contiguous graphene sheets making up the nanotube walls. Coalescence of oxidatively etched holes in the sidewalls and caps could then account for the peak and downturn behavior observed in the samples of short nanotube arrays (4 & 5). The ratio of edge to bulk atoms on the graphene layer increases, causing increased reactivity and accounting for the decrease in kinetic component values observed.

As such, the fact that a peak and decrease is not observed in Samples 1-3 and 6 as it is in Samples 4 and 5 may be a result of the homogenization of kinetic parameters, as the many different tubes experience oxidation at different individual reaction coordinates. It is noted, however, that even the “average” activation energy
and frequency factor for an overall reaction coordinate in a long array is generally higher than that found by averaging the kinetic parameters for the short array samples. This study also mapped the change in kinetic parameters as a function of the nanotube array length, via Sample 6, looking for any direct relationship between the two parameters and expecting that the peak observed for short arrays would progress gradually to higher reaction coordinates as the length of the array was increased. However, in view of the nature of floating-catalyst CVD, it is not a surprise that no peak progression was observed. Instead, it is expected that no peak progression will occur, but rather the peak will become obscured as the array length surpasses the point at which individual nanotube length becomes limited by catalyst poisoning instead of growth time.

Indeed, the “peak and decline” behavior were not observed over the length scales examined, indicating the nanotubes making up the arrays are, in fact, shorter than 1mm.

This has positive implications for the spinning of nanotubes into thread for composite reinforcement [4, 5]. In this type of application, the thread strength is governed by Equation 2.2 and is dependent upon the nanotube length (Equation 2.3), with longer nanotubes allowing for a higher ratio of tube to yarn tensile strength. As such, increased nanotube lengths would be doubly beneficial through decreased defect density (improving the constituent fiber’s mechanical strength) and increased yarn modulus.
Figure 4-5. TEM micrographs of Sample 1b after partial oxidation. Raw nanotubes from Sample 1 were oxidized at 450°C for 6 hrs, treated with acid for the removal of metallic particles, rinsed and dried. Nanotube end-caps were observed to be removed in some places, but, just as frequently, holes were etched in the nanotube walls (arrows), probably around structural defects such as kinks, dislocations, etc. Scale bar in top is 100 nm and in bottom is 50 nm.
The treated nanotube sample (1b) does not show the initial rapid increase in activation energy or frequency factor, but each parameter increases at a relatively constant rate, similar to the “refinement” stage in the raw samples. It must be kept in mind that Sample 1b began as a completely different structure when compared to the raw nanotubes. Sample 1 was partially oxidized to open the tubes, exposing and probably oxidizing some of the iron catalyst particles. This treatment removed some portion of the carbonaceous structure of the nanotubes and would have consumed the more reactive forms of carbon as well as (at least temporarily) any pre-adsorbed oxygen. Thus, the data for a given relative mass in the treated samples would correspond to a higher degree of oxidation when compared with a raw nanotube sample.

The catalyst removal process (partial oxidation, cooling to room temperature, exposure to atmosphere, and acid and water washes) changed the oxidation behaviour of the nanotubes, increasing the overall reactivity of the sample to a degree higher than would be expected if the nanotubes were continually oxidized without these interruptions. As such, measured activation energies and frequency factors were significantly lower than those observed for any of the raw nanotube samples. The change is a direct result of the treatment steps, including the partial oxidation, where holes were etched in the tube walls at defect sites, causing an increased number of dangling bonds. These holes would allow the penetration of oxygen deeper into the multi-walled nanotube, exposing and allowing oxidative attack on the inner walls, which might otherwise have been shielded by outer tubes. Perhaps more importantly,
dangling bonds at these edges serve as reactive sites for the attachment of functional groups, which increase the reactivity and lower the activation energy. FTIR spectra on this sample indicate the presence of carbonyl (C=O) and hydroxyl groups (-OH), as well as C-O bonding, showing that some functionalization occurred during the treatment process. With further experimentation, it was found that the oxidation, acid wash, and rinsing caused no significant change in the oxidative stability of the nanotubes when performed separately. Only when partial oxidation was followed by aqueous immersion was the oxidation profile of the nanotubes impacted.

Oxidation of nanotube caps has been previously observed [6, 7] and found to be preferential to oxidation of nanotube walls due to the increased strain energy present in these more curved structures [8]. An oxidation model was proposed wherein the caps oxidized first, followed by the “layer by layer peeling of outer layers” [6]. However, these results were later shown to be inadequate for a complete description of the oxidation of nanotube structures. Shimada et al. showed that defects in nanotube walls such as cracks, vacancies, and dislocations play a significant role in the gasification of the structure and may be more reactive than pentagonal defects in the graphene sheet, potentially leading to the initiation of oxidation along nanotube walls instead of end caps [9].

Examination of a sample after partial oxidation (Figure 4-5) shows that oxidative etching takes place at the tube ends, but also initiates at points along the nanotube walls, suggesting the presence of reactive defects, in agreement with the findings of Shimada et al. [9].
For purposes of comparison, the activation energy of MWNT’s have been previously measured at 225 kJ/mol [6] (arc-discharge generated, measurement by unknown method) and 292 kJ/mol [2] (unknown synthesis method, measurement by a non-isothermal method). Park et al. computed activation energies for the oxidation of carbon from a single-walled nanotube structure to lie between approximately 239 and 386 kJ/mol [10]. It should be noted, however, that the values of activation energy and frequency factor will often depend upon the analysis method.

In order to represent the present samples by a single activation energy value for comparison purposes, the respective data points from Figures 4-3 and 4-4 may be averaged together. Sample 1b shows the lowest activation energy barrier at 162 kJ/mol, only slightly increased over amorphous carbon at 144 kJ/mol [2] and coal chars at 155 kJ/mol [1]. Samples 4 and 5, CVD synthesized using very different carrier gas flow rates, but of roughly equivalent length (approximately 40-50 μm), show very similar activation energies to each other: 208 and 209 kJ/mol, respectively. The longer array samples show somewhat higher values for activation energy: 256, 253, 237, and 237 kJ/mol for Samples 1, 2, 3, and 6, respectively. Samples 1 and 2 show oxidation activation energy barriers comparable to that measured for purified and high-temperature annealed carbon (251 kJ/mol) [1].

In the previous chapter, it was shown that the synthesis temperature used for Samples 2 and 3 results in a more defected structure than the higher synthesis temperatures used for Samples 1 and 6, and thus an increased reactivity as well. In this case, increased structural reactivity is balanced by the lower catalyst content used
in the synthesis feedstock. Less catalyst in the feedstock yields fewer catalyst particles in the nanotube sample, which in turn provide fewer sites for oxidation catalysis. This decreases the overall reactivity of the sample, resulting in kinetic component values comparable to Samples 1 and 6.

Certain limitations served to define the temperature window in which these experiments were conducted. At the low end of the temperature scale, the rates of mass loss became so low that seismic vibrations and signal noise from the equipment and environment became a considerable problem over the time required to achieve a sufficient reduction in mass. Larger mass samples (~1.5mg) showed decreased susceptibility to error as these events caused smaller fluctuations relative to the overall mass. This allowed the collection of data in the proximity of 700 K, while low mass (~0.5mg) samples showed sufficient stability only above 725 K. In order to smooth the signal and obtain a more representative data set, mass loss rates were averaged over a period of 5 minutes at temperatures less than 800 K and over a period of 1 minute for temperatures between 800 and 850 K.

Conversely, on the high end of the temperature scale, thermal runaway proved a challenge at temperatures above approximately 900 K, with the samples of larger initial mass more susceptible than those of smaller initial mass. Heat generation by the oxidation of the nanotubes exceeds the heat dissipation rate from the reaction zone, causing the reaction to shift from a thermally limited reaction rate to an oxygen mass-transfer limited rate. As these reactions operate by different mechanisms, data from these occurrences has been excluded from the calculations performed here. Thermal
runaway typically occurred as the temperature ramp began to level off and was marked by a sharp, temporary rise in the sample temperature beyond equilibrium along with an acute increase in the rate of burn-off. As combustion subsided (when the oxygen within the diffusion zone was depleted), the temperature returned to equilibrium. If any sample remained, oxidation would continue with the likelihood that runaway would reoccur. Attempts to control or eliminate this by altering the heating rate in the furnace met with little success.

4.5 Conclusions

Kinetic parameters for multi-walled, CVD generated carbon nanotube arrays were measured as a function of reaction progression within a range of 700 to 900 K and subsequently replicated with little variation. The measurements were found to be limited by a low signal to noise ratio at low temperatures and thermal runaway at high temperatures. The nanotubes examined were found to have comparable activation energies for oxidation to multi-walled nanotubes from prior art, with differing synthesis methods. Nanotube length has been shown to impact the measured activation energy of oxidation, suggesting decreasing defect density with increasing length. Evidence of oxidative etching was observed at points outside of the nanotube caps, indicating probable locations of nanotube wall defects. These results provide insight on the mechanisms of the nanotube nucleation and formation, oxidation kinetics of carbon nanotubes, as well as provide an upper limit to the window for the oxidative purification of CVD generated nanotubes. Perhaps the most important
implication of the current results is that the mechanical strength of carbon nanotubes may increase directly with their length, approaching some ideal value. This would be a very promising result for ultra-long carbon nanotube reinforced composites.

