CONTROLLED GROWTH OF UNIFORM DIAMETER MULTI-WALL CARBON NANOTUBE ARRAYS VIA CHEMICAL VAPOR DEPOSITION FOR APPLICATION IN FIELD EMISSION DEVICES

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Jonathan Gar-Sing Leong

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ABSTRACT

With the flat panel display industry eclipsing $101$ Billion in 2007 and consumer demand for improved picture quality ever growing, field emission has received increased attention. Traditional field emitters have higher pixel density than current displays, but their contrast ratio suffers due to insufficient emission current. An ordered array of multi-wall carbon nanotubes (MWCNTs) should produce much higher emission currents due to their $>100x$ increase in aspect ratio. However, such a device has not yet been demonstrated due, in part, to the challenge of fabricating an ordered vertical array of straight, uniform diameter MWCNTs.

MWCNTs were grown in a chemical vapor deposition (CVD) reactor by exposing nickel nanoparticles, formed by annealing thermally evaporated nickel thin films under 20 cm$^3$/s (STP) hydrogen flow at 1173 K for 5 minutes, to a mixture of 6 gases (CH$_4$, CO$_2$, CO, H$_2$, and H$_2$O) with a gas phase carbon activity of 20 at 900 K and a total flow rate of 20 cm$^3$/s (STP) for 90 minutes. Spaghetti-like MWCNTs grew on substrates with 10.2 ± 1 nm nickel nanoparticles in a gas mixture with O/H ratio 0.1. An increase in the O/H ratio to 0.5 resulted in the formation of both spaghetti-like MWCNTs and straight MWCNTs. Substrates with 6.1 ± 1 nm nickel nanoparticles and the same O/H ratio, resulted in preferential growth of straight, uniform diameter MWCNTs. Thus, the fabrication of straight, uniform diameter MWCNTs with CVD requires a nickel nanoparticle diameter less than 10 nm and an O/H ratio of 0.5.

Arrays of 43 nm wells were obtained through electron-beam lithography (EBL) after optimization of the thickness of the resist layers and e-beam dosages in addition to hard-baking of the resist. Subsequently, catalyst was deposited within the wells to enable
site-specific growth of the MWCNTs. Hard-baking prevented the resist layer from collapsing during the EBL process, but also prevented its removal during lift-off. Electrical characterization of candidate devices within a custom-built high vacuum chamber showed the need for voltages above 162 V in order to achieve measurable emission.
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1.0 INTRODUCTION

Tubular carbon allotropes have been studied in great detail since their discovery in 1952 by Radushkevich and Lukyanovich [1]. In 1976, Oberlin et al. [2] published transmission electron micrographs (TEM) clearly showing carbon nanotubes with hollow cores. However, interest in utilizing carbon nanotubes as a means to revolutionize modern-technology was minimal prior to their ‘discovery’ by Iijima in 1991 [3], who showed the hollow, tubular, nanometer sized morphology typical of carbon nanotubes through high-resolution transmission electron micrographs (HR-TEM). Due to their excellent mechanical (e.g. high tensile strength that is comparable to diamond and represented by a Young’s Modulus of 1-1.2 TPa [4]) electrical (e.g. resistivity comparable to nickel-chromium on the order of $10^6 \Omega\cdot\text{m}$ [5]), and thermal (e.g. thermal conductivity exceeding that of diamond by a factor of two at greater than 3000 W/m-K [6]) properties, carbon nanotubes have become instrumental in research aiming to make improvements in many applications such as field-effect transistors (FET) [7], interconnects [8], and particularly, field emission devices (FED) [9,10,11]. Several methods for fabricating field emission devices utilizing carbon nanotubes as emitters (CNTFEDs) exist with each differing in the types of carbon nanotubes used as well as their ease in scaling for high-rate manufacturing. It is, therefore, critical to evaluate the performance differences caused by utilizing different types of carbon nanotubes as well as the impact the methods of fabrication have on high-rate manufacturing. Without a clear understanding of the performance and manufacturability of these devices, it would not be possible to incorporate CNTFEDs within the consumer electronics industry.
1.1 Tubular Allotropes of Carbon

