Design and Construction of Plasma Enhanced Chemical Vapor Deposition Reactor and Directed Assembly of Carbon Nanotubes

by

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Keywords: lithography, patterning, sputtering, thermal process, catalyst, precursor

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Saving the best for last, I would like to thank my parents, who taught me everything I know about life and living (and some stuff about science too). I wouldn’t have what I do if it wasn’t for you.
# Table of Contents

Lists of Tables .................................................................................................................. iii

Lists of Figures .................................................................................................................. iv

ABSTRACT ...................................................................................................................... vii

Chapter 1. Introduction ....................................................................................................... 1

Chapter 2. Background ....................................................................................................... 4

2.1 Carbon Nanotube Properties ..................................................................................... 4

2.1.1 Electronic Properties ............................................................................................ 4

2.1.2 Physical Properties ............................................................................................... 7

2.2 Growth Processes ....................................................................................................... 8

2.2.1 Laser Vaporization ............................................................................................... 8

2.2.2 Carbon Arc Discharge ......................................................................................... 11

2.2.3 Chemical Vapor Deposition (CVD) .................................................................... 14

2.2.3.1 Thermal CVD .................................................................................................. 14

2.2.3.2 High-Pressure CO Conversion (HiPco) ......................................................... 17

2.2.4 Plasma-Enhanced Chemical Vapor Deposition (PECVD) ................................. 19

2.2.4.1 Microwave/RF PECVD ................................................................................ 20

2.2.4.2 High-Voltage PECVD .................................................................................. 22

2.3 Growth Mechanisms ................................................................................................. 26

Chapter 3. Experimental ................................................................................................... 29

3.1 Reactor Design ......................................................................................................... 29
Lists of Tables

Table 1. Effects of Plasma Power on Nanotube Diameter and Growth Rate [14]............... 23
Table 2. Effects of Ammonia Flow Rate on Nanotube Diameter [14].......................... 24
Table 3. Effect of Total Flow Rate on Nanotube Growth Rate [14]............................. 24
Table 4. Effects of Substrate Temperature on Nanotube Diameter and Growth Rate [14]. ........................................................................................................... 25
Lists of Figures

Figure 1. Chiral Vector Orientation Effects Carbon Nanotube Diameter and Atomic Arrangement [17] ........................................................................................................ 5

Figure 2. Carbon Nanotube Structures [3] ........................................................................................................ 6

Figure 3. Chiral Vectors Determine Electronic Properties [3]........................................................................ 6

Figure 4. SEM Image Showing the Setup of Young’s Modulus Test of a Multi-Wall Carbon Nanotube [1]........................................................................................................ 8

Figure 5. Laser Vaporization Reactor Schematic [8]......................................................................................... 9

Figure 6. Transmission Electron Microscope (TEM) Image of Products from Laser Vaporization [8] ......................................................................................................................... 10

Figure 7. High Resolution TEM Cross Section of SWNT Bundle Grown by Laser Vaporization [8] ......................................................................................................................... 11

Figure 8. Carbon Arc Discharge Nanotube Growth Chamber [24] (Originally from [25])....................................................... 12

Figure 9. Scanning Electron Microscopy (SEM) Image of Products of Carbon Arc Discharge Method [9]......................................................................................................................... 13

Figure 10. High Resolution TEM Image of Single Wall Nanotube Bundle Resulting From Carbon Arc Discharge Growth Method [9].......................................................................................... 14

Figure 11. Thermal CVD Schematic Showing Base Growth Mechanism and Precursor Diffusion into the Catalyst Through Porous Silicon [20]......................................................... 16

Figure 12. Different SWNT on the Same Sample Demonstrating the Base Growth Mechanism [11]................................................................................................................................. 17

Figure 13. HiPco Reactor Schematic with Enlargement of Injector Nozzles [12] ............................................... 18

Figure 14. TEM Image of Products from the HiPco Method [12]........................................................................ 19

Figure 15. SEM Image of Radially Grown Nanotubes on an Optical Fiber [13]............................................. 22
Figure 16. Illustrations of Base Growth and Tip Growth Mechanisms [21]. ............... 26

Figure 17. Nanotubes Grown by Microwave PECVD Showing Straight and Aligned Growth, followed by Disorderly Growth after Plasma Deactivation [13]. ....... 28

Figure 18. Simplified Reactor Schematic ................................................................. 29

Figure 19. Sample Holder/Heater Showing Bulb Operation .............................................. 31

Figure 20. (Right) High Voltage Electrode (Red Arrow) Showing Linear Motion Stage ............................................................................................................. 32

Figure 21. Computer Aided Design (CAD) of the Chamber and Rack ...................... 33

Figure 22. Gas Manifold and Plexiglas Cover ............................................................. 35

Figure 23. Gas Flow Simulation of Reaction Chamber .................................................. 36

Figure 24. Heater Test Plots Showing Surface and Side Temperatures ..................... 38

Figure 25. Low Chamber Pressure Results in Plasma Distributed Over Sample Holder, Not Confined to Area Under Upper Electrode. ........................................ 39

Figure 26. Images of Plasma Resulting from Different Gas Mixtures Under Various Chamber Pressures ..................................................................................... 40

Figure 27. Sample Preparation Stages for Catalyst Patterning .................................. 43

Figure 28. Standard Growth Temperature Profile as Measured on the Side of the Sample Holder. ...................................................................................................... 44

Figure 29. Aligned CNT Growth from Patterned Catalyst .......................................... 45

Figure 30. NPGS Pattern with Different Colors Representing Different Doses........... 46

Figure 31. Atomic Force Microscopy (AFM) of the Hole Matrix Pattern. .................. 46

Figure 32. Resulting CNT Matrix Grown from 400nm Hole Pattern ....................... 47

Figure 33. CNT Growth from Holes of Different Diameter ....................................... 48

Figure 34. Control Sample with Damaged Nanotubes ............................................. 49

Figure 35. Sample After 15-Minute Regrowth Showing Realignment of a Portion of Damaged Nanotubes (Left) and Lengthening of Remaining CNT .......... 49
Figure 36. Nickel Cross After Initial 15-minute Growth

Figure 37. Nickel Cross After Second 15-minute Growth (30-min total)

Figure 38. Nickel Cross After Third 15-minute Growth (45-min total)

Figure 39. Nickel Cross After Fourth 15-minute Growth (60-min total)

Figure 40. Etching Effects of NH3 Plasma on Sputtered Ni Catalyst Layer Showing Smooth Sputtered Surface (Left) and Surface After 3 Minute Etch (Right) [15].

Figure 41. CNT Dimensions after First Growth, showing Average and Std Deviation

Figure 42. CNT Dimensions after Second Growth, showing Average and Std Deviation

Figure 43. CNT Dimensions after Third Growth, showing Average and Std Deviation

Figure 44. CNT Dimensions after Fourth Growth, showing Average and Std Deviation

Figure 45. Average CNT Nickel Cluster Diameter per Run

Figure 46. Average CNT Height per Run

Figure 47. Branching of CNT as a Result of Nickel Cluster Fracturing
Design and Construction of Plasma Enhanced Chemical Vapor Deposition Reactor and Directed Assembly of Carbon Nanotubes

Joshua David Schumacher

ABSTRACT

The goals of this research project were the design and construction of a carbon nanotube (CNT) reactor based on the plasma enhanced chemical vapor deposition (PECVD) principle and the development of a method for directed assembly of CNTs by catalyst patterning. PECVD was selected as the growth method due to the requirement of a catalyst for the growth process, thereby facilitating directed assembly and controlled diameter CNT growth at well-defined locations.