Chapter 4, in part, is a reprint of the material as it appears in “Length and the Oxidation Kinetics of Chemical-Vapor-Deposition-Generated Multiwalled Carbon Nanotubes”, McKee G. S. B., Flowers J. S. and Vecchio K. S. J. Phys. Chem. C 112 10108-10113, 2008. The dissertation author was the primary investigator and author of this paper.

4.6 References

5. **Dimensional control of MWNT in Floating-Catalyst CVD**

5.1 Summary

Dimensional control in CVD synthesis of MWNT’s is significant and relevant to a number of different applications. This study examines the dimensional impacts of catalyst concentration in the feedstock and nanotube growth time on the products of floating-catalyst CVD. Extensive diameter surveys are performed by TEM and compared with results from thermo-gravimetric analyses and Raman spectroscopy. Results indicate nanotube diameters are inversely proportional to the catalyst concentration with weak correlation and are directly proportional to growth time. Carbon deposition occurs in two stages, the first characterized by accelerating deposition and increases in nanotube diameter and length, the second by etching of the array and carbon deposition at a constant rate.

This work examines the dimensional impact of variables relevant to the synthesis of vapor-grown carbon fibers, with regard to the similar synthesis variables for multi-walled carbon nanotubes. Analysis is accomplished through extensive TEM diameter surveys, Raman, and thermo-gravimetric analyses. Structure, reactivity, and nanotube dimension trade-offs are identified in terms of catalyst concentration and nanotube growth time.
5.2 Experimental:

Carbon nanotubes were synthesized through the pyrolytic decomposition of a benzene-ferrocene feedstock solution in a CVD furnace as described in Chapter 3 and shown in Figure 3-1. All synthesis runs for this study were conducted in a “low-flow” fashion, using approximately 100ccm 99.5% Ar and a synthesis temperature of approximately 850°C. Feedstock was introduced into the furnace at a rate of 0.347ml/min.

The catalyst concentration and growth time were examined separately. In each set of experiments, all variables not under examination (furnace temperature, growth time, substrate, etc) were held approximately constant.

In order to examine the significance of catalyst concentration, the ratio of ferrocene to benzene in the feedstock was systematically varied, from 4.75g ferrocene per liter benzene (0.227% molar ratio) up to the room temperature solubility limit at approximately 200g ferrocene per liter benzene (9.58% molar ratio). Multiple synthesis runs were made for each catalyst to carbon ratio for purposes of analysis duplication.

Growth time experiments made use of a catalyst to carbon ratio of approximately 15g/L. Nanotube growth time was determined by controlling the time over which the carbon/ferrocene feedstock was introduced into the furnace (at constant rate). This was varied between 5 and 240 minutes.

Residual iron content in as-produced nanotubes was calculated through complete oxidative removal of the carbonaceous component. Large samples (5-100+)
mg) were held at 650°C in air for several hours and the total mass change recorded. Assuming complete catalyst conversion to Fe$_2$O$_3$, the residual mass results were subsequently corrected for oxygen mass and the mass of retained iron calculated.

Deposition rates were calculated from the amount of carbon deposited on a 3”x1” quartz slide placed at the beginning of the growth zone in the reactor.

Nanotube dimension measurements were made via SEM (Philips XL20, 15kV accelerating voltage) or TEM (Philips EM420, 120kV accelerating voltage, or JEOL JEM-2011, 200kV accelerating voltage) observations. TEM samples were prepared through sonication in MeOH for 2.5 minutes and dripped onto a 200 mesh Cu grid. Micrographs were collected between 70,000 and 150,000 times magnification and nanotube diameters in each measured and tabulated. At least 250 individual and distinct nanotubes from each sample were measured to provide a statistically accurate representation.

Oxidation mass-loss profiles were obtained in a Perkin-Elmer Pyris Diamond TG/DTA. Masses of approximately 1mg were placed in open-top alumina pans under a purge gas of 2% O$_2$, balance He. The thermal program initiated the purge gas, raised the temperature to 200°C at 40°/minute, soaked for 10 minutes, then increased to 1000°C at the rate of 1°/minute (in order to simulate the reaction equilibrium state and allow direct comparison between these data and those found in other works) [1-3]. Each sample was analyzed twice to ensure repeatability of the results.

Raman spectroscopy (Renishaw Raman) was performed at room temperature using an argon ion laser (514.5nm, ~0.35mW @ sample). Data was collected from
three distinct locations of the exposed side of an aligned array of nanotubes for each sample. Three spectra collected for each location were normalized to the D-band (~1350 cm\(^{-1}\)) peak and averaged together to eliminate minor variations in the individual spectra.

In order to examine the relationship between catalyst concentrations, carbon levels in the furnace, and nanotube diameters, a two-stage CVD synthesis was performed with the goal of creating an environment of excess carbon for the cases of high and low catalyst concentration. In the first stage of synthesis, a growth feedstock with either 12.5 or 151g ferrocene/L benzene was initially used. After 2.5 minutes of growth, the feedstock containing ferrocene was removed and replaced with pure benzene for an additional 27.5 minutes. Dimensions of the resulting deposits were then found via TEM.

5.3 Results & Discussion:

Nanotubes were deposited in aligned arrays with thicknesses from ~100 µm to a few millimeters. Each sample was tested as-synthesized (excepting mechanical processing for TGA & sonication for TEM sample prep) without treatment for the removal of non-nanotube impurities. Samples were observed to be generally free of non-nanotube carbonaceous impurities at SEM levels of magnification. At higher magnifications in the TEM, however, certain samples were observed to have potentially significant levels of carbonaceous and catalyst particle impurities, as will be discussed later.
For the purposes of this investigation, cleaning of the tubes by refluxing or another partial oxidation technique may have removed excess catalyst particles and non-nanotube carbonaceous impurities, but would have resulted in significant damage to the nanotube structures, such that any meaningful structural analysis would have been impossible.

5.3.1 Catalyst Concentration

As might be expected, a strong correlation between the catalyst to carbon ratio and the retained iron content is observed (Figure 5-1). The relationship roughly follows a parabolic curve, with a rapid increase in the retained iron content at low catalyst concentrations (0 to 25 g/L), followed by a more gradual increase at higher concentrations. Some variability in iron content is evident for synthesis runs at a given catalyst concentration, but the overall pattern shows a proportional increase in one with the other. In only one of the many synthesis runs did the retained iron content ever drop below 1.25 wt% Fe, possibly suggesting a minimum iron content for nanotube formation.

Altering the catalyst concentration in the feedstock without modifying other synthesis conditions does not appear to directly change the resulting deposition rate (Figure 5-2). Large changes in the catalyst concentration produce no predictable change in the yield, when performed under similar circumstances. Similarly, a large range of deposition rates can be obtained using very similar concentrations (Fig. 5-2, note yield range at 15 g/L) by varying the growth time. Thus, it is apparent that the
relationship between yield and ferrocene concentration, if any, is minimal in comparison with the relationship between yield and growth time.

Figure 5-1. Retained iron content plotted as a function of the ferrocene to benzene ratio in the synthesis feedstock. The curve shows a direct proportionality between the two variables and is roughly parabolic up to the room temperature solubility limit of ferrocene in benzene (~200 g/L).

Results of the survey of diameter distribution as a function of retained iron content are summarized in Figure 5-3. Significant scatter in the data suggest no dependence of the diameter on the iron content. However, if one chooses to except the 12 wt% Fe data point, a trend is weakly suggested, where the mean diameter shows a slight decreasing trend with increasing iron content. In either case, the diameter’s standard deviation remains roughly constant. This trend is in agreement with previous results from Bai et al. [4], but contrary to results by Sinnott et al. [5].
Deposition rate (yield) is plotted as a function of catalyst concentration. Wide variations of the catalyst concentration produce no predictable change in yield. However, by varying the growth time, large changes in yield may be obtained without altering the catalyst concentration. Thus, yield appears to be independent of the iron to carbon feedstock ratio, but is strongly dependent upon growth time.

Bai et al. [4] suggest that the increased catalyst content creates a finer dispersion of catalyst particles as well as a carbon deficiency in the reaction zone, resulting in a smaller mean nanotube diameter. In order to test this hypothesis, a two-stage CVD synthesis was performed with the goal of creating an environment of excess carbon for the cases of high and low catalyst concentration, as described previously. Nanotube dimensions resulting from these runs fell generally in line with the other diameter measurements shown in Figure 5-3: the 12.5g/L sample showed a mean diameter of 37.24 nm and a standard deviation of 15.30 nm; the 151 g/L sample showed a mean diameter of 33.81 nm and a standard deviation of 19.29 nm.

The observed differences in standard deviation falls within the scatter observed for all catalyst concentrations and cannot be considered significant. The difference in
diameters is approximately 10% of the overall diameter and as such, falls above the approximate margin of error of 6% for a 95% confidence level. If the theory put forward by Bai et al. [4] were accurate, the two samples should have statistically similar diameters, but, as a difference has been observed, it must be due to causes other than a carbon deficiency during synthesis.