Allotropes of carbon with a tubular structure can be categorized in two categories: carbon nanofibers (CNFs) [12,13] and carbon nanotubes (CNTs) [3,14] the latter which includes both single-wall (SWCNTs) and multi-wall (MWCNTs) varieties. The difference between CNFs and CNTs is, particularly, the structure of the tube walls. More specifically, the walls of CNFs are at an angle from the axis of the tube where they form a “[coffee] cup-stacked” structure [13]. On the other hand, the walls of CNTs are parallel with the tube axis; SWCNT being formed by a rolled single graphene sheet while MWCNT having concentric graphene sheets [3]. Typically, the CNFs can only be grown via chemical vapor deposition (CVD) methodologies while CNTs can be grown by CVD and other methods such as direct-current arc discharge or laser ablation.

1.1.1 Carbon Nanofibers

Carbon nanofibers are produced in CVD processes and are carbon tubes formed from stacked truncated cones of graphite (Figure 1). These CVD processes utilize metal...
nanoparticles as growth promoters (catalysts) and are found at one extremity of the filament. The diameter of the CNF is roughly the same as that of the catalyst nanoparticle [12,15]. Additionally, CNFs only grow from catalyst nanoparticles with diameter greater than 20 nm [15]. Generally, the growth of CNFs requires temperatures in the range of 773 K to 973 K, the presence of carbon gases (e.g. methane, acetylene, ethylene, benzene, and carbon monoxide), and transition metal catalysts (e.g. Iron, Nickel, Cobalt) [12,16,17]. The growth mechanism has been extensively studied [12,15,16,17,18] and consists of three basic steps: decomposition of hydrocarbons on the surface of the metal nanoparticles, diffusion of carbon into the metal nanoparticles, and precipitation of carbon out of the metal nanoparticles to form carbon filaments. CNFs mostly grow in a “spaghetti-like” [19] fashion where they are not particularly aligned with each other, contain many structural defects, and bend many times throughout their length [11].

1.1.2 Single-wall Carbon Nanotubes

As mentioned previously, single-wall carbon nanotubes can be produced via CVD and other methods such as direct current arc discharge and laser ablation. The later two methods were the original methods to produce SWCNTs while CVD was introduced as a method to facilitate mass-production. Since direct current arc discharge and laser ablation techniques require time-intensive purification/filtration of the end product to obtain the desired samples, these techniques are not favored when seeking a method for mass-producing devices where a more continuous process with minimal manipulation of the devices is favored. The method of producing SWCNTs via CVD is similar to that of producing CNF, although, higher temperatures (> 1500 K) are typically needed to
facilitate growth [20]. SWCNTs are made of a single rolled graphene sheet and depending on the angle of this roll as defined by the wrapping vector, C, of the nanotube (Equation 1); they can have semiconducting (bandgap of 0.4-0.7 eV [8,21]) or metallic properties due to the resulting structure [22] (Figure 2). While the armchair conformation

\[ C = na_1 + ma_2 \]

**Equation 1:** The wrapping vector, C, where \((n,m)\) are integers that specify the angle of the graphene sheet roll and \(a_1, a_2\) are unit vectors. If \(n = m\), the tube is of the armchair conformation. If \(m=0\), the tube is of the zigzag conformation. All other tubes are of the chiral type. [8]

![Figure 2: SWCNTs of differing configurations](image)

(a) (b) (c)

Figure 2: SWCNTs of differing configurations (a) armchair has metallic properties while (b) zigzag and (c) chiral can both have either semiconducting or metallic properties. *Adapted from [22]*

results in the respective tubes to have strictly metallic properties, zigzag and other chiral conformations can be either semiconducting or metallic. If the difference between \(n\) and \(m\) results in an integer that is divisible by 3, the tube will have metallic properties [8]. Since SWCNT diameters are typically in the range of 0.7 nm to < 5 nm and their lengths
can be up to several millimeters, they can have aspect ratios (defined as the length divided by the diameter) beyond $10^7$.