The reactor was built in accord with horizontal flow design using standard ultra high vacuum components. The controllable parameters of the reactor include sample temperature, DC plasma intensity, chamber pressure, gas flow ratios, and total gas flow. The most favorable parameters for growing CNTs of well defined length, diameter, and separation were obtained by initially using parameter values obtained from literature, then optimized by changing a parameter and noting the effect on CNT growth.
Catalyst patterns for the directed assembly of CNTs were prepared by electron-beam lithography (EBL). Experiments were performed that demonstrated the feasibility of using lithographic methods to achieve directed assembly of carbon nanotubes for the manufacture of CNT devices. Experiments focusing on growth interruption and regrowth of CNTs were conducted to investigate methods of introducing tailored branching points into carbon nanotubes during the growth process. These experiments clearly demonstrate that growth interruption increases the occurrence of CNT branching. An analysis of the relationships between CNT diameter, branching points, and the number of growth steps was conducted.
Chapter One

Introduction

Carbon nanotubes (CNT) have been the focus of intense research by many groups, primarily because the electronic and physical properties of a carbon nanotube are unique and have been shown to be superior to currently used materials. These properties include a Young’s modulus value on the order of diamond [1, 2], the ability of a nanotube to behave as either a metal or a semiconductor [3], and unique band-gap values based on structure [4].

The physical characteristics of carbon nanotubes are ideal for use in structural applications such as reinforcement of polymer-based composite materials, mechanical devices on the nanometer scale, and for the enhancement of probe-based metrology. Electronic devices based on single wall carbon nanotubes have been created, such as a Field Effect Transistor (FET), a logic inverter and a NOR gate [5]. A multi-level random access memory (RAM) structure composed of SWCNTs has been proposed [6]. The device would use Van der Waals forces to attract and keep orthogonal nanotubes in contact. The attraction mechanism has been shown to be reversible with no permanent deformations in the CNT, and the concept demonstration device operated continuously for extended periods of time [6]. Two multi-wall carbon nanotubes have been manually attached to an insulated probe tip to form nano-tweezers, utilizing the electrical and mechanical properties of MWCNTs in one device [7]. The nanotube tips are attracted to
each other when a bias voltage of 8.5 V is applied to the gold contacts at the base of the CNTs. Manipulation of different nano-clusters and the resistivity measurement of the captured objects has been demonstrated [7].

The early methods of producing carbon nanotubes by laser vaporization [8] and arc discharge [9] lacked control of the CNT length, diameter and alignment relative to the surface structure. This prevented the large-scale use of nanotubes in devices. CNT production by chemical vapor deposition was developed (earliest example shown by Li et al. [10]), and gave rise to three new methods of nanotube growth; thermal CVD [11], High-Pressure Carbon Monoxide (HiPco) [12], and plasma enhanced CVD [13-15]. A key result to this work was the demonstration of using PECVD to produce aligned carbon nanotubes grown in specific locations on a patterned catalyst substrate [16].

The focus of this work was to design and construct a CNT reactor based on the PECVD process, and to develop a technique suitable for wafer-scale integration and alignment of CNT structures. Plasma Enhanced Chemical Vapor Deposition using high voltage was selected for the production of CNTs in this thesis based on the ease of implementation of the method and the ability to control CNT location based on catalyst patterning. After construction of the reactor, the CNT growth parameters were optimized to produce repeatable films of carbon nanotubes with desired diameter and length, aligned perpendicular to the sample surface.
A method was developed for patterning a metallic catalyst by the creation of cavities into thermally grown SiO$_2$. Carbon nanotubes were grown from the catalyst patches in the cavities and the relationship of cavity diameter to CNT diameter was measured. This relationship should allow the diameter of CNTs to be designed before growth as well as permit the simultaneous growth of carbon nanotubes of different diameters on the same sample for use as interconnects or CNT arrays for sensors.

Furthermore, the novel growth continuation of carbon nanotubes was demonstrated and performed in a systematic manner. Metrology of the sample between growth steps showed an increase in the length of the CNTs. The length and diameter was measured and averaged and the data plotted with respect to the number of growth steps. Branching of the CNT was also displayed, with the branched nanotubes included in the statistical data set. The number of branches per nanotube was plotted as a function of the growth to show the effect of continuing growth on the catalyst particle on the CNT tip.
Chapter Two

Background

2.1 Carbon Nanotube Properties

A carbon nanotube is a nano-sized (1 to 100 nanometers) structure that consists entirely of carbon atoms in a hexagonal arrangement with unstressed 120° bond angles. The carbon hexagons of each nanotube are arranged in a helical manner about the length axis of the tube [4], so that the tube resembles a rolled up sheet of graphene (a single planar graphite layer). A nanotube is characterized by a chiral vector (chiral meaning not identical to its mirror image), which defines the distance between two lattice points in a defined rotational direction (see Figure 1). The length of the chiral vector is equivalent to the circumference of the nanotube. Different orientations of the vector determine the different possible nanotube structures (see Figure 2).

2.1.1 Electronic Properties

The electronic properties of the nanotube are also determined by the chiral vector (see Figure 3). Carbon nanotubes that consist of a single wall of carbon atoms (SWNT) have been shown to behave either as a metal or a semiconductor based on the orientation of the chiral vector. Each lattice point has a unique energy band structure associated with it [4]. Carbon nanotubes with a structure of concentric tubes are referred to as multi-wall nanotubes (MWNT). Each wall is assumed to have independent electrical properties,
however the nanotube usually posses metallic properties as a result of the high probability that one or more of the walls behave as a metal and dominates the conductivity of the CNT.

Figure 1. Chiral Vector Orientation Effects Carbon Nanotube Diameter and Atomic Arrangement [17].

The chiral vector \( (C=n_{a_1}+m_{a_2}) \) is based on unit vectors \( a_1 \) and \( a_2 \). The orientation of the chiral vector is shown relative to a sheet of graphene in figure 1a. Rolling the sheet to form a tube shows the basic structure of CNTs (see figure 1b). The structure of the CNT corresponding to the chiral vector from (a) shows that the ends of the vector are joined and define the circumference (see figure 1c).
Figure 2. Carbon Nanotube Structures [3].
The structures are named according to their appearance, namely armchair (a), zigzag (b), and chiral structures (c).