![Diagram showing nanotube diameter and standard deviation versus retained iron content.](image.png)

Figure 5-3. Nanotube diameter and standard deviation are plotted versus the retained iron content. A weak decreasing trend is observed in the mean diameter as retained iron content increases. Significant scatter is apparent in the standard deviation and no direct relation to the retained iron content is observed. Data points represent a simple random sample of at least 250 data points, excepting the highest iron content sample, for which 206 tubes were examined.

There exists considerable scatter in the mean nanotube diameters for all catalyst concentrations investigated. As such, while the catalyst concentration may impact the nanotube dimensions, it does not appear to be a reliable method for controlling the dimensions of the resulting nanotubes, as it is in the case of vapor
grown carbon fibers. Other variables appear to have significantly larger and more reliable impacts.

Raman spectroscopy results are summarized as G:D peak ratios in Figure 5-4a and as G’:D peak ratios in Figure 5-4b. While the Raman spectroscopy results show a wide range of G:D and G’:D peak ratios at low retained iron content, as the iron content is increased, the data range decreases, with approximately the same minimum for all iron contents measured. This suggests that nanotubes with lower iron content have the potential for significantly improved structural perfection versus those with larger amounts of retained iron, but are not guaranteed to be so improved. This also contradicts a finding by Bai et al. [4] that impurity content in CVD generated nanotubes decreases when the catalyst to carbon source ratio is increased. However, that study appears to have been performed by SEM observations, so results may have been more representative of localized areas rather than bulk materials.

While the as-synthesized nanotube arrays were observed to be clean on the micron scale (Figure 5-5a), nanoscale impurities were observed in certain samples. For example, samples using catalyst concentrations equal to or greater than approximately 75g ferrocene per liter benzene were often found to contain significant quantities of carbon coated catalyst particles, in addition to those observed enclosed within nanotubes (Figure 5-5b). As this type of contamination was generally limited to the higher catalyst ratios used and not observed in other samples, it is likely a direct result of the higher concentrations used in synthesis.
Raman studies of nanotube structure are summarized in terms of the (a) G:D and (b) G':D peak ratios, plotted versus the retained iron content in the sample. The same approximate minimum of peak ratios is observed across all iron contents, however, as iron content is decreased, the maxima of the data range increases as well. This suggests the potential, but not guarantee, for improved nanotube structures with decreasing iron contents.

A summary of thermo-gravimetric oxidation analyses appears in Figure 5-6. As the mass-loss curves are asymmetric over temperature and in order to concisely compare oxidation profiles for many samples, the data points plotted in Figure 5-6...
correspond to a reaction coordinate of \( x = 0.5 \) (each profile showed only a single oxidation peak indicative of nanotube burn-off). The oxidation profiles reveal an increase in the oxidation temperature with decreasing iron content. This indicates a decreased reactivity in the nanotube, which stems from at least two different mechanisms.

Figure 5-5. (a) An example SEM micrograph of a nanotube sample. The nanotubes examined appear free of impurities on the micron scale. Scale bar is 2\( \mu \)m. (b) Samples synthesized using the higher catalyst concentrations analyzed were frequently observed to contain significant quantities of carbon coated catalyst particles in addition to those observed enclosed within nanotubes. Scale bar is 100nm.
Figure 5-6. Thermo-gravimetric burn-off of nanotube samples is summarized and plotted versus the sample iron content. In order to summarize the oxidation curve with a single number, the temperature corresponding to oxidation of half the sample mass is used. As iron content in the sample decreases, burn-off temperatures increase, indicating less reactive structures. This change occurs through diminished defect densities and less catalytic oxidation by the iron particles.

The first arises from the presence of iron particles catalyzing the oxidation of carbon nanotubes [6-8]. As the amount of retained iron increases, the amount of catalytic material is increased, resulting in a higher density of catalytically active sites. As the number of sites is diminished (by decreasing iron content), the reactivity of the nanotube structure decreases and is reflected by an increase in the temperature of oxidation.

The second mechanism arises from the improved structural perfection demonstrated in the Raman spectroscopy analyses reported here. Defects in nanotubes serve as sites of increased reactivity [9], so as the peak ratio increases, indicating a smaller density of defect structures, the reactivity of the nanotube structure will
decrease. Both mechanisms serve to decrease the reactivity of the nanotubes and thus increase the sample’s temperature of oxidation.

5.3.2 Growth Time

Elongation of the nanotube array and carbon deposition rate appear to exhibit two distinct stages as growth time is increased (Figure 5-7). Throughout the first stage (stage 1 growth), array length increases linearly and the deposition rate accelerates. In the second stage (stage 2 growth), array length begins to drop off while the mass continues to increase, but now at a linear rate.

Deposition and growth during stage 1 may be understood if one considers the changing morphology of the deposition surface. Initially, only the deposition substrate is present. At this point, carbon is deposited onto the substrate surface, generally as nascent nanotubes, or is incorporated into the elongation of these nanotubes. As the tubes elongate, wall area is increased, thereby increasing the available surface area for carbon deposition proportionately with length. Carbon continues to be incorporated into the elongation of the nanotubes, but will also deposit onto the sidewalls of the nanotubes, thus increasing nanotube diameters (and further increasing the area available for deposition). Diameter survey results (Figure 5-8) confirm an increase in tube diameter and standard deviation with increasing growth time. Thus, as the available surface area for deposition increases, so the rate of deposition increases. The increase in the standard deviation with growth time may be attributed to the constant nucleation of nanotubes. Carbon deposition will occur on the surfaces of existing
nanotubes, increasing their diameters, but will also contribute to the formation of new tubes which will grow in diameter with passing time.

Figure 5-7. Nanotube array length (a) and deposition rate (b) are plotted as a function of growth time. Both may be separated into two phases of growth and deposition. Stage 1 growth shows linear array elongation and accelerating deposition rate with increasing time. Stage 2 growth shows etching of the nanotube array and continued carbon deposition, but now at a linear rate.

Growth changes to stage 2 at approximately 120 minutes. Two potential reasons behind this change include: (1) carbon and new catalysts can no longer reach
the substrate and base of the array due to nanotube thickening or (2) all active catalyst particles have become poisoned and can no longer support nanotube growth. Possible reasons for the observed decrease in nanotube length include preferential etching of the more exposed surface or redistribution of carbon as unsaturated iron particles continue to deposit. In either case, carbon continues to deposit, but mostly in its amorphous form and is not incorporated into the nanotube structures. Thus, the deposition surface morphology does not significantly change, yielding a linear increase in mass and constant deposition rate. For these reasons, with increasing growth times, synthesis products transition from aligned arrays of nanotubes to aligned arrays of nano-fibers to a nanotube-reinforced-carbon composite material.

Figure 5-8. Nanotube diameter and standard deviation are plotted versus the growth time during stage 1 growth. Accelerating carbon deposition during stage 1 occurs as the surface area available for deposition increases as nanotubes elongate. This results in an increase in average nanotube diameters as well as in the diameter’s standard deviation as growth time increases.
Nanoscale carbonaceous contamination was observed on larger tubes in certain samples (Figure 5-9a). In this case, there is no obvious link between the catalyst concentration ratio used and the contaminated samples as several samples across the range of ratios examined displayed varying degrees of carbonaceous deposits attached to the nanotube walls. Instead, this is a result of longer growth times, showing the impact of additional carbon deposition on nanotube walls. Additionally, some samples with this type of contamination showed an interesting bi-layer structure on certain nanotubes, similar to that noted elsewhere [4, 10]. The outer layer varies significantly in thickness, while the inner layer’s thickness and the tube’s inner diameter remain approximately constant (Figure 5-9b). In these cases, the tube structure appears to be an inner set of organized graphene layers coated with an outer layer of carbon, probably amorphous (Figure 5-9c), supporting the proposed mechanism for stage 1 growth.

5.4 Conclusions:

Given the similarity to floating catalyst CVD synthesis of vapor-grown carbon fibers, it was expected that nanotube diameter would similarly depend upon the catalyst to carbon source ratio. Catalyst particle dimensions are traditionally understood to directly impact the diameters of the nanotubes formed, however in this case, a higher catalyst concentration in the feedstock does not necessarily translate to larger catalyst particles and thus, larger nanotube dimensions. The results of the TEM diameter survey indicate a relatively weak correlation between nanotube dimensions
and catalyst concentration, but with an opposite proportionality to what was expected. It has been shown that this dependence is not a result of carbon depletion within the reaction zone.

It is evident that there are trade-offs for catalyst concentration and growth time. As catalyst concentration increases, diameter decreases, but stability and structural perfection decrease, raising the reactivity of the nanotubes. As nanotube growth time increases, the overall CNT array length increases, but so do the average diameter and its standard deviation. Carbon deposition rate appears to be independent of the catalyst concentration, but increases in two stages with the growth time, with nanotubes yielded only during the first growth stage.

These results should allow for improved control in the floating-catalyst chemical vapor deposition synthesis of nanotubes.