1.1.3 Multi-wall Carbon Nanotubes

As with single-wall carbon nanotubes, multi-wall carbon nanotubes can be produced by CVD processes as well as the non-manufacturing-friendly direct current arc discharge and laser ablation techniques. MWCNTs do not typically require the higher temperatures that are used to grow SWCNTs; however, it is possible that higher growth temperatures enhance the crystallinity of the MWCNT and reduce defects so that straight nanotubes can be obtained [23]. In the case of large diameter MWCNTs (> 20 nm), it is often difficult to distinguish them from CNFs without the aid of instruments like the HR-TEM. Large-diameter MWCNTs typically have many defects (unless grown at elevated temperatures) and the resulting growth has been described as “spaghetti-like” or “bamboo-like” [19,24]. MWCNTs are comprised of several concentric graphene sheets (Figure 3) and electrical conduction favors the outermost shell since it is in direct contact with the external electrodes [25,26]. In vacuum, without the presence of oxidants,

![Schematic of a multi-wall carbon nanotube with three concentric graphene sheets. Adapted from [25]](image)

MWCNTs have excellent electrical stability due to the stabilizing effect of the multiple graphene shells which slow degradation which generally results from resistive heating of
the structure during current emission [11]. MWCNTs are generally incorrectly regarded to be metallic; they are more accurately classified as non-semiconducting since the large diameter of the outer wall causes the bandgap of the MWCNT to approach 0 eV [25]. However, the electrical properties of MWCNTs may not be as straight-forward for MWCNTs that have smaller diameters. For example, Collins and coworkers [26] have reported on the conformation of the shells of the MWCNT having an effect on the overall electrical properties of smaller diameter MWCNTs.

For a 9.5 nm diameter MWCNT with intershell spacing of 0.34 nm and 14 shells total as determined by TEM, the authors reported on the effects on the electrical properties of the MWCNT when the shells were removed one at a time by oxidation in air under applied voltage of 1.7 V. The destruction of the shells was marked by regular step-wise drops in the measured current with step sizes of approximately 12 µA [27]. By plotting capacitance vs. gate voltage, the authors demonstrated the difference in the conformation of the individual shells as each shell was removed. Metallic behavior on a capacitance vs. gate voltage curve appears as a close to zero-slope trend whereas pure semiconductor behavior is noted by regions of zero conductance where the charge carriers are completely depleted. The original 9.5 nm diameter MWCNT exhibited metallic behavior until the third outermost shell was removed (Figure 4). It is important to note the authors did not claim that the three outermost shells were of the arm-chair conformation. It is possible that the three outermost shells were not of the arm-chair conformation, but had diameters large enough so that their bandgap approached 0 eV as suggested by other authors [25]. Since there were still metallic inner shells, the capacitance did not drop to zero as would be expected for a semiconductor, but was
Figure 4: Electrical characterization of a 9.5 nm diameter MWCNT comparing capacitance vs. gate voltage showing the effects of removing individual shells. $n$ is the total number of shells and equals 14 for this particular MWCNT [26].

marked with a negative slope which eventually leveled to the capacitance level of the metallic shell beneath it. Upon removal of the semiconducting shell, the MWCNT exhibited purely metallic behavior. These results suggest that MWCNTs with diameters 7.48 nm or less are small enough such that the conformation of the individual shells are non-negligible and can determine the overall electrical properties of the MWCNT. The authors noted that the trend was random due to the shells being of random orientation (chirality). Nevertheless, the authors were able to show that in their specific MWCNT, the 5th shell, counting from the inner most shell, was the inner most metallic shell since the MWCNT began to exhibit complete semiconducting behavior upon removal of this shell (Figure 4).
1.2 Field Emission

Field emission (FE) is the emission of electrons from the surface of a condensed phase into a vacuum due to the presence of high electrical fields. In FE, the applied electrical field is high enough to allow electrons with energies below the Fermi level to tunnel through the potential barrier at the surface, known as the work function of the material. Field emission is also known as cold emission or Fowler-Nordheim tunneling and is very different from other forms of emission like thermionic emission or photoemission. Thermionic emission requires thermal energy to be provided to the material while photoemission requires the material to absorb photons of light to induce the tunneling effect. FE offers several additional characteristics that are attractive for vacuum electronics such as instantaneous response to changes in the electric field, resistance to small fluctuations in temperature, good on/off ratio, and ballistic transport [28]. In 1928, Fowler and Nordheim [29] accurately described field emission leading to the formation of field emission theory. The Fowler-Nordheim theory predicts extremely high current densities from emitters, far greater than what would be possible with thermionic emission, and has led to an abundance of research to create devices (e.g. Field Emission Displays) that not only take advantage of FE, but push the envelope in terms of maximizing the emitted current densities while minimizing power requirements.