Figure 3. Chiral Vectors Determine Electronic Properties [3].
2.1.2 Physical Properties

The physical properties of carbon nanotubes have also been measured. The stress versus strain response (Young’s modulus) and strength-at-failure of a single MWCNT was measured inside a scanning electron microscope (SEM) [1]. Stress is defined as the applied force per unit area and strain is the ratio of elongation to starting length. The measurement was performed by manually attaching a multi-wall carbon nanotube, synthesized by the Carbon Arc Discharge method (see Section 2.2.2), to two atomic force microscope (AFM) cantilever tips by means of depositing carbonaceous material with the electron beam of the SEM (see Figure 4). This carbonaceous material adhered the ends of the nanotube to the two cantilever tips and was strong enough to allow testing of the MWCNT before the attachment broke. The rigid upper cantilever was controlled by a linear pico-motor, while the lower softer cantilever was fixed [1]. The upper cantilever was retracted and the CNT was stressed to the breaking point. The deflection of the soft cantilever and the length change of the nanotube was recorded and used in the calculation of the strain on the nanotube [1]. Analysis of the data from nineteen repetitions of the experiment yielded a Young’s modulus range for MWCNT between 270 to 950 gigapascals (GPa) [1]. This is similar to that of diamond (approximately 1143 GPa), with the upper result overlapping the lower range of measured diamond films (940 to 1040 GPa) [2].
2.2 Growth Processes

Carbon nanotubes have been grown by three major techniques, Laser Vaporization [8, 18], Carbon-arc Discharge [9], and Chemical Vapor Deposition[10, 11, 19-22]. Other growth methods are derived from these three. An overview of each process is presented and the advantages and disadvantages of each method are reviewed.

2.2.1 Laser Vaporization

Laser ablation was originally used to simulate the conditions for carbon condensation in the atmosphere of a carbon-rich red giant star [23]. This experiment led to the discovery of the $C_{60}$ molecule. A refinement of that process, the Laser Vaporization method focuses the beam of a laser onto a mixture of metallic catalyst and graphite particles to synthesize single wall carbon nanotubes. Many different setups have been used, but the most recent design [8] uses a 2-kW continuous wave CO$_2$ laser focused by a...
NaCl lens with a 20 cm focal length to focus the beam into a tube with a 4 mm diameter (see Figure 5). Nitrogen or argon flows through the tube from the direction of the laser and the mixture of metallic catalysts (an even part mixture of nickel and cobalt) and graphite powders is injected into the stream of gas, passing through the focal point of the beam. The laser beam vaporizes the 40 um carbon particles in approximately 20 milliseconds [8]. The metal catalyst is also reduced to nano-sized particles. Single wall carbon nanotubes with diameters of approximately 1.22 nanometers (nm) are found growing from metal clusters that have a diameter less than 20 nm [8]. The larger metal clusters are encased in thick graphitic shells that prevent the growth of carbon nanotubes. The walls of the reaction tube are kept at 1100°C to prevent the deposition of soot. The products flow through a baffle (to block any stray laser energy) and are collected. In a 10-minute run of this approach, 500 mg of material was produced, approximately 20 to 40% of which was SWNT, the remainder being soot and metallic particles (see Figure 6).

Figure 5. Laser Vaporization Reactor Schematic [8]

Using a mixture of reactants in powder form is the biggest advantage of this process. Previous laser-based techniques used a solid target [23], and the majority of the
laser energy was lost to thermal conductivity of the bulk solid. Using micron-sized
particles reduced the thermal conductive losses and provided for a faster reaction. The
ability to produce between 100 and 200 mg of single wall carbon nanotubes in 10
minutes (600-1200mg per hour) is a significant improvement in yield over older methods,
and is higher than other growth techniques such as the HiPco process (see section 2.2.3),
which averages 450 mg per hour.

The carbon nanotubes produced were clustered together to form densely packed
bundles (see Figure 7). These bundles have more nanotubes than those produced by the
Carbon Arc Discharge method (see section 2.2.2), and the structure of the bundles is not
as well defined.

Figure 6. Transmission Electron Microscope (TEM) Image of Products from Laser
Vaporization [8].
2.2.2 Carbon Arc Discharge

An early method for generating single wall carbon nanotubes was the use of an electric arc between two graphite rods or electrodes (see Figure 8). The rod that served as the anode was partially bored along its length to create a cavity to hold a mixture of metallic catalyst and powdered graphite. Mixtures of nickel and cobalt were originally used as catalysts, however using either of these metals mixed with Yttrium provided an increase in the yield of single wall carbon nanotubes [9]. The rods are held in close proximity to each other (approximately 3 mm) in a low-pressure atmosphere of helium (500 Torr). A current of 100 Amps was passed through the rods, which were continuously moved to keep a constant electric field of ~100 V/cm across the electrodes. The growth process took approximately two minutes.
The products of this method consisted of a quantity of soot deposited on the chamber walls, and a deposit of very fine material around the cathode. Scanning electron microscopy of this material showed an entangled growth of SWCNTs with an average diameter of 1.4 nm [9] (see Figure 9). While the nanotubes were not aligned in any particular direction in the chamber, it was discovered that the nanotubes had formed “bundles” of approximately 20 nanotubes that were all parallel to each other (see Figure 10). The bundles had diameters ranging from 5 nm to 20nm, and the nanotubes displayed a triangular packing arrangement with an average nanotube separation of 1.7 nm.

The advantages of using the carbon arc discharge method for nanotube production are the ease of implementation and minimal cost. The SWCNTs produced are very similar to those produced by laser ablation [9]. In the past, the nanotube yield was low,
but has increased dramatically as a result of reaction optimization to the point that a gram of nanotube bundles may now be produced in a two-minute run. The bundles themselves also offer an interesting structure that may be utilized in future applications.

The main disadvantage of this technique, and the technique of laser vaporization, is the inability to use the nanotubes in their as-grown state. Further work must be done to separate individual nanotubes to be able to use them in electronic applications and devices.

Figure 9. Scanning Electron Microscopy (SEM) Image of Products of Carbon Arc Discharge Method [9].
2.2.3 Chemical Vapor Deposition (CVD)

2.2.3.1 Thermal CVD

Chemical Vapor Deposition is the heterogeneous decomposition of gaseous reactants by the thermal energy of the substrate and subsequent deposition of a solid on the surface of the substrate [26]. For nanotube growth, a catalyst provides the mechanism for carbon absorption and CNT growth. A metallic catalyst, such as iron, nickel, or cobalt, is deposited onto a substrate. The sample is placed in a furnace and heated to a temperature between 700 to 1000°C. The reacting gasses, called precursors, are introduced into the chamber where they are decomposed primarily at the catalyst particles.
by thermal energy. The carbon is absorbed into the catalyst and forms a solid solution with the metal. When the catalyst becomes supersaturated, the carbon precipitates out as a nanotube (see Figure 11). This mechanism applies to all forms of CVD, including the HiPco and plasma enhanced CVD methods.