Chapter 5, in part, has been submitted for publication of the material as it may appear in Carbon, McKee, Gregg S. B., Deck Christian P. and Vecchio, Kenneth S., 2008. The dissertation author was the primary investigator and author of this paper.
Figure 5-9. (a) Nanoscale non-nanotube carbonaceous contamination was observed on larger tubes in several samples. This type of contamination occurred in samples with increased growth times, across the spectrum of catalyst concentrations examined. (b) A bi-layer structure was observed on some of the nanotubes examined, causing significant variation in the outer diameter of the nanotube, while the inner diameter and inner layer thickness remained approximately constant. (c) The inner layer appears to be organized graphene layers, while the outer layer appears to be a less organized form of carbon, probably amorphous. White lines indicate the approximate boundaries of each layer.
5.5 References


6. **Catalyst-Substrate interaction in CVD Synthesis**

6.1 **Summary**

Carbon nanotube growth substrates interact directly with synthesis catalysts, impacting the resulting nanotube diameters, based upon the mobility of the catalysts on the substrate surface as well as other interactions between the catalyst and substrate. Alumina and silica (as quartz) were found to generate nanotubes with diameters significantly different from most substrates. Catalyst particle formation from a thin film was examined on alumina, silicon, and silica substrates, and was found to correlate well with the relative nanotube diameters. Surface roughness was evaluated and found not to limit agglomeration of the catalyst particles in this experiment.

Significant differences between interactions of the iron catalyst with the alumina or silica substrates were found. These appear to result from the nature of the inter-atomic bonds in the materials, allowing electron transfer and easing the chemical oxidation of the catalyst on ionic alumina surfaces more than on covalent silica. Once formed, iron ions behave similarly to iron oxide, which is predominantly ionic, and will continue to interact with alumina more strongly than silica, further limiting agglomeration of the catalyst material and resulting in smaller catalyst particles for nanotube growth.

Thus, the use of ionically bonded substrates appears to assist partial catalyst oxidation and thereby favor smaller catalyst particle formation during the sintering
phase. Inter-diffusion of the catalyst oxide into the substrate may also assist in limiting agglomeration of metal catalyst particles.

This study examines nanotubes synthesized by floating-catalyst CVD (FC-CVD) on a range of substrates. In-depth analysis focuses upon the most common substrate materials, including silicon, silica (as quartz), and alumina. Theories governing interactions between substrate and catalyst are examined in light of the results of a nanotube diameter survey, and a new theory is proposed.

6.2 Experimental

Carbon nanotubes were synthesized by FC-CVD through the pyrolytic decomposition of a benzene-ferrocene feedstock solution as described in Chapter 3 and shown in Figure 3-1. All synthesis variables other than substrate materials were held approximately constant for this study. Synthesis runs were conducted in a “low-flow” fashion, using approximately 100sccm 99.5% Ar and a synthesis temperature of approximately 830°C. Feedstock (15g ferrocene per liter benzene) was introduced into the furnace at a rate of 0.347ml/min. Growth was allowed to progress for 60 minutes.

A variety of substrates were examined, including silicon, quartz, alumina, NiO, mullite (3Al$_2$O$_3$·2SiO$_2$), graphite, an alumina-kaolinic clay mixture (approximate composition 91.5% Al$_2$O$_3$, 7.8% SiO$_2$, 0.2% Fe$_2$O$_3$, 0.2% TiO$_2$, 0.5% Na$_2$O & K$_2$O), a machinable ceramic with approximate composition of 55% fluorophlogopite mica in a
borosilicate glass matrix, and a soda-lime glass (approximate composition 72.2% SiO$_2$, 14.3% Na$_2$O, 6.4% CaO, 4.3% MgO, 1.2% K$_2$O, 1.2% Al$_2$O$_3$, 0.3% SO$_3$). All bulk substrates were polished to at least 4000 grit prior to nanotube deposition. The soda-lime glass was molten at synthesis temperatures.

Nanotube dimension measurements were made via SEM (Philips XL20, 15kV accelerating voltage) or TEM (Philips EM420, 120kV accelerating voltage, or JEOL JEM-2011, 200kV accelerating voltage) observations. TEM samples were prepared through sonication in MeOH for 2.5 minutes and dripped onto a 200 mesh Cu grid. Micrographs were collected between 70,000 and 150,000 times magnification and nanotube diameters in each measured and tabulated. At least 250 individual and distinct nanotubes from each sample were measured to provide a statistically accurate representation.

To confirm the link between substrate and catalyst particle sizes and thus substrate and nanotube diameters, thin catalyst films (3-10nm) were simultaneously e-beam evaporated (Temescal BJD 1800) onto Al$_2$O$_3$, Si, and bulk quartz (SiO$_2$) substrates. Film thickness was measured during deposition using an Inficon I/C5 controller. Each thin-film/substrate batch was then sintered at synthesis temperatures for 10 minutes under approximately 150 ccm of 10% H$_2$ 90% Ar, in order to mimic the reducing atmosphere present in the synthesis chamber during nanotube growth without introducing carbon onto the surfaces.
Catalyst particle size measurements were then made by contact-mode atomic force microscopy (AFM, Nano-R, Pacific Nanotechnologies). Substrate surface roughness measurements were similarly performed by AFM.

6.3 Results

Carbon nanotubes were deposited upon all substrates except graphite. Aligned arrays were deposited upon silicon, quartz, alumina, mullite, and the machinable ceramic. Figure 6-1 summarizes the results of the diameter survey on the substrates tested. A simple random sample was used, with an approximate margin of error of 6% for a 95% confidence level. While most substrates yielded mean nanotube diameters of approximately 25nm, a significant difference in mean nanotube diameter is observed in the cases of alumina and quartz. These substrates fell significantly outside this range, with mean diameters of 15.8nm and 36.1nm, respectively. TEM micrographs of nanotubes from quartz, silicon, and alumina substrates appear in Figure 6-2.

The observed diameter difference between alumina and quartz is contrary to that reported previously [1] when aluminum was used as a buffer layer on silica and believed to oxidize to Al$_2$O$_3$. Nanotubes grown by FC-CVD in that study are significantly larger diameter when compared to the nanotubes here, but show a lower average diameter on SiO$_2$ substrates compared to Al$_2$O$_3$. 
Figure 6-1. Mean nanotube diameter and standard deviation are compared across several different deposition substrates. Substrate impact on nanotube dimensions appears to be related to the mobility of the catalyst particles on the substrate surface, which governs the ability of the catalysts to sinter and agglomerate.

Figure 6-2. TEM micrographs showing nanotube size and structure for FC-CVD nanotubes grown on (a) alumina (Al₂O₃) (b) silicon, and (c) quartz (SiO₂). Scale bars in each pane are 50nm.
It is commonly accepted that nanotube diameters are directly related to the size of the catalyst particle from which they grew [2, 3]. Thus, the catalyst particle sizes on the substrates should vary proportionately with the observed nanotube diameters.

Examination of the iron thin-films deposited on alumina, silicon, and quartz then sintered for 10 minutes confirms the relationship between nanotube diameters and the catalyst particle sizes (Figure 6-3). Modeled as semi-ellipsoidal shapes, particles increase in size from alumina (radii: 275nm, 271nm, 31nm) to silicon (radii: 315nm, 280nm, 45nm) to quartz (radii: 429nm, 364nm, 69nm).

Figure 6-3. AFM scans of (a) alumina, (b) silicon, and (c) quartz substrates. 10nm of iron was e-beam evaporated onto each of the substrates, which were then annealed at 850°C for 10 minutes under 10% H₂, 90% Ar gas stream. Processing was performed simultaneously on each thin film batch. Resulting particle volumes increase, left to right, indicating increasing mobility of the catalyst on the substrate surface and explaining the difference in nanotube dimensions observed. Particles are modeled as semi-ellipsoid shapes; alumina: radii: 275nm, 271nm, 31nm; silicon: radii: 315nm, 280nm, 45nm; silica: radii: 429nm, 364nm, 69nm.

Since all synthesis parameters, except substrate, remained consistent from one synthesis to the next, the substrate is the only logical cause of size differences in the
catalyst particles. This confirms that substrate choice has a direct impact on the catalyst particle size, and thus on the resulting dimensions of carbon nanotubes grown from those particles.

It is apparent that catalyst mobility differs significantly from one substrate material to another, accounting for the catalyst particle size variations observed. Lower catalyst mobility on the substrate would limit sintering and agglomeration of the catalyst particles, thereby yielding smaller catalyst particles and a lower mean nanotube diameter. Given the particle sizes found by the AFM scans, it is expected that iron mobility on alumina would be lower than on silicon, which, in turn, would be lower than on quartz.

Quartz, silicon, and alumina substrate surface roughness were examined by AFM to evaluate potential relationships with final catalyst particle size. Each surface was quite smooth, with very limited surface features. Root-mean-square roughness measurements were 12.0nm for quartz, 4.1nm for silicon, and 2.6nm for alumina.