1.2.1 Fowler-Nordheim Theory

The Fowler-Nordheim theory is used to quantitatively describe the FE process for metals, more specifically, elastic tunneling through a triangular barrier, with the electron distribution described by Fermi-Dirac statistics [29,30]. There are several assumptions that Fowler and Nordheim made when formulating their theory: the metal obeys the free
electron model of Sommerfeld with Fermi-Dirac statistics, the metal surface is planar (reduces the problem into 1-D), the potential in the metal is constant, and the temperature of the system is 0 K [29,30]. The derivation of the Fowler-Nordheim (FN) equation is non-trivial and can be found in the literature [29,30,31]. The final simplified form relates current density to the electric field (Equation 2) [32,33]. The FN equation is often more

\[ J = K_1 E^2 \exp\left( -\frac{K_2}{E} \right) \]

\[ K_1 = \frac{1.56 \times 10^{-6}}{\Phi}; K_2 = 6.87 \times 10^9 \Phi^{\frac{3}{2}} \]

**Equation 2:** Fowler-Nordheim equation where \( J \) is the current density in mA/cm², \( E \) is the electric field (V/m), \( \Phi \) is the work function of the material (eV)

useful in a linearized form with measurable quantities as variables. This is accomplished by utilizing the definition of field enhancement factor \( \beta \), substituting in applied voltage and measured current, and linearizing the resulting expression with the natural logarithm (Equation 3). With the known measured current readings and known applied voltage,

\[ \ln\left( \frac{I}{V^2} \right) = \ln(\zeta_1) - \zeta_2 \left( \frac{1}{V} \right) \]

\[ \zeta_1 = \frac{1.56 \times 10^{-6} A \beta^2}{d^2 \Phi}; \zeta_2 = \frac{6.87 \times 10^9 d \Phi^{\frac{3}{2}}}{\beta} \]

**Equation 3:** Fowler-Nordheim equation where \( I \) is the measured current (mA), \( V \) is the applied voltage (V), \( A \) is the emitting area (cm²), \( \beta \) is the field enhancement factor (E*d/V), \( d \) is the distance between the emitting area and the counter-electrode (m)
it is possible to plot \( \ln(I/V^2) \) against \( 1/V \) in what is known to be a F-N plot [11]. A constant negative slope in the resulting plot demonstrates that the electrical characterization is dominated by field emission.

1.2.2 Prior Art: Field-Emitter Arrays

Based on F-N theory, the field enhancement factor and work function are variables that affect emission characteristics of the field emitter. Ideal field-emitters are based on materials that minimize work function while ensuring excellent geometry (e.g. high aspect ratio) to allow for maximum field enhancement [34]. It is important to note that the field emitter must be electrically, thermally, and mechanically stable in order to prevent large changes in its work function throughout its use. Since the late 1960’s when Spindt [35] described a thin-film field emission cathode, much work has been done to understand FE as it applies to arrays, as well as improve the performance of such arrays. While Spindt’s early work [35] focused on micrometer-dimensioned molybdenum tips, further improvements were desired in terms of understanding the importance of the tip geometry, manufacturability, increasing sharpness of the tips, and increasing aspect ratio to be much better than one. Much work has been done with conductively-doped silicon emitters whose tips could accurately and reproducibly be made very sharp by lateral high temperature thermal oxidation, although, with aspect ratios still around one [36,37]. Other groups successfully deposited thin-films of metal [38], or used diamond [39,40,41] to enhance the FE ability of the emitting tips. Most of these emission tips varied in geometry but were generally pyramidal with varying apex angles. Utsumi [42] introduced a figure of merit based on the theoretical best emitter being a metallic floating sphere where the typical emitter tips were ranked. Pyramidal tip geometries ranked better
with decreasing apex angle, while whisker-like geometries with hemispherical caps fared the best (Figure 5). Utsumi’s observation occurring almost coincidentally with Iijima’s “discovery” of carbon nanotubes sparked the beginnings of the utilization of carbon nanotubes as field emitters.