Single and multiple wall carbon nanotubes have been grown using thermal CVD. Numerous groups have demonstrated that the diameter of the nanotube is directly related to the size of the catalyst particle. Efforts have been made by various researchers to reduce the catalyst size, thereby growing smaller diameter nanotubes. One technique utilizes nanoporous silicon (with 3nm pores) covered with 5nm of iron evaporated through a shadow mask to produce a catalyst pattern [22]. The iron layer forms nanoparticles in the pores of the silicon, which interact strongly with the substrate and remain on the surface during growth. Nanotube growth is further enhanced by the ability of the precursor gas to permeate into the pores of the silicon that do not contain an iron nanoparticle and to diffuse into the catalyst from the sub-surface level, thereby effectively increasing the catalyst absorption area and boosting the growth rate [22].
Nanotubes grown by thermal CVD have been shown to exhibit a base growth mechanism, in which the catalyst particle remains on the surface while the closed end of the nanotube increases in length (see Figure 12). The carbon is precipitated out of the top of the catalyst particle in a continuous manner, as more carbon is diffused into the catalyst to replace the carbon that formed the nanotube. Growth ceases when carbon is no longer supplied to the catalyst. The cause of stunted growth is thought to be a result of an amorphous carbon coating of the catalyst particle, inhibiting further precursor diffusion.
2.2.3.2 High-Pressure CO Conversion (HiPco)

Chemical vapor deposition can also be used without a substrate with the products being formed in the midst of the flowing gasses. High-pressure carbon monoxide conversion uses iron pentacarbonyl (Fe(CO)$_5$) as the catalyst and pre-heated CO as the carbon source. Carbon monoxide at room temperature is flowed through a bubbler filled with liquid Fe(CO)$_5$ (to collect and transport the catalyst) and is injected into a heated quartz tube. Carbon monoxide is flowed along the length of the reactor where it is heated to 1050°C. This is then injected into the reactor via a multiport “shower head” at the point of injection of the Fe(CO)$_5$. The iron pentacarbonyl is rapidly heated by the carbon monoxide, which has been shown to enhance the formation of nanotubes. The reactor is kept at a very high pressure of 2.3x10$^4$ Torr (30 atm). The Fe(CO)$_5$ decomposes and forms iron clusters, which act as the catalyst for nanotube growth. The products are flowed out of the reactor and collected downstream in a filter. The carbon monoxide is recovered and recycled into the process after purification.
The primary advantage of the HiPco method is the high level of carbon nanotube output. Production rates for a parametrically optimized reactor have been shown to be 450 mg per hour (upwards of 10 grams of nanotubes per day). The reaction produces single walled nanotubes and iron particles over-coated with carbon. The nanotubes do not have the amorphous carbon coating that is present on nanotubes produced by laser ablation or arc discharge.

Maintaining the optimal temperature over the length of the reactor appears to be the major difficulty of the HiPco process. If the temperature is too high, the iron clusters do not form, and nanotube growth does not occur. At lower than optimal temperatures, the iron clusters become overgrown with a graphitic shell which prevents diffusion of carbon monoxide into the particle, also preventing CNT growth. The carbon nanotubes
that are produced and collected are not aligned or straight and are mixed with a high concentration of iron particles, which must be separated physically before the nanotubes may be used.

![Figure 14. TEM Image of Products from the HiPco Method [12].](image)

2.2.4 Plasma-Enhanced Chemical Vapor Deposition (PECVD)

Coherent films of aligned carbon nanotubes have been grown by microwave or high voltage-based plasma enhanced chemical vapor deposition. The growth processes of both methods are similar, with the exception of the method of plasma production. The introduction of the precursor gasses into the chamber combined with either high voltage
or microwaves excites a plasma, which decomposes the precursor gasses into their components. The carbon migrates from the precursor gas to the catalyst on the sample and produces carbon nanotubes.

2.2.4.1 Microwave/RF PECVD

Microwave PECVD uses microwave radiation to initiate a plasma. A typical process uses a 2-3 GHz source with output power between 600W to 1 kW, which is comparable to a microwave oven with a frequency of 2.4 GHz and similar power range.

A catalyst of ferric nitrate [27], cobalt [13], nickel, or layered aluminum and iron [28] is deposited on a substrate of silicon (or Alumina [27]). The sample is placed on a graphite susceptor and heated, most often by a radio-frequency (RF) inductive coil, to a temperature between 800 to 900°C. This range of temperatures has been shown to be necessary in the growth of carbon nanotubes by microwave plasma enhanced CVD (see Section 2.3). After the chamber is pumped down to the milli-torr (1x10⁻³) base pressure range, the precursor gasses, controlled by mass flow controllers, are introduced in a specified ratio. The most commonly used gas mixtures are Acetylene (C₂H₂) with Ammonia (NH₃) [13] and Methane (CH₄) with Hydrogen (H₂). Acetylene is usually mixed in a 1:4 ratio with Ammonia. Gas ratios for the Methane/Hydrogen mixture have varied dramatically in recent years, with the majority of the gas changing from Methane (60% of total in 1998) [27] to Hydrogen (80% of total in 2002) [28]. The alignment of carbon nanotubes has also improved, with the results changing from soot and randomly ordered nanotubes (resembling the results from early arc-discharge methods) to fields of
uniformly aligned CNTs. The chamber pressure has also decreased over time (from 15 to 3 Torr), which when combined with the changing chemistry, results in approximately the same quantity of Hydrogen present in the chamber, while the amount of Methane is greatly decreased.

Carbon nanotube growth can occur in the absence of a plasma if the other growth conditions are present. As shown in the experiment by Bower et al. (2000) [13], once the precursor gas is no longer energized, the carbon nanotubes can continue to grow. However, further CNT growth in these conditions is not aligned as it was previously, and the growth mechanism is shifted to conventional CVD. This resulting growth occurs at the same temperature (825°C) as the plasma enhanced growth occurred, but at tremendously reduced rate (150nm/min compared to the plasma enhanced 6000nm/min).

The field of carbon nanotube growth by microwave plasma enhanced CVD has progressed considerably in a relatively short period of time. Early results were similar to that of arc-discharge, the nanotubes produced were tangled and randomly oriented [27] but were grown over the total surface of the sample, not just at the cathode. Recent results have shown that carbon nanotubes can be grown on a variety of substrate contours parallel to the normal of the surface (with slight degree of variation) [13].
2.2.4.2 High-Voltage PECVD

The process of plasma enhanced chemical vapor deposition is similar to that of thermal CVD. A cleaned substrate (usually silicon or glass) is coated with a metal that has been shown to act as a catalyst for CNT growth, such as Ni, Fe, Co, etc., using various deposition methods (evaporation, sputtering, etc.). The coated samples are placed into the PECVD reactor, which is then pumped down to a low base pressure (~1mTorr). Simultaneously, the substrate is heated to a temperature shown to produce carbon nanotubes (450 to 700°C depending on process and chemistry [14, 29]). The decrease in required substrate temperature for CNT growth compared to other growth methods is
thought to be a result of the energy added to the system from the high-voltage plasma. The carbon containing and reacting gasses are introduced into the chamber through a network of mass flow controllers to regulate the flow rate and gas composition of the mixture. The high voltage causes an ionization avalanche resulting in plasma formation, which acts to decompose the gas into its components. The exact growth mechanism of CNT formation is not exactly known, however it is thought that carbon enters into the catalyst until it is supersaturated. Finally, the carbon is precipitated out of the catalyst in the form of a carbon nanotube.

This method has more variables than the other techniques and allows for independent control of growth parameters. It has been shown that substrate temperature, catalyst thickness, chamber pressure, precursor flow rate, gas ratio, order of gas introduction, applied high voltage and current, and electric field orientation have effects on nanotube growth rate, diameter, and alignment.