6.4 Discussion

Through comparison of the resulting catalyst particle sizes and the measured surface roughness of the quartz, silicon and alumina substrates, it is apparent that surface roughness does not limit agglomeration of the catalyst in this experiment.

\[ \text{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (Z_i - \overline{Z})^2} \]

where \( Z_i \) is the height of a given point, \( \overline{Z} \) is the average height of all points, and \( N \) is the number of points.
Catalyst particle sizes vary oppositely from what would be expected if roughness formed physical barriers to diffusion. All three substrates are extremely smooth by most measures, so surface roughness may play a more significant role in substrates of a rougher nature.

Formation of iron-oxygen compounds has been observed on silica, silicon, and alumina [1], and it is expected that iron oxide will limit catalyst agglomeration on the substrate. However, there exists a limited amount of oxygen under typical nanotube CVD synthesis conditions (e.g. substrate, catalyst oxide, water vapor for purification), so it must be considered where oxygen could derive from and what reactions it might be subjected to.

In typical thin-film based synthesis, substrate and catalyst are both exposed to atmosphere during processing. Storage of a substrate under ambient atmosphere exposes it to both oxygen and water vapor, leading to the formation of native oxides of silicon or catalyst. Water vapor will also adsorb to alumina with significant energy (~140kJ/mol) and remain through temperatures of 500°C [4]. When placed into the synthesis furnace, any of these may react with substrate, catalyst, carrier gas, or carbon source.

When floating-catalyst processes are used, catalyst is introduced with the carbon source, typically in vapor form, directly into the reducing atmosphere of the furnace. The possibilities for oxidation of the catalyst are thus substantially more limited.
Reduction of oxide substrate by catalyst has been suggested [5], but the conditions surrounding this observation appear to suggest that atmospheric exposure is a more likely catalyst oxidation route. Evidence for the reduction of iron oxide by silicon under nanotube synthesis conditions has been previously reported [6, 7]. Further, while kinetics would play a major role on this size scale, bulk reduction of SiO₂ or Al₂O₃ by iron, carbon, or hydrogen gas (H₂) is thermodynamically very unfavorable with large positive free energies associated (Figure 6-4). Indeed, the reduction of alumina by iron would be a well-known thermite reaction run in reverse. Temperature dependent thermodynamic values for these reactions were obtained from [8-10].

Figure 6-4. Thermodynamics of the reduction of silica and alumina by carbon, iron, and hydrogen gas (H₂) to Si or Al and CO, FeO, and H₂O, respectively. All reactions are thermodynamically unfavorable at these temperatures, with large positive free energy of reaction.
Bulk silica and alumina may be reduced by atomic hydrogen (Figure 6-5), which is expected to be present as an intermediate by-product of hydrocarbon decomposition [11], however amounts of atomic hydrogen present during synthesis are expected to be quite low and would be consumed rapidly by this and other reactions. Nonetheless, oxygen freed in this manner, as water vapor, would be available to react with catalyst materials.

There exists a significant difference in the inter-atomic bonding in silica versus in alumina. The bond character in Al\textsubscript{2}O\textsubscript{3} is extremely ionic and polar [4, 12]. As a result, an exposed alumina surface will have a high concentration of lewis acid (Al\textsuperscript{3+}) and base (O\textsuperscript{2-}) sites on its surface, increasing the likelihood of electron transfer leading to chemical oxidation or reduction of the metal catalyst particle [13]. Bond character
in SiO$_2$ is predominantly (65% - 89%) covalent [14]. Further, above 600°C, amorphous (sputtered) forms of SiO$_2$ are known to transform to non-polar, 4-membered siloxane rings [12]. Thus, a silica surface lacks the active sites allowing for the oxidation of the catalysts.

Once formed, the catalyst ions may interact with oxygen in the substrate to form surface moieties that would behave like oxides (particularly on an ionic surface), without necessitating the reduction of the substrate, potentially pinning catalysts and preventing agglomeration.

By examining the phase diagrams for Fe-Si-O and Fe-Al-O systems, other significant differences in how the catalyst ions will interact with the substrate become apparent. It should be noted that the bulk phase diagrams are used here only to indicate the tendency (or lack thereof) of the catalyst ions to dissolve into the substrate. The reactions between the substrate and the catalyst ions to form other phases will be dominated by kinetic variables and is not rigorously discussed here.

The FeO-SiO$_2$ system is shown in Figure 6-6 [15, 16]. For low-iron composition mixtures around nanotube synthesis temperatures (up to ~1200°C), the system consists of a two phase mixture of $\beta$-quartz and fayalite (olivine structured Fe$_2$SiO$_4$) or tridymite and fayalite ($\beta$-quartz is stable from ~573°C to ~870°C at which point it transforms to $\beta$-tridymite), with no solid solubility of FeO in SiO$_2$. This suggests that the incorporation of the catalyst ions into the substrate will require the formation of a two phase mixture, which would then be subjected to capillarity or Gibbs-Thompson effects.
Figure 6-6. The SiO$_2$-FeO phase diagram [15, 16]. At low iron concentrations, a two-phase mixture is formed.

The FeO-Al$_2$O$_3$ system is shown in Figure 6-7 [16, 17]. Alumina accommodates the presence of small amounts of iron ions (here, in the form of FeO) through the formation of a solid solution. Since no secondary phase is created, there are no capillarity or Gibbs-Thompson effects acting to prevent the mixing of the materials. Further, diffusion and solubility of FeO/Fe$_2$O$_3$ into alumina has been noted and studied extensively in prior art [18-20]. Cooper and Nastasi report a high degree of thermally activated mixing between oxides of iron and aluminum around nanotube synthesis temperatures, particularly in amorphous alumina [18].

Thus, it is proposed that the observed difference between alumina and silica substrates is a result of the nature of the inter-atomic bonds in the substrates. Chemical and electronic interactions are more likely to occur on the ionic alumina surface, allowing easier oxidation of iron, which would then act to pin catalyst particles, preventing agglomeration. Iron ions, behaving like iron oxide would also experience inter-diffusion with alumina substrates, further acting to bind the catalyst particles to a particular location. Silica substrates experience weaker interactions with
iron catalyst particles, making the formation of ions more difficult. Without ion formation and strong interaction with the substrate, significant pinning of catalyst particles does not occur, allowing higher mobility across the surface and more agglomeration.

Figure 6-7. The Al$_2$O$_3$-FeO phase diagram [16, 17]. At low iron concentrations, Fe$^{2+}$ ions are soluble in the alumina matrix. At slightly higher concentrations, Al$_2$O$_3$ and FeO·Al$_2$O$_3$ are formed, in both of which Fe$^{2+}$ ions are soluble.

In further support of this theory is the behavior of nanotube diameters grown on substrates with varying alumina-silica compositions. Average diameters increase with increasing amounts of silica in a silica-alumina system. Pure alumina shows the lowest average nanotube diameter at 15.8nm, followed by the alumina-koalinic clay mixture (~91.5% Alumina, 7.8% SiO$_2$) with 24.8nm, mullite (3 Al$_2$O$_3$ · 2 SiO$_2$) with 27.0nm, and pure silica with 36.1nm. However, three (or more) oxide component interaction relationships begin to get quite complex, so the composition might be best understood as a measure of what “most” of the catalyst particles are interfacing with.
In order to test this theory, the mobility of nickel on silica and alumina substrates was examined in the same fashion. Thin films of nickel (10nm) were e-beam evaporated onto quartz and alumina substrates and annealed in the same fashion as the iron thin films previously. Phase diagrams for NiO-SiO$_2$ and NiO-Al$_2$O$_3$ (Figure 6-8) bear a strong resemblance to the FeO phase diagrams [21-23], indicating the formation of a two-phase mixture for the accommodation of Ni$^{2+}$ ions in the silica system and spinel NiO·Al$_2$O$_3$ + Al$_2$O$_3$ in the alumina system. As with iron, nickel can form a trivalent oxide in addition to the divalent NiO. No solid solution of NiO in Al$_2$O$_3$ or NiO·Al$_2$O$_3$ is indicated in the phase diagram, but would be expected due to the ionic nature of nickel oxides. This may be an omission due to the fact that the NiO-Al$_2$O$_3$ system has not been as extensively studied as the FeO-Al$_2$O$_3$ system. It is expected that the nickel catalyst layer will behave in the same fashion as the iron catalyst layer, forming smaller particles on alumina than silica upon annealing. Indeed, AFM scans indicate that this is the case (Figure 6-9), showing increased interaction between the nickel and the substrate, validating the theory proposed as discussed above (silica supported catalyst radii: 426nm, 398nm, 68nm; alumina supported catalyst radii: 248nm, 215nm, 110nm).

Silicon, as an elemental solid, experiences catalyst pinning through a different mechanism, specifically, the formation of iron silicides as noted elsewhere [5, 24]. The consumption of iron catalysts to form silicides acts to poison nanotube growth, but given a large enough amount of iron as a relatively thick thin-film, or a long enough introduction as a floating catalyst, conversion of iron to iron silicide is
incomplete, allowing nanotube formation and growth on an iron-silicide coated substrate [5]. The use of diffusion barriers to limit chemical interaction between catalysts and silicon substrates has been studied extensively [5, 25, 26].