**Figure 5:** Various field emission geometries with performance factor, $f$, given as a fraction of the theoretical floating sphere. (a) Rounded whisker. (b) Sharpened pyramid. (c) Hemi-spheroidal. (d) Pyramidal. *Adapted from [42]*
2.0 CRITICAL LITERATURE REVIEW

Investigators have studied field emission phenomena, as well as carbon nanotube growth for several decades. It wasn’t until the early 1990s when both of these concepts were understood well enough to allow for “Gedanken” devices incorporating FE and CNTs to come into fruition. In 1995, de Heer et al. [9] demonstrated the first known device that utilized CNTs as the emitters in a field emission device (FED). Throughout the earlier portion of the past twenty years, much work had been done to tackle the challenge of creating FEDs based on CNTs (CNTFED) that produced repeatable results that could be explained by FE theory while, the latter decade has seen a shift in focus towards production methods that are reproducible and amenable to high-rate manufacturing. Unfortunately, as of present, there is no standard for manufacturing and testing CNTFEDs. The quality of the device depends on factors such as the chemical vapor deposition (CVD) technique employed to grow the CNTs and the catalyst patterning technique used. Different CVD techniques produce CNTs of varying vertical alignment and morphology while the use of different catalyst patterning techniques affects the spacing between the CNTs. Device benchmarking can vary among research groups due to differences in electrical characterization technique, high vacuum equipment, and background electrical noise. Thus, it is important to consider these differences to determine the effects they have on the performance of the device and to gain a better understanding of the device characterization so that direct comparisons with similar devices can be made.
2.1 Carbon Nanotube Field Emission Device Fabrication

The evolution of CNTFEDs over the past twenty years has been marked with a dramatic shift from devices being conceptual to being manufacturable. Early devices typically made use of CNTs grown by either arc discharge or laser ablation due to an inadequate understanding of controlled CNT growth in CVD processes. At that time, both arc discharge and laser ablation techniques were capable of producing CNTs that were well graphitized, straight, and low in structural defects while, in contrast, CVD processes grew CNTs that were not well graphitized, had spaghetti-like growth, and high in structural defects [11,19,23]. The main problem with non-CVD growth of CNTs is the requirement for a very time-consuming purification step and subsequent manipulation of the purified CNTs onto appropriate substrates. While this was not a problem for the early devices since the research focus at the time was on discovering and demonstrating interesting physical properties [43], it became a significant hurdle when the focus switched towards high-rate manufacturing of CNTFEDs. In addition, as the understanding of CNTFEDs increased, other hurdles including vertical alignment of CNTs and control of the density of CNTs on the substrate were discovered and studied.

2.1.1 Ex situ Fabrication

*Ex situ* fabrication of CNTFEDs refers to the devices where the carbon nanotubes have to undergo purification processes and be manipulated onto the device substrate. The carbon nanotubes can be purchased from specialty companies (e.g. Unidym [44], Nano-C [45], and NanoLab [46]) or fabricated from arc discharge or laser ablation. The latter two procedures are discussed below.
Fabrication procedures for arc discharge of MWCNT were published by Ebbesen and Ajayan in 1992 [47] and has been used or improved upon by several other groups [11,48,49]. Ebbesen and Ajayan reported on the generation of arcs between two graphite electrodes in a He atmosphere ranging from 20 Torr to 500 Torr (reference standard not provided) with an applied voltage of 16 V and current of roughly 100 A, the latter of which depends on the size of the rods, their separation (typically 1mm) and the gas pressure. The authors reported that no CNTs were formed at pressures of 20 Torr He. Instead, sheet-like amorphous, glassy graphitic material was found. When the pressure was increased to 100 Torr He, they found some CNTs although the yield was very low. Upon further increase to 500 Torr He, they reported both a mixture of CNTs and other nanoparticles. They found 500 Torr He to be optimal in terms of conversion of consumed graphitic starting material into CNT and similar sized nanoparticles (roughly 75% conversion). Increasing the pressure to 2500 Torr did not improve the quality of the CNTs, but instead lead to a decrease in conversion. The author’s did not propose any growth mechanisms to explain their results. The resulting CNTs were found to have diameters ranging 2 nm to 20 nm under TEM with well-graphitized, straight walls with length exceeding 1 µm.