A comprehensive study of the effect on nanotube growth of changing a single parameter and holding the others constant was performed by Han et al. in 2002 [14]. This work provided insight into the complex, interdependent system of growth parameters and a starting point for successfully growing nanotubes.

<table>
<thead>
<tr>
<th>Plasma Power Settings</th>
<th>Average CNT Diameter</th>
<th>Growth Rate (µm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550V / 0.08A</td>
<td>180 nm</td>
<td>5.8</td>
</tr>
<tr>
<td>605V / 0.12A</td>
<td>90 nm</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Table 1. Effects of Plasma Power on Nanotube Diameter and Growth Rate [14].
The other growth parameters were held constant: Flow Rate of NH$_3$ (240 sccm) and C$_2$H$_2$ (60 sccm), NH$_3$ pre-growth etch (4 minutes), growth time (6 minutes), IR lamp temperature (450°C).

The decrease in nanotube diameter is suggested to be caused by enhanced hydrogen etching from dissociated NH$_3$ due to increased plasma intensity. The increased growth rate is a function of increased amounts of C$_2$H$_2$ being dissociated and absorbed into the catalyst.

<table>
<thead>
<tr>
<th>NH$_3$ Flow Rate</th>
<th>Average CNT Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 sccm</td>
<td>200 nm</td>
</tr>
<tr>
<td>300 sccm</td>
<td>100 nm</td>
</tr>
</tbody>
</table>

Table 2. Effects of Ammonia Flow Rate on Nanotube Diameter [14].

The other growth parameters were held constant: Flow Rate of C$_2$H$_2$ (60 sccm), NH$_3$ pre-growth etch (4 minutes), growth time (6 minutes), IR lamp temperature (450°C), and Plasma Intensity of 605V / 0.12A.

The nanotubes grown at 120 standard cubic centimeters per minute (sccm) of NH$_3$ resembled nanofibers with coarse structure and short length. The growth rate increased slightly with higher flow rates of ammonia. Above 240 sccm of NH$_3$, the CNT density decreased while the diameter remained constant. This behavior is thought to be the result of the etching effects of ammonia. Results from other groups indicate that the use of NH$_3$ is critical for nanotube formation. Without it, the catalyst forms an amorphous carbon layer that prevents CNT growth.

<table>
<thead>
<tr>
<th>Total Flow Rate</th>
<th>Growth Rate ($\mu$m/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 sccm</td>
<td>13.5</td>
</tr>
<tr>
<td>350 sccm</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Table 3. Effect of Total Flow Rate on Nanotube Growth Rate [14].
The other growth parameters were held constant: the ratio of NH$_3$ to C$_2$H$_2$ at 4:1, NH$_3$ pre-growth etch (4 minutes), growth time (6 minutes), IR lamp temperature (450°C), and Plasma Intensity of 605V / 0.12A.

The average nanotube diameter for both growth runs was approximately 90 nm [14]. This indicates that the rate of growth is a function of total flow rate, while carbon nanotube diameter is more dependent on the gas ratio.

<table>
<thead>
<tr>
<th>Substrate Temperature</th>
<th>Average CNT Diameter</th>
<th>Growth Rate (μm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td>40 nm</td>
<td>2</td>
</tr>
<tr>
<td>550°C</td>
<td>110 nm</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 4. Effects of Substrate Temperature on Nanotube Diameter and Growth Rate [14].

The other growth parameters were held constant: the ratio of NH$_3$ to C$_2$H$_2$ at 4:1, the NH$_3$ and C$_2$H$_2$ flow rates, the total flow rate (300 sccm), NH$_3$ pre-growth etch (4 minutes), growth time (6 minutes), and Plasma Intensity of 605V / 0.12A.

A lack of distinct carbon nanotubes was observed at temperatures of 350°C under the current growth conditions. As temperature was increased to 450°C, nanotube definition improved. Further increase of the sample temperature yielded large diameter carbon nanofibers [14].

Finding the optimal balance of parameters for growth of well aligned multiple wall carbon nanotubes requires tuning the process to grow CNTs with a designed diameter at a high rate of growth. Based on the results from the above experiments, a starting recipe for carbon nanotubes of approximately 75 nm diameter should include: NH$_3$ to C$_2$H$_2$ ratio of 4 to 1 with total flow of 300 sccm, sample temperature of approximately 450°C, and a plasma intensity of 605V at 0.12 A DC.
2.3 Growth Mechanisms

A theory of the interaction between catalyst and gaseous carbon resulting in carbon nanotube growth was proposed by Qin et al [27]. The paper concluded that the amount of carbon that can be contained in a catalyst is a function of the temperature of the catalyst and is highly localized. The bottom of the catalyst particle is in contact with the sample surface and is held at a relatively constant temperature. The act of decomposition of the carbon containing precursor gas removes heat from the surface of the catalyst, which is then locally supersaturated. This results in the precipitation of carbon in the form of a nanotube from the upper surface of the catalyst (see Figure 16).

Figure 16. Illustrations of Base Growth and Tip Growth Mechanisms [21].
This accounts for the apparent bottom-up growth of the nanotube seen in experiments using thermal chemical vapor deposition and some experiments where microwave plasma enhanced CVD was used. No catalyst particle is observed at the tip of the carbon nanotubes. In these experiments, the thermal energy of the sample dominates the growth processes. In other microwave PECVD chambers, the substrate temperature is 50 to 100°C less, and the microwave energy to the plasma is increased. These conditions result in carbon nanotubes that have a catalyst particle at the tip and have been shown to grow with a tip growth mechanism (as demonstrated by Delzeit et al. [28], Figure 16, and in section 4.5 of this thesis).

The alignment mechanism of nanotubes is another well-discussed topic. The original cause of alignment of CNTs was thought to be the interaction of Van der Waals forces between closely grown nanotubes. In an experiment by Bower et al. (2000) [13], it was shown that carbon nanotubes will grow randomly in the absence of an electric field, after being grown previously aligned, when the growth conditions are present. It was suggested that if Van der Waals forces were responsible for alignment, continuous growth of aligned nanotubes should remain aligned after the removal of the electric field. Bower also suggested that ammonia provides a stronger local surface field than that of hydrogen because the self-bias potential of a surface is proportional to the mass of the ions and the ammonia ion is heavier than that of hydrogen [13]. Carbon nanotubes grown by thermal CVD were recently demonstrated to grow aligned to an electric field that did not establish a plasma.
An important decision is the choice of catalyst. Carbon nanotubes have been demonstrated to grow from iron (Fe), nickel (Ni), and cobalt (Co). These metals are used primarily due to the fact that they form meta-stable carbides, and that the diffusivity of carbon in these metals is very high [21]. The aim of most of the research into carbon nanotube growth is to build devices and incorporate CNT technology into integrated circuit processing. Iron is typically avoided by IC manufacturers due to the negative effects caused by iron diffusing into silicon, Nickel ($0.28/gram) is less expensive than cobalt ($0.503/gram) and therefore is the more cost effective choice.
Chapter Three

 Experimental

3.1 Reactor Design

The reactor was constructed using a horizontal flow design. A sample is located in the center of the vacuum chamber on a heating element (see Figure 18). The precursor gasses flow horizontally across the surface of the sample and a high-voltage plasma is applied above the sample, perpendicular to the gas flow. In the initial design, sample loading occurred through the bottom by removing the sample holding plate and heating assembly. However, changing to a side-loading design with a loading door simplified the process.