6.5 Conclusions

Catalyst-substrate interaction during nanotube synthesis by CVD has been examined. Average nanotube diameter was measured and on most substrates is approximately 25nm. Alumina and silica (as quartz) were found to generate nanotubes with significantly different diameters of 15.8nm and 36.1nm, respectively. Catalyst particle formation from a thin film was examined on alumina, silicon, and quartz substrates, and was found to correlate well with the relative nanotube diameters.

Surface roughness was evaluated and found not to have a significant role in particle formation. Catalyst oxide formation was then examined. Significant differences between interactions of the catalyst with the alumina or silica substrates appear to result from the nature of the inter-atomic bonds in the materials. The ionically bonded Al₂O₃ substrate eases the chemical oxidation of the metal particles through electron transfer with the surface in comparison with the covalently bonded SiO₂ substrate. Once formed, the catalyst ions may behave similarly to metal oxides, also ionic in the examined cases of iron and nickel, and will continue to interact with alumina more strongly than silica, resulting in limited agglomeration of the catalyst material and smaller catalyst particles for nanotube growth.
Figure 6-8. The phase diagrams for the NiO-SiO$_2$ and NiO-Al$_2$O$_3$ systems [21-23]. As in iron systems, nickel ions would be expected to form a solid solution with Al$_2$O$_3$ and a two phase mixture with silica.
Thus, the use of ionically bonded substrates appears to assist partial catalyst oxidation and thereby favor smaller catalyst particle formation during the sintering phase. Inter-diffusion of the catalyst ions into the substrate may also assist in limiting agglomeration of metal catalyst particles.

Figure 6-9. AFM scans of a 10nm layer of nickel on (a) silica and (b) alumina substrates, annealed in 10% H\textsubscript{2}, 90% Ar for 10 minutes at 850°C. Catalyst particle are significantly smaller on the alumina substrate.

Chapter 6, in part, is currently being prepared for submission for publication of the material. McKee, Gregg S. B., Deck, Christian P. and Vecchio, Kenneth S. The dissertation author was the primary investigator and author of this paper.
6.6 References


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7. **Discussion, Revised Synthesis, & Summary**

7.1 **Introduction**

This thesis proposed to explore and develop enhancements to the structure and arrangement of carbon nanotubes to improve their spinnability. The research detailed in Chapters 3-6 have each contributed to this goal and to the general knowledge of the field. Initial hopes were to apply the findings of these experiments to the floating-catalyst CVD of carbon nanotubes, which had already been tuned to yield ultra-long arrays. This chapter discusses two particular findings from the experiments not specifically discussed previously, which show their true significance operating in concert with each other. These include auto-pyrolysis of the carbon source and the growth mechanisms of the tubes themselves. Auto-pyrolysis and the FC-CVD method in particular were found to be incompatible with the growth of spinnable nanotube arrays. Thus, a revised synthesis process is developed by combining these results with findings from previous chapters, allowing the generation of well-aligned nanotube arrays, which lend themselves to the drawing or spinning of nanotube threads.

7.2 **Auto-pyrolysis**

Decomposition of hydrocarbons is a thermally activated process [1, 2] and generally follows an Arrhenius relationship with respect to temperature. At low temperatures, the reaction products are vanishingly small, but above some critical temperature range, the reaction rate increases exponentially. At high temperatures, cracking and reformation reactions occur between the hydrocarbon molecules to
produce different hydrocarbon molecules, as described in Section 2.4.1.2.1. The amount of carbon generated depends upon the temperature and hydrocarbon species present (or subsequently generated).

In idealized carbon nanotube synthesis, hydrocarbon decomposition to form carbon occurs only on catalyst particles, however it has been observed that a variety of surfaces (including substrates and nanotube walls) can also catalyze the breakdown of hydrocarbons [3] and gas-phase reactions generating free carbon are apparent.

### 7.2.1 Observed Evidence

Evidence for the auto-pyrolysis of the carbon source (benzene) used in the experiments of Chapters 3-6 may be observed in several places. First, in Chapter 3, a significant quality decrease was observed by Raman spectra and TGA oxidation profiles when the nanotube synthesis temperature was increased from 850°C to 900°C, suggesting an increase in the deposition of sp³-hybridized carbon with increasing temperature (see Figures 3-8 and 3-11).

Further evidence for the auto-pyrolysis of benzene is shown in Chapter 5. Deposition rate is shown to be proportional to the second power of the growth time during stage one growth (Figure 5-7b), indicating, as previously discussed, that carbon is depositing on all available surfaces. Direct evidence of this is shown in the nano-scale carbonaceous deposits in Figures 5-9. If carbon deposition were occurring only through catalytic decomposition and the elongation of the nanotubes, it would be expected that the yield would be linearly proportional to the nanotube length. In order
for the yield to increase as observed, the hydrocarbon must break down to form carbon exclusive of the catalyst particles.

Excessive over-coating of catalyst particles observed in the TEM surveys of Chapter 5 also indicates the deposition of auto-pyrolyzed carbon. It is expected that catalyst particles will eventually become poisoned in the synthesis atmosphere, but this would generally result in a contiguous thin coating of carbon over the surface of the particle, preventing the hydrocarbon from making contact with the catalyst particle and decomposing thereupon. However, catalyst particles were frequently observed in these experiments having carbonaceous shells with thicknesses on the same scale of, or larger than, the catalyst particles themselves.

The original proposal for this thesis suggested experiments to evaluate and minimize the strength of the bond between nanotube arrays and their supporting substrates, following the reasoning discussed in Section 2.4.3. These experiments were undertaken, but halted when it became apparent that the data acquired was not representative of the information sought.

The experimental setup consisted of a razor blade attached to a load cell mounted on a translation stage (Figure 7-1). The razor blade was inserted into an aligned array of nanotubes, parallel to the nanotube axis, and then pulled parallel to the substrate via the translation stage. The force required to separate the nanotube array from the substrate was recorded and a stress calculated based on the area of mat removed.
Figure 7-1. The experimental setup for measuring shear strength between nanotube arrays and substrates consisted of a razor attached to a load cell with a pair of translation stages. The razor was inserted parallel to the tube axes by raising the array/substrate from underneath until the substrate and razor were within approximately 25 microns. The razor/load cell stage was then withdrawn horizontally and the force required to separate the array from the substrate was measured.

Examination of the substrates after nanotube removal showed significant, continuous layers of carbon ("crusts") from which the array had separated, indicating the strength of attachment measured was of that between the array and this base layer rather than between the array and the substrate (Figure 7-2a). These basal crusts are very similar to the carbonaceous crusts frequently observed on the top surfaces of nanotube arrays (Figure 7-2b).

When this evidence is taken together, it becomes obvious that excess carbon is being deposited in the synthesis methods used for these nanotubes.

7.2.2 Impacts of Auto-pyrolysis

There exists a competitive relationship between beneficial structural annealing of the nanotube and the detrimental auto-pyrolysis of the hydrocarbon. Higher
synthesis temperatures enable the annealing of defective, high-energy structures out of the nanotube’s graphene walls. However, as discussed above, above a certain temperature, the amount of carbon released into the synthesis zone becomes excessive and unmanageable, leading to the rapid poisoning of the synthesis catalysts and unwanted carbon deposition onto the tube’s wall structures. The synthesis temperature experiments discussed in Chapter 3 again exemplify this. As synthesis temperature increases from 760°C to 850°C, the structural improvements due to increased annealing outweigh the declinations due to excess carbon deposition. Above 850°C, the situation reverses and annealing cannot keep pace with the rate at which carbon is deposited.

Carbon deposition on the catalyst particle may or may not be useful. Depending on the rate of carbon deposition and the rate of tube growth, deposits on the catalyst may be incorporated into extending the nanotube wall structure or may cause a graphitic coating over the particle, terminating growth of the tube. Deposition onto nanotube surfaces is particularly detrimental as it increases the diameter of the nanotubes as well as surface roughness (Figures 5-8, 5-9). Deposition onto other surfaces can cause the formation of a carbonaceous crust on the surface or base of the array. Any carbon deposition other than tube elongation adversely impacts the spinnability of the nanotube array.
Crusts were observed at the base (a) and top surface (b) of nanotube arrays. Shear experiments were aborted as the measured force of separation was between the array and the basal crust, rather than between the array and the substrate.

This problem with carbon deposition is further compounded by the fact that TGA and SEM analyses are incapable of detecting impurity levels detrimental to nanotube spinnability. SEM resolution depends upon the microscope being used, but in general has a limit of several tens of nanometers. As such, while micron scale particles may be observed in reasonable detail, deposits on nanotube surfaces may easily go undetected. Similarly, thermo-gravimetric analysis requires impurity levels
be at least a small percentage of the overall mass. Thus, nano-scale impurities, such as those shown in Figure 5-9a, are below the resolution threshold for either method and may not be apparent. Only examination by TEM has shown effective at determining the level of nano-scale impurities in a sample.

7.2.3 Amelioration

Three methods of addressing carbon deposition through auto-pyrolysis are available: lowering the synthesis temperature, decreasing the partial pressure of the carbon source, and changing the carbon source. Through careful adjustment of the synthesis temperature, the amount of carbon introduced into the system is reduced, however, the deposition rate will be sensitive to small fluctuations in temperature and lower temperatures limit the removal of defects through annealing. On the positive side, lower temperatures will also limit other gas-phase cracking and recombination reactions that may produce toxic substances.