While the arc discharge method mentioned worked well for producing MWCNTs, it was shown to have extremely low yields for SWCNT production [50]. Using this method, SWCNTs are formed in the gas phase rather than physically on the carbon cathode. By utilizing metal catalysts (Co, Pt, Y) akin to CVD growth of CNTs, the yield of SWCNT was improved, although the growth was plagued with an abundance of fullerenes and the yield was still relatively low compared to MWCNT growth under arc
discharge [50,51,52,53]. Bethune and coworkers [51] reported on the generation of arcs between two graphite electrodes in a 100-500 Torr (reference standard not provided) He atmosphere with a current of 95-105 A. In order to incorporate the metal catalyst into the arc discharge system, one of the graphite electrodes was modified with a ~4 mm hole filled with a catalyst mixture consisting of graphite and the catalyst metal. The authors reported that Co-graphite mixtures facilitated growth of SWCNTs while Fe-graphite, Ni-graphite, Ni-Cu-graphite mixtures did not [51]. Instead, these other mixtures only facilitated growth of larger carbon fibers when exposed to hydrocarbons as expected from typical CVD process utilizing hydrocarbons as the carbon source gas [12]. They also found that their tubes were encased in amorphous carbon. Lambert and coworkers [43] further affirmed that Co-graphite mixtures were superior to other one-metal mixtures by showing that iron, copper, platinum, ruthenium, and nickel mixtures with graphite formed no SWCNTs. They additionally discovered that binary metal mixtures could significantly enhance SWCNT yields. By using a mixture of 18.75 wt% of each Co and Pt with balance being graphite, they were able to double their SWCNT yield. They also showed that Co-Ru did not grow any SWCNTs. The authors speculated that the effectiveness of the bi-metallic catalyst relied on the formation of a single-metallic phase (alloy). Using X-ray diffraction, they reported that when Co-Pt bi-metallic mixtures were used, there was only a single metallic phase within the SWCNT. However, when Co-Ru bi-metallic mixtures were used, there was a mixed metallic phase within the carbon soot product.

An alternative method, laser ablation (laser vaporization), was introduced by Guo and coworkers [54] to increase the SWCNT yield and to minimize the amorphous carbon
overcoat that was common in SWCNTS produced by metal-catalyzed arc-discharge method [50,51,52,53]. The laser-vaporization apparatus consisted of a Continuum DCR-16S laser and a 1” quartz tube mounted in a 12” Lindberg furnace capable of temperatures up to 1473 K. The laser was 300 mJ/pulse, and the focus spot was 6-7 mm on a graphite target comprised of the metal catalyst mixtures being tested. The nature of this setup allowed for continuous operation with better control over the vapor phase compared to the traditional arc discharge setup which was a batch process by nature and relied on accurate current inputs based on the consumption of the graphite rods. They found that the yield of SWCNT compared to fullerenes was greatly enhanced in both single metal and bi-metal catalysts and bi-metal catalysts enhanced the yield by 10-100 times. Their process typically yielded 15% SWCNTs for all carbon vaporized using Co/Ni (0.6/0.6 at%) and Co/Pt (0.6/0.2 at%) catalysts. Moreover, their tubes lacked the thick layer of amorphous carbon that was typical in the traditional arc discharge production method. This work was further refined by Thess and coworkers [5] where the overall yields were increased to beyond 70 percent. They used Co-Ni (0.6/0.6 at%) catalyst and operated the furnace at 1473 K under flowing Ar at 500 Torr (reference standard not provided). Their gains in yield for SWCNT growth was facilitated by their implementation of a double-laser pulsing scheme. More specifically, the initial laser vaporization pulse (532 nm, 250 mJ in a 5 mm diameter spot at 10Hz) was followed 50 ns later by a second pulse (1064 nm, 300mJ, in a 7 mm diameter spot coaxial with the first laser). This double-laser ablation scheme was shown to provide a more uniform vaporization of the graphite-metal target [55,56].
The laser ablation technique requires special equipment and is more expensive and difficult to operate than arc discharge [48]. Journet and coworkers [48] expanded on the work of Lambert and coworkers [43] to incorporate bi-metallic catalyst mixtures consisting of graphite and Ni-Co, Co-Y, or Ni-Y in various atomic percentages [11,48,43,57]. They found that a mixture of Ni-Y (1.0/4.2 at%) granted the highest yields (between 70-90%) [48] with comparable amount of amorphous carbon coating to previous work by Thess and coworkers [5]. Their results suggested that arc discharge could still be used for growth of SWCNT with high yield; however, they did not discuss how this batch process could be scaled up appropriately to compete with the continuous laser-ablation process.