Figure 18. Simplified Reactor Schematic
3.1.1 Reactor Chamber

One of the design specifications was to make the chamber big enough to process four inch diameter wafers. This required that the inside diameter of the chamber be at least ~4.5 inches to provide adequate clearance. To keep costs down, a standard chamber was used rather than a custom design. A stainless steel Ultra High Vacuum (UHV) six-way cross with eight-inch flanges (six inch inside diameter) was selected as the main reaction chamber. This design provides ample interior space as well as isolation of the process from the laboratory environment.

3.1.2 Sample Holder and Counter-Electrode

The sample holder/heater was designed using AutoCAD® 2002 (by AutoDesk) and manufactured by the USF machine shop. The design limitations were very strict as a result of the design temperature and process chemistry. The only materials used in the heater construction were copper, stainless steel and glass. Ceramics were used initially, but discarded after a calcium containing film was found deposited on the chamber walls after the first heater test.

The sample holder itself is a 4 1/8 inch square piece of ¼ inch thick stainless steel. A circular depression was machined into the top to contain a four-inch wafer. Four tubes were welded to the underside of the top, which ride on four threaded legs that are height adjustable and provide a means to change the angle of the sample relative to the flow of the input gasses.
Four 500-watt halogen bulbs, spaced closely to the bottom of the sample holder, provide heat for the sample (see Figure 19). The bulbs are held in place by a stainless steel reflector, which serves to reflect and contain the heat to the underside of the sample holder. Power is routed to the bulbs by a high current copper electrical feedthrough. To monitor the temperature without causing interference with the plasma, a K-type thermocouple is mounted on the side of the sample holder.

Figure 19. Sample Holder/Heater Showing Bulb Operation.
Note height-adjustable threaded legs.
The upper high voltage electrode is currently a 1-inch diameter stainless steel disk mounted on a high voltage feedthrough parallel to the sample holder. The entire sample holder acts as ground for the high voltage. The feedthrough is bolted to a graduated linear motion stage, which enables the electrode-to-sample distance to be varied in-situ from 0 to 30 mm to tailor the plasma.

Figure 20. (Right) High Voltage Electrode (Red Arrow) Showing Linear Motion Stage

Originally, the plasma was induced using a heated filament to cause electron emission. The high voltage between the filament and the sample holder accelerated the electrons to form the actual plasma. However after testing multiple current settings to optimize the heating current for the filament, it was discovered that the plasma also occurred in the absence of the heating current. This discovery allowed the replacement of the filament with a parallel plate electrode, which provided an increase in plasma area.

Another factor influencing the growth of carbon nanotubes was the choice of electrode polarity. Originally, the electrode was held at a negative voltage and CNT growth was poor. Once the polarity was reversed, significant CNT growth occurred.
3.1.3 Support Equipment

The whole reactor chamber and system is mounted on a custom designed and fabricated extruded aluminum rack (see figure 21). The power supplies are mounted on aluminum shelves built into the stand. The plasma is excited by a high-voltage Glasman Series KL power supply. The power supply for the heater is a Sorensen DCS 150-20 and the process temperature is displayed on an Omega CNi 3254 thermocouple display. The stand also accommodates the high-volume Edwards® 30 series roughing pump.

Figure 21. Computer Aided Design (CAD) of the Chamber and Rack.
3.1.4 Gas Input Manifold

A primary decision was the choice of precursor gasses to be used. The atomic absorption grade of acetylene (C$_2$H$_2$) was used as a carbon source in addition to anhydrous ammonia (NH$_3$). Experiments were conducted using only acetylene, but no carbon nanotube growth was observed [30]. Ammonia is thought to serve as an etching agent, preventing the formation of amorphous carbon [31], preparing the Ni surface for growth, and etching the CNT’s while they grow, to help remove defects and keep the diameter small [14].

The precursor gasses are controlled by a custom designed and fabricated stainless steel manifold, using Swagelok® tubing connectors and manual shut-off valves (see Figure 22). Unit Instruments UFC-1660 Metal-Seal Mass Flow Controllers (MFC) provide both measurement and accurate digital control of individual and total gas flow. The MFCs are powered by Unit Instruments URS 100-5 five-channel MFC controller and power supply. The gasses are mixed by a Koflo® Stratus static tube mixer. The entire manifold is mounted on ¼ inch thick aluminum plate.

The gas manifold is housed in a custom designed and fabricated Plexiglas box that contains Sierra Process Control ammonia (2001-10) and combustible (2050-10) gas leak detectors and is under constant suction from the air handler that evacuates the gas storage cabinets and the exhaust of the roughing pump for the reactor. The box was designed to fit into the grooves of the aluminum stand and have a hinged lid to enable access to the manual shut off valves for the gas manifold. The box is reinforced at every
corner to provide structural rigidity when opening the lid or removing the box from the stand.

Figure 22. Gas Manifold and Plexiglas Cover. The MFC’s (in blue), supply lines, shut-off valves, and ammonia leak detector can easily be accessed.
3.1.5 Chamber Exhaust

Initial gas flow simulations were performed using Fluent’s FIDAP flow modeling software (see Figure 23). It was decided, based on the results from those simulations, that the exhaust length needed to be increased to achieve a more laminar gas flow. Adding an extension nipple increased the length by 13 inches to a total of 21 inches. Placing stainless steel vanes in the nipple also helped to reduce turbulence in the gas flow. A glass viewport was placed at the end of the extension to visually access the conditions inside the chamber without directly exposing the viewport to thermal radiation from the heater.

Figure 23. Gas Flow Simulation of Reaction Chamber.
The reactor is pumped down to a millitorr base pressure by an Edwards® 30 series roughing pump. A butterfly-type throttling valve is installed between the chamber and pump to control the exhaust gas flow rate and regulate the pressure in the chamber. The pump exhaust is routed to the air handler/scrubber by 1 inch O.D. stainless steel pipe.

### 3.2 Optimization

#### 3.2.1 Pressure Testing

The chamber was pumped down and thoroughly helium leak tested and registered no leaks above the $1 \times 10^{-8}$ sccm He detection level.

#### 3.2.2 Operational Testing

The mass flow controllers were tested for flow rates at a constant supply pressure determined by the gas cylinder regulators. The zero and full flow rates of the mass flow controllers were also checked and found to match the calibrated specifications. No leaks were detected from the manual gas shut-off valves in the supply lines.