Decreasing the partial pressure of the hydrocarbon in the synthesis furnace is a method pursued by other research groups. Both Zhang et al. and Zhang et al. make use of extremely low hydrocarbon flows in their synthesis methods [4, 5]. However, changes in the partial pressure of the hydrocarbon through adjustment of the carbon source flow rate must be coordinated with the overall flow rates of other carrier and reactive gases, as well as the furnace size, such that the residence time of the hydrocarbon within the furnace is not changed. Further, changing the hydrocarbon partial pressure without altering the synthesis temperature will only alter the rate at
which carbon is introduced into the system, potentially lengthening catalyst life, but will not alter the proportions of useful and detrimental carbon introduced.

Altering the carbon source is a significant and often overlooked way of addressing carbon deposition in the synthesis furnace. As discussed in Chapter 2, different carbon sources have different deposition behaviors, with respect to residence time and furnace temperature. Further, these properties have already been investigated for a variety of hydrocarbons for petroleum industry purposes. While the objective of nanotube synthesis is considerably different from those of petroleum refining (where carbon deposition is generally to be avoided), this data is useful and may be applied with relatively small considerations. However, as each carbon source will have differing decomposition behaviors with respect to temperature, the carbon source and synthesis temperature must be carefully coordinated.

According to the data put forward by P. Tesner [2], all aromatic hydrocarbons examined show low temperature sensitivity for carbon deposition and thus have higher deposition rates at lower temperatures, indicating temperature changes will be of less utility when addressing carbon deposition. Benzinger [1] also indicates that these are primary carbon formers. For these reasons, aromatic hydrocarbons are less favorable than others (e.g. methane, ethylene, acetylene) and should generally be avoided in nanotube synthesis.
7.3 Nanotube Growth in FC-CVD

Conventional discussion of carbon nanotube growth mode generally revolves around tip or basal growth, as described in Section 1.1.9.4. Chapter 6 presents strong evidence that there is some catalyst interaction with the substrate prior to or during nanotube growth, however evidence of both tip and base growth mechanisms is observed. Many instances of enclosed catalysts at the tips of nanotubes, implying tip growth, are observed (Figure 7-3), but many instances of catalyst-free nanotube ends, implying basal growth, are similarly observed in tubes grown by the same method (Figure 7-4).

![Figure 7-3. Catalysts were frequently observed enclosed at the tips of nanotubes, suggesting the tip growth mechanism.](image)

Additionally, it may be expected that nanotubes will form from catalyst particles suspended in the vapor phase, which will be referred to as “floating growth” herein. These defy traditional classification as tip or basal growth as either requires the use of the substrate as a reference point. Further, as the catalysts are not supported, distinct nanotubes might be expected to grow from opposite ends of the catalyst particles, as shown schematically in Figure 7-5. While explicit evidence of
dual-tube growth is lacking, observations over the course of these experiments strongly suggest this growth mechanism. Catalyst particles enclosed within the length of nanotubes are common in both base and tip grown nanotubes, but if a catalyst particle were sucked into a growing tube, the inner diameter would remain constant. Differing inner diameters of tubes on either side of a catalyst particle indicate distinct structures on opposing sides and thus dual-tube growth (Figure 7-6). Outer diameters of these structures are generally similar or the same, but this would be expected in situations where extra carbon is being deposited onto the outer walls of the nanotubes through auto-pyrolysis, as described earlier.

Floating growth causes additional problems with regard to creating nanotube arrays conducive to spinning. Floating catalysts and nanotubes may attach to whatever they contact, especially given the presence of free carbon, which can act as “glue”. If the structure touches down on the substrate, it may anchor itself and simply become another tube in an aligned array. However, if a floating tube or catalyst particle makes contact with the wall of another tube, it may anchor there, adding significantly to the surface roughness of the tube and preventing the close contact of other adjacent nanotubes. Catalyst particles depositing onto the sides of existing tubes may serve as nucleation sites for nanotube growth. Due to TEM sample preparation procedures involving sonication, observing a tube anchored to the side of another tube is relatively rare. However, there is ample evidence of locations where a tube anchored, but broke off during sample preparation, leaving behind a hemispherical shell of its outermost layers (Figure 7-7).
Figure 7-4. Nanotubes were also frequently observed without catalyst particles at their capped ends, suggesting a basal growth mechanism.

Interestingly, it appears that carbon generated through auto-pyrolysis may also contribute a small amount of tube growth by another mechanism. It is occasionally observed that the outermost shells of a MWNT will continue for a short distance after the vast majority of inner walls have been capped (Figure 7-8). Catalyst particles in these tubes are much smaller than the outer diameter of the nanotube, suggesting that
they do not contribute to the growth of these shells, but rather the layers’ growth is fueled by auto-pyrolytic carbon. It is expected that carbon is introduced to the tubes’ outer surfaces, either through auto-pyrolysis or through decomposition of the hydrocarbon on the tube surface. This carbon may then organize itself into a graphene layer, becoming another shell of a multi-walled tube. Since this layer is forming independently of the primary tube, the conditions which cause or caused the closing of the tube may not be present for the new outer layer, allowing it to continue extending in a linear fashion. However, once these layers extend beyond the initial structure, structural support from it is lost, and the outer layers will lose linearity and be more apt to close, explaining why only short extension lengths are observed.

![Figure 7-5. Dual-ended growth from a single catalyst particle. During floating catalyst synthesis, catalyst particles are suspended in the vapor phase, allowing growth to occur without the restrictions imposed by contact with a substrate. Hydrocarbons decomposing on the particle will diffuse across the surface and, depending on particle morphology, may nucleate nanotubes of differing sizes in opposite directions.](image)

7.3.1 Amelioration

If nanotubes are to be spun into a thread or yarn via pulling from an aligned array on a substrate, the location of the catalyst must be controlled. This is a realistic
impossibility in floating catalyst CVD as the catalyst will always be present in the vapor phase. The only option for growing spinnable nanotubes on a substrate is to use thin-film catalyst layers. This simplifies synthesis by a small amount by removing the catalytic spatial distribution and concentration variables from the synthesis considerations, but it also introduces an additional obstacle for continuous nanotube synthesis. On the other hand, if spinning is performed directly from the vapor phase, such as described in Section 2.3.2.5, floating catalyst CVD remains an option.

Figure 7-6. TEM micrographs show distinct changes in the inner diameter of nanotubes from one side of a catalyst particle to another, suggesting dual-tube growth from the vapor phase. Scale bar = 50 nm.

7.4 Revised Synthesis Process

As it was determined that both auto-pyrolysis of the hydrocarbon source and the floating-catalyst CVD method in general are detrimental to the creation of nanotube arrays amenable to spinning and drawing, complete revision of the nanotube
A synthesis process was undertaken. These and other lessons learned through the course of the reported experiments were taken into account.

**Figure 7-7.** Arrows and hemispheres mark sites where nanotubes are believed to have anchored or attached during floating catalyst synthesis, but broken off due to sonication forces during TEM sample preparation. Scale bars are each 50 nm.

**Figure 7-8.** Carbon generated by auto-pyrolysis of the hydrocarbon may deposit onto the outside of existing nanotubes, forming additional graphene walls which may extend beyond the capping of the supporting nanotube. Two examples are shown here. Scale bar = 50nm.
7.4.1 Synthesis Conditions

The revised synthesis method is a thin film CVD process similar in many ways to those used by [4-6]. A 5nm thin film of iron was e-beam evaporated (Temescal BJD-1800) onto 50-300nm sputter deposited (Denton Discovery 18) $\text{Al}_2\text{O}_3$ layer, supported on a silicon wafer. Benzene and other aromatic hydrocarbons were abandoned for their carbon forming characteristics, as discussed above. Instead, acetylene ($\text{C}_2\text{H}_2$) and ethylene ($\text{C}_2\text{H}_4$) were examined as potential sources at various flow rates. Synthesis temperatures between 660°C and 940°C have been attempted in order to find an appropriate temperature for the new carbon source. The carrier gas was switched from 99.5% Ar to a 60/40 mix of 99.999% Ar (in order to control possible oxidants such as carbon dioxide and water) and Hydrogen gas. Carrier gas flow rates were increased from ~100sccm to approximately 1000sccm total flow (no hydrocarbon). Finally, synthesis was moved from the 50mm tube furnace used in most prior synthesis runs to a 25mm or 31mm tube furnace.

As a result of these changes, the velocity of the synthesis gasses through the furnace was increased by an approximate factor of 18 times, with a corresponding reduction in their residence time within the growth zone. The change in carrier gas flow rates also dramatically reduces the partial pressure of the hydrocarbon in the synthesis stream.

Initially, the revised synthesis process was designed to duplicate each of the processes described in the three reports of spinnable nanotubes, however deposits from each of these attempts were non-existent or wholly inappropriate for spinning.
due to non-nanotube carbonaceous deposits. For example, despite the fact that two groups use acetylene as a carbon source for spinnable nanotubes, results with this hydrocarbon showed very little carbon deposition on either silicon or alumina substrates, even despite significant auto-pyrolysis at temperatures above ~800°C.