It is important to note that all of the CNT products from the above processes require post-processing to remove unwanted carbon side-products such as fullerenes [52,43,58] or metallic SWCNTs. While metallic SWCNTs could serve to short out devices, they are typically not a problem because they can be easily burned out with the application of current densities exceeding $10^9$ A/cm$^2$ [26]. The semiconducting SWCNTs are protected during this process since their carriers are depleted by the gate layer. The purification process involves oxidation processes (i.e. high temperature exposure to air or oxygen [59] or chemical oxidation by HNO$_3$, KMnO$_4$, or OsO$_4$ in water [60]) or filtration and flocculation (suspension in ultrasonicated aqueous solution of sodium dodecyl sulfate to remove large debris followed by flocculation in concentrated surfactant where the purified product settles out [58]). These techniques have been employed by most groups [11,49,43,61] and has been explored and explained in greater detail by Duesberg and coworkers [62]. In short, dry oxidation can grant very pure materials, however the yield
is low. Chemical oxidation can chemically alter the product which introduces surface functionality, tolerable for some applications, but unacceptable for others. Filtration and flocculation allows physical sorting methods to be employed, but requires a multitude of steps to grant high purity, representing a very time consuming process on the order of several weeks. Certainly, the purification step is the bottleneck of the process and not amenable to high-rate manufacturing.

Finally, purified CNTs are placed on a substrate forming the device to be tested. Typically this is done by evaporating suspensions onto a substrate [11] or preparing the substrate with conductive epoxy containing the CNTs [49]. Without the ability to manipulate the CNTs to stand vertically on the substrate, CNTFEDs based on \textit{ex situ} methods have shown themselves to be extremely limited in value outside of simple electrical characterization due to the haphazard placement of the CNTs on the substrate. The multitude of steps requiring manipulation of the CNTs precludes the possibility of making identical devices and as such, \textit{ex situ} fabrication is not a viable solution for commercialization. Additionally, the inability to tune CNTFEDs by placing the CNTs such that they are spaced optimally to prevent electrostatic interference is an unacceptable design constraint inherent in the \textit{ex situ} fabrication process.

\subsection*{2.1.2 \textit{In Situ} Fabrication}

\textit{In situ} fabrication techniques expand on the previous work completed on CVD-based growth of carbon filaments [12,15,16,17,18]. Due to the inability of \textit{ex situ} techniques to be utilized for high-rate manufacturing, there was a great need to improve the understanding of CVD fabrication techniques. CVD’s main benefit is that it offers the flexibility to be adapted to producing CNTs for virtually all known applications
without the need for manipulation or purification steps [19]. By carefully controlling the carbon-source gases, temperature, and other constraints, it is possible to obtain repeatable results. Additionally, the CNT’s diameters can be roughly set by controlling the size of the catalyst nanoparticles [12,15]. The introduction of templating and, especially, Plasma-enhanced CVD (PECVD) technology has enabled the ability to align CNTs vertically while advances in lithography have allowed for careful patterning of the catalyst to create ordered arrays, qualities necessary for FEDs.