The heater was tested to the design temperature of 800°C (the actual growth temperature used is not that high). The four halogen bulbs heated the sample holder to 826°C (measured on the surface) after 5 minutes at full power (120V at 16.67A) (see figure 23), however sustaining this temperature stressed the glass of the bulbs (combination of heat and differential pressure of halogen gas in vacuum), which resulted in bulb disintegration. The temperature was measured both on the side and surface of the sample holder to enable calibration of the side temperature reading relative to the
temperature at the sample. During a growth run, the process temperature is measured on the side of the sample holder to prevent interference with the plasma. This test was conducted without a sample on the holder and without a plasma. Figure 24 shows the results of the heater test. The maximum temperature was achieved after five minutes, followed by bulb failure. The temperature at the sample holder surface initially falls, then stabilizes. The data for the calibration was taken from this area of the graph where both temperatures were stable (between the eight and ten minute marks). The sample temperature was calculated to be approximately 120% of the side temperature. Power was removed from the heater and the sample holder was allowed to cool.

Figure 24. Heater Test Plots Showing Surface and Side Temperatures.
3.2.3 Plasma Optimization

The optimized parameters of Han [14] and others were used as a starting point for establishing a recipe for a stable plasma. Literature research indicated that moderate plasma current was best for optimal carbon nanotube growth. The high voltage power supply was set for a 10 milli-Amp current limit, while the voltage was adjusted to produce a plasma. The ratio of input gasses was set for 4:1 NH₃:C₂H₂ as per the literature while the total input flow rate was varied between 125 and 250 sccm. The chamber pressure was varied by the exhaust-throttling valve. The shape and distribution of plasma was shown to be strongly dependent on the pressure in the chamber. Low chamber pressure resulted in evenly distributed plasma between the high voltage electrode and the sample holder (see Figures 25 and 26 A &B).

![Image of plasma distribution](image_url)

Figure 25. Low Chamber Pressure Results in Plasma Distributed Over Sample Holder, Not Confined to Area Under Upper Electrode.
High chamber pressure caused an extremely focused, high density plasma between the electrode and the sample holder (see Figure 26D), followed by rapid electrical arcing as the gaseous dielectric of the capacitance between the electrodes broke down and allowed the maximum current, 10 mA, to flow (red arrow in Figure 26D shows formation of arc discharge). Optimal plasma was established with an input gas flow rate of 250 sccm and a chamber pressure of approximately 2 torr (see Figure 26C).

Figure 26. Images of Plasma Resulting from Different Gas Mixtures Under Various Chamber Pressures.
Chapter Four

Results and Discussion

The goal of this work was to produce a method for integrating carbon nanotubes into devices on the wafer scale. Producing CNTs without the use of an electric field resulted in structures of interwoven nanotubes that needed to be physically separated before single tubes could be used. This has been quite a challenge in the past. The two main advantages of using the PECVD technique is nanotube alignment to the electric field and the catalyst dependency of CNT growth, allowing definition of the growth location [16].

4.1 Pattern Generation

The challenge of growth on a patterned catalyst is to make a pattern with 300nm and smaller features. Electron beam lithography was used to write a customized pattern into a polymethylmethacrylate (PMMA) copolymer resist, which served as the mask for the subsequent process steps.

The dose of the electron beam is very important to the success of the pattern. The dose is a function of both electron current and dwell time (the amount of time the beam is striking the same part of the sample). Patterns with very small features require a small dose with a focused beam and very tight control. The first patterns to be designed and written (using the JOEL JSM-840) were to study the effects of different doses on the
developed pattern. The pattern was changed to a rectangular matrix to study the effects of hole size on nanotube growth.

Before patterning the sample was cleaned in an ultrasonic cleaner with Acetone, Isopropanol, and Methanol sequentially to remove organic contaminates. After the cleaning procedure, 130nm of silicon dioxide (SiO$_2$) was thermally grown on the sample, after which a 20nm thick layer of Chromium (Cr) was deposited. Finally, the PMMA was spun onto the sample to a desired thickness (roughly 150nm, see Figure 27a). The sample was then baked in an oven for 2 hours at 175$^\circ$C. The sample was placed into the scanning electron microscope and the writing area was identified. The pattern was loaded into the Nano-Pattern Generation System (NPGS), which controls the lithographic process, and the pattern was written.

After writing, the resist was then developed in a solution of 1:3 methyl isobutyl ketone (MIBK) in Isopropyl Alcohol (IPA). This opened up windows to the underlying Cr layer (see Figure 27b). Exposing the sample to a 15-second chromium etch transferred the pattern through the chromium (see Figure 27c). Finally, a buffered oxide etch (BOE) formed a cavity in the SiO$_2$, exposing the bare silicon and widening the hole due to the isotropic nature of BOE (see Figure 27d). A layer of nickel (Ni) was deposited onto the sample using electron beam deposition (see Figure 27e). Finally, the PMMA was removed with acetone, leaving a Ni layer in a socket of SiO$_2$, with a surrounding masking layer of chromium (see Figure 27f).
Figure 27. Sample Preparation Stages for Catalyst Patterning

A. Sample Layer Structure

B. After E-Beam Litho and Develop

C. After Chromium Etch

D. After Buffered Oxide Etch

E. After Nickel Deposition

F. After PMMA Removal
4.2 Directed Assembly

Samples were run in the PECVD reactor for a standard 15-minute growth run using the optimized growth parameters from section 3.2.3. A standard run temperature profile is shown in figure 28 and involves temperature ramp up under vacuum, constant temperature for 15 minutes while the gasses are flowing and the plasma is active, and the cool down period after the shutdown of the reactor. The calibrated temperature at the center of the sample holder is approximately 550°C. Carbon nanotubes grew from the nickel patch up through the mask (see Figure 29). The alignment of the nanotubes was affected by variations in the electric field between the electrode and the sample holder. Changes in plasma dynamics as a result of slight chamber pressure fluctuations are thought to be the cause of the electric field variations (see section 3.2.3).

![Standard 15-min. Growth Run Profile](image)

Figure 28. Standard Growth Temperature Profile as Measured on the Side of the Sample Holder.
4.3 Nucleation Threshold

The diameter of the hole was also varied in the patterning experiment. The goal was to determine the correlation of hole diameter to CNT diameter.

Six hole matrices were patterned on the same sample using the above technique with hole diameters of 50, 100, 150, 200, 300, and 400nm. Each matrix contained four sub-matrices with different doses — minimum dose in upper left, 33% dose in upper right, 66% in lower left, and maximum dose in lower right (see Figure 30). The dose was controlled by the dwell time of the electron beam as determined by the Nano-Pattern Generation Software (NPGS) and the beam current was held constant at 15 pA. The objective was to simultaneously optimize the dosage and hole diameter.
Figure 30. NPGS Pattern with Different Colors Representing Different Doses

Figure 31. Atomic Force Microscopy (AFM) of the Hole Matrix Pattern.
After the pattern was created and the catalyst deposited, AFM was performed to examine the surface profile and catalyst patch dimensions (see Figure 31). The sample was processed in the CNT reactor for 15-minutes, and then imaged with an SEM. The pattern was not visible for the 50 and 100nm diameter hole matrices, however carbon nanotubes were observed growing from the other hole matrices (see Figure 32). The diameters of the carbon nanotubes and holes were measured and compared (see Figure 33). The average hole diameter is approximately 2.5 times that of CNT growing from the hole.