Significantly improved results were obtained with ethylene as the hydrocarbon source, but with substantially different flow ratios than those proposed by Li et al. [6]. Carbon nanotubes were deposited in aligned arrays perpendicular to the substrate. These nanotubes are much more easily removed from the substrate than those grown through FC-CVD methods and will stick to many things they come into contact with. At synthesis temperatures of 940°C, small amounts of white smoke were observed in the exhaust stream, indicating auto-pyrolysis of the hydrocarbon.

7.4.2 Characterization

SEM analysis shows the tubes of the array tending to bundle together much more than has been observed in FC-CVD arrays (Figure 7-9). Alignment of the tubes appears better in the tubes synthesized at 750°C, compared to those grown at 940°C, which appear to have significantly greater variability of the axial direction (Figure 7-10). Arrays generated in this manner have thus far been significantly shorter than those generated through previous FC-CVD methods (which were up to 6.5mm tall), with average lengths ranging between ~20μm – 120μm. Array lengths appear to be more consistent over the deposition area than those created via FC-CVD, but thin-film substrates larger than ~1 cm² have yet to be investigated. The top surface of the arrays
grown at either synthesis temperature appears to be crust free. However, a basal crust is apparent through SEM observations for the higher synthesis temperature (Figure 7-11).

Figure 7-9. (a) Nanotubes generated by the revised synthesis method show a significantly increased tendency to stick together when the mat is separated, compared to (b) nanotube arrays generated through FC-CVD methods used previously.

TEM analysis of these two samples reveals interesting differences in structure. Both sets of tubes appear to have significantly thinner/fewer walls than those grown by FC-CVD. Nanotubes from the sample generated at 940°C exhibit bamboo-like structure, where the inner diameter of the tube is periodically segmented by one or more graphene layers, much like the bamboo plant (Figure 7-12), while nanotubes generated at 750°C show a hollow core (Figure 7-13). This difference in morphology is not unexpected. As temperature rises, the solubility limit of carbon in an iron catalyst particle and the bulk diffusivity of carbon through the particle both increase. Thus, as carbon diffuses through the catalyst to the nanotube-forming side of the
particle, a graphene layer will form, get picked up and carried away by the extending nanotube. The thickness of the tube walls may be very significant to the spinnability of the nanotubes themselves. Nanotubes with thicker walls will generally be stiffer due to the additional wall layers. Flexibility in the tubes allows them to laminate to adjacent tubes with less difficulty, improving spinnability.

Figure 7-10. (a) Nanotubes generated at 750°C exhibit improved alignment of the array. Scale bar = 20 µm. (b) Nanotubes generated at 940°C show increased variability of the axial direction. Scale bar = 10 µm.
Figure 7-11. A basal crust was observed when nanotubes were generated with ethylene at 940°C, binding the nanotubes to the substrate and indicating auto-pyrolysis of the carbon source. Scale bar = 20 µm.

Figure 7-12. Nanotubes grown at 940°C exhibit a bamboo-like structure due to increased diffusion of carbon through the catalyst particle bulk. Typical diameter of tubes was about 30-35nm. Scale bar = 70nm.
Figure 7-13. Nanotubes grown at 750°C show continuous hollow structures with thin walls. Typical diameters were approximately 20nm. Scale bar = 70nm.

Raman spectroscopy on the two samples indicates a significant amount of sp\(^3\)-hybridized carbon present in the nanotubes (Figure 7-14). In neither case do the G:D or G’:D ratios of these samples (940°C: 1.25 & 1.17, respectively, and 750°C: 1.45 & 1.55, respectively) surpass those obtained via FC-CVD processes, indicating that the actual ratio of sp\(^3\)- to sp\(^2\)-hybridized carbon may not be as significant as the size and flexibility of the tubes.
Figure 7-14. Raman spectra for samples grown by thin-film CVD at differing synthesis temperatures. Neither sample approaches the G:D or G':D ratios achieved via FC-CVD synthesis, suggesting that the actual amount of sp³ carbon is not as significant as originally thought.

7.4.3 Spinnability

Both synthesis temperatures produce nanotubes significantly more conducive to spinning than FC-CVD methods. The observations detailed above indicate that synthesis at or around 750°C is preferable to that at or around 940°C due to improved nanotube structure, size, array alignment, and the elimination of crusts. With regards to spinning threads from aligned arrays of nanotubes, the most significant limitation at this point in time arises from the length of the arrays and the corresponding lengths of the tubes. This is primarily a practical matter, as the manipulation of tubes and arrays with lengths of tens of microns is generally quite difficult. As lengths are extended, manipulation becomes easier and thread quality will improve.
Thus far, spinnability has been strongly suggested by SEM microscopy, but not yet done by hand. Micrographs, such as shown in Figure 7-9a and in Figure 7-15 show the natural tendency of the tubes to draw subsequent tubes from the array to form the thread. Thread drawing has been observed on a small scale (Figure 7-16). Here, a continuous length of approximately 100µm was drawn from an array of 20µm nanotubes, requiring the repeated draw of at least 5 individual nanotubes. Further efforts to improve on this achievement continue.

Figure 7-15. Arrays grown via the revised synthesis method show a strong propensity to cling and draw adjacent nanotubes, indicating their amenability towards spinning or drawing into threads.
Figure 7-16. A 100 µm thread drawn from a 20 µm long array of carbon nanotubes, showing the ability of nanotubes grown by the revised synthesis method to form thread structures.

7.4.4 Limitations & Improvements

It should be kept in mind that the FC-CVD process was honed and optimized over a period of 4-5 years, whereas the thin-film CVD process is still quite new to this lab. Significant improvements to the process may be expected with time as the details of various synthesis conditions are evaluated. For example, further reductions in the carbon source flow rate (all other variables constant) have been found to increase catalyst life, allowing significant increases in the length of the nanotubes. Where 100sccm ethylene flow leads to growth termination by catalyst poisoning in approximately 10 minutes for a total length of ~65 µm, a flow rate of 50sccm allows growth to continue through at least 30 minutes with a total length of ~120µm.

Further improvements might be achieved by switching the carbon source from ethylene to methane. As discussed previously, nanotube structural quality increases with synthesis temperature. The drawback is that auto-pyrolysis of the hydrocarbon
increases exponentially with temperature as well. Thus, it is desirable to utilize a hydrocarbon that requires higher temperatures for decomposition. According to data put forward by Benzinger and Tesner [1, 2], methane appears the most well suited (of examined hydrocarbons) to fit this requirement. Since methane does not deposit carbon directly, it is required to undergo various reformation reactions prior to deposition, which require higher temperatures. These would form the rate limiting step for carbon deposition, allowing temperature increases of approximately 200K, per Tesner’s deposition rate data. For the same reason, however, synthesis gas residence time would need to be adjusted (increased) to allow time for reformation reactions to occur.

7.5 Summary

The theoretical criteria for spinnability proposed in Section 2.4.3 are supported by the results of the revised synthesis process, however the FC-CVD process used in early experiments has proven incompatible with the generation of spinnable nanotube arrays. While significant improvements were accomplished for floating-catalyst CVD synthesis, primarily through substrate choice and growth time, these gains were still outweighed by the excess carbon deposition from auto-pyrolysis and random catalyst deposition inherent to the FC-CVD method.

Auto-pyrolysis was brought under control by changing the combination of carbon source, synthesis temperature, partial pressure of the hydrocarbon, and its residence time within the furnace. TEM observations show significantly improved
nano-scale cleanliness on nanotube walls and the formation of crusts on the surface or base of the nanotube array has been eliminated.

Nanotube diameters were decreased through substrate choice, catalyst film thickness, and adjustment of the nanotube growth times. The revised synthesis process also generates nanotubes with significantly thinner/fewer walls, improving flexibility of the tubes and improving spinnability.

Formation of crusts was found to be a direct result of excess carbon deposition, which, in this case, was primarily due to auto-pyrolysis of benzene and thus was eliminated with the changes described previously.

Through elimination of auto-pyrolytic decomposition of the hydrocarbon during synthesis and switching from a floating-catalyst process to a thin-film based process, significant improvements were made with regard to the nanotube surface cleanliness, dramatically improving inter-tube attractions.

Further improvements to the spinnability of nanotubes grown through thin film CVD may be achieved through further optimization of the synthesis conditions. The results of the experiments reported in this thesis offer a general understanding and guidelines about the impact of the synthesis conditions, but due to the sensitivity of the process to a large number of variables (as well as internal variations, e.g. furnace set point versus actual temperature, temperature variations as a function of location within the furnace), fine tuning is necessary and unavoidable. The potential for significant improvement to the structural quality of the nanotubes exists and may be
achieved by switching to a methane carbon source and increasing the synthesis temperature.

This document has reported research undertaken to improve the CVD synthesis of carbon nanotubes to the point where the self-sustaining drawing or spinning of yarns or threads is achievable. Significant findings with regard to the oxidative stability of nanotube arrays as a function of length, synthesis catalyst, and other synthesis conditions have also been reported. Improvements to nanotube length and quality have been documented and presented, and arrays amenable to spinning or drawing have been generated.

7.6 References