Figure 32. Resulting CNT Matrix Grown from 400nm Hole Pattern
4.4 Growth Interruption and Regrowth

The regrowth of carbon nanotubes was performed on a sample from a previous run. Scanning electron microscopy was performed on the sample to check the accuracy of the plasma parameters. Tweezers had crushed part of the forest of nanotubes (see Figure 34). During the characterization of this sample, a “landmark” was found that could be used for locating the same area after each growth run. The CNT growth was continued using the same growth conditions and imaged in the SEM. The comparison to the original image revealed lengthening of the undamaged nanotubes and realignment of some of the damaged tubes to the electric field. (see Figure 35).
Figure 34. Control Sample with Damaged Nanotubes

Figure 35. Sample After 15-Minute Regrowth Showing Realignment of a Portion of Damaged Nanotubes (Left) and Lengthening of Remaining CNT.
The tight spacing of the nanotubes was unsatisfactory for accurate length measurement and characterization. A 30 nm thick Ni catalyst pattern was designed to grow carbon nanotubes with sufficient spacing to simplify characterization. The pattern was in the shape of a cross with line dimensions of 0.5µm width by 10µm length.

This sample was run using the optimal growth parameters for 15-minutes, then was imaged and measured in the SEM (see Figure 36). The sample was placed back into the reactor and run for another 15-minutes with the same parameters. Again, it was imaged and measured in the SEM (see Figure 37). This process was repeated two more times, with the results imaged (see Figures 38 and 39).

Figure 36. Nickel Cross After Initial 15-minute Growth
Figure 37. Nickel Cross After Second 15-minute Growth (30-min total)

Figure 38. Nickel Cross After Third 15-minute Growth (45-min total)
Images were taken from the side of the sample for accurate measurement of the CNT height and nickel cluster diameter. Each nanotube on the distinguishable axis of the cross pattern was measured, and the data was plotted (see Figures 41 through 44) along with the average CNT height/diameter value and standard deviations. Figure 41 shows the CNT dimensions from the first growth run. The majority of CNTs were 1 to 2µm in length, with values close to the average of 1.475µm ±0.3µm. The measured Ni cluster diameters were between 200 and 325nm. Figure 42 shows the additional growth of the CNTs as the average CNT length increased approximately 2.5µm in the second run. The average Ni cluster diameter simultaneously decreased by 44nm. Figure 43 shows a slight increase (400nm) in average CNT length with a slight reduction in Ni cluster diameter (22nm). The average CNT length was increased by 1.1µm in the fourth growth run (see
Figure 44) and the average Ni cluster diameter was reduced slightly (7nm). The standard deviation values increased with each successive growth for CNT length (from 0.321µm to 1.153µm) and Ni cluster diameter (from 45.6nm to 52.2nm). The average nickel cluster diameter and standard deviation after each run is shown in Figure 45. It was shown that the Ni particle size shrinks after each growth run, as a result of Ni cluster fracturing and the formulation of new carbon nanotube branches. Figure 46 shows the CNT length increased with the number of growth runs. It appears that the slope of the graph is reduced with later growth runs, indicating a reduction in average growth rate.

Other groups have shown the etching effect of ammonia-based plasma on nickel films [15]. Ren et al. have demonstrated that NH$_3$ is responsible for fracturing a smooth surface of Ni into clusters (see Figure 40). This is mechanism is thought to be responsible for the fracturing of the Ni cluster and subsequent loss of Ni particles from CNT tips, interrupting the growth of select carbon nanotubes. Without the Ni cluster, CNT growth cannot be continued.

Figure 40. Etching Effects of NH$_3$ Plasma on Sputtered Ni Catalyst Layer Showing Smooth Sputtered Surface (Left) and Surface After 3 Minute Etch (Right) [15].
Figure 41. CNT Dimensions after First Growth, showing Average and Std Deviation.

Figure 42. CNT Dimensions after Second Growth, showing Average and Std Deviation.
Figure 43. CNT Dimensions after Third Growth, showing Average and Std Deviation.

Figure 44. CNT Dimensions after Fourth Growth, showing Average and Std Deviation.
Figure 45. Average CNT Nickel Cluster Diameter per Run.

Figure 46. Average CNT Height per Run.
The etching effects of ammonia is thought to cause the nickel pattern (originally 500nm wide), to split and form the Ni clusters that were transported upward on the tips of the nanotubes during CNT growth. This same mechanism is also thought to be responsible for the Ni cluster splitting, causing the formation of CNT branches. The number of Ni clusters per CNT base (see Figure 46) was a ratio of the number of branches in a CNT that contain a Ni particle at the tip to the original number of CNTs without branches, as counted from the cross pattern after each run. The graph is almost linear for the first three runs with increased branching as the Ni clusters fracture into smaller particles (from Figures 36 through 38). The fourth run shows a large decline in the number of remaining nickel clusters as a result of Ni cluster removal from NH$_3$ etching (from Figure 39).

Figure 47. Branching of CNT as a Result of Nickel Cluster Fracturing.
Chapter Five

Summary

In this work, the products and processes of CNT growth methods were compared to select the ideal growth method for implementation based on the goal of growing nanotubes in well-defined locations. Due to demonstrated CNT growth from a patterned catalyst [16], the PECVD method was selected for implementation in the reactor.

The design issues and points of construction of each element of the reactor have been discussed and the plasma optimization and CNT growth parameters were addressed. It was found that the plasma is strongly dependent on chamber pressure, which directly influences the quality of the CNT with regard to alignment and constant diameter over the length of the nanotube.

A method for patterned growth of nanotubes based on a lithographically patterned catalyst was presented and the results of the method were investigated. Successful growth of a single MWCNT from the catalyst patch in the hole demonstrated the success of the method for precise control over the location of CNT growth. The growth diameter of the CNT varied with the hole diameter, and showed a direct relationship of catalyst size to nanotube diameter and the potential to design and control the growth diameter of a nanotube. The method could be used to simultaneously grow carbon nanotubes of different diameters at various locations on the same substrate.
The ability to grow MWCNT from a hole shows promise for developing CNT interconnects for integrated circuits. Using this method to produce CNT-based field emission devices should provide an increase in the resolution and efficiency over current technology. The ability to design the CNT diameter by lithographic patterning and control the CNT length by means of growth time should allow fabrication of CNT-based nanoantenna arrays for high-frequency communication and sensing. Incorporating CNTs into the structure of a solar cell would increase the surface area of the device, and should increase the collection efficiency and power production.

A novel concept of the regrowth of carbon nanotubes was demonstrated and characterized. The nanotubes showed an increase in growth at the tips, while the bases remained stationary. This displayed the dominance of the tip-growth mechanism in this process. Branching of the carbon nanotubes resulted from fracturing of the Ni cluster at the CNT tips after consecutive growth runs. Further experiments should be conducted to refine the technique to control the branching points and introduce junction-type defects in the MWCNT. A physical junction often produces changes in the band-gap or resistivity of the nanotube and could be utilized in future device applications.

The reactor with optimized parameters may be used in future experiments for the production of prototype device structures. Mass production of such device structures on wafer sized substrates using the electron beam lithographic process should be attainable after further modification and optimization with regard to the enlargement of the electrode.
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