2.1.2.1 Thermo-CVD Approach

Much of the earlier efforts in CVD based growth of CNFs were based on understanding the thermodynamics of the non-equilibrium system [63,64,65,66,67] in order to be able to predict the product of the CVD experiment. Tevenbaugh and Cairns [63] found that within the CHO system, the five gases that were the most thermodynamically stable at carbon growth temperatures (typically 700-1400 K [19]) were H₂, CH₄, CO₂, CO, and H₂O by many orders of magnitude. Subsequent work by Jablonski and coworkers [66] showed that the effectiveness of Ni, Fe, Co catalyst foils were affected by the presence of some or all of these gases during carbon growth. Notably, the kinetics of the carbon growth using Ni catalyst was not affected when the five-gas mixture was switched to binary mixtures of CO-CO₂ or CH₄-H₂ or a ternary mixture of CO-H₂-H₂O. In contrast, when the gas mixture was switched from five gases to the aforementioned binary gases, the kinetics of the Fe system dropped two orders of magnitude while that of the Co system dropped one order of magnitude. Additionally, when the gas mixture was switched from five gases to the aforementioned ternary gas mixture; both Fe and Co systems’ kinetics changed proportionally to the product of the
partial pressures of CO and H₂. Since the temperature was fixed at 900 K, it is possible that this temperature allowed for optimal catalytic activity of the Ni, but sub-optimal catalytic activity for the other metals. It is reported in the literature that different metal catalysts have their optimum catalytic activity at different temperatures [19].

In an effort to control and differentiate the growth of CNFs and CNTs, Bazzana [68] supported the catalyst on fused quartz substrates. Thin-films (> 5nm) of Ni catalyst were deposited onto the fused quartz substrates and the five gas mixture as mentioned above was used with varying compositions. Since the thin film breaks up and forms nanoparticles under high temperatures [64,69] and the diameters of the nanoparticles can be controlled by the thin-film thickness [69,70], the method of using a catalyst support such as fused quartz successfully enables reasonable control of the diameters of the carbon nanotubes. The effects of Ni diameter, temperature, compositions of the five gas mixture, and ratio of oxygen species to hydrogen species were studied to reveal the optimal conditions for growth of MWCNTs. It was reported that MWCNTs of diameter 8-12nm and lengths 200 nm – 2 µm with density of up to 10⁹ CNT/cm² were grown with five gas mixture composition determined by setting the gas phase carbon activity to 20, the growth temperature at 900 K, an O/H ratio of 0.5, and overall feed gas flow rate of 20 cm³/s (STP: 1 bar, 273 K). The investigator didn’t reveal thickness of Ni thin film although the mass of the Ni evaporated was given as 0.5 mg without error or standard deviation. The position of the 0.5 mg of Ni within the tungsten wire basket was not given. It is possible for any deviation in these details to alter the total Ni that deposits onto the substrate leading to potential deviations in the CNT growth. While TEM was used to ascertain diameter measurements, the investigator did not reveal how the lengths
of the carbon nanotubes were estimated. The reported results showed MWCNTs growing in a disordered fashion standing at various angles to the substrate. Without the growth aligned in at least two dimensions it is very difficult to estimate the length of carbon nanotubes by inspection (e.g. SEM). Nevertheless, the author was able to grow CNFs and CNTs with reasonably uniform diameters in a controlled and repeatable fashion.

While all of the factors were important in the outcome of the results, the major factor for determining the diameter of the tubes was the amount of Ni deposited onto the substrate. When the nanoparticles exceeded 20 nm in diameter, no CNTs were formed, rather, spaghetti-like CNF grew in abundance covering the substrate in a carpet-like manner with densities in the $10^9$ CNF/cm$^2$ range. When the nanoparticles were in the range of 10-20 nm in diameter, there was a resulting mix of CNFs and CNTs. Their relative ratio was shown to be adjustable by the O/H ratio. At an O/H ratio of 0.1, only CNFs formed. As the O/H ratio increased to 0.5, the amount of CNTs increased then leveled-off while the CNFs decreased. An infinite O/H ratio was tested by changing the carbon source gas mixture from the five gases to a binary CO-CO$_2$ system and showed only CNF growth suggesting that the five gas mixture plays a significant role in the formation of CNTs. Throughout these tests, the overall population density was in the range of $10^7$-$10^9$ cm$^{-2}$. When the diameter of the catalyst nanoparticles was further decreased to below 10 nm, the selectivity towards growth of MWCNTs was increased drastically. It was reported that the formation of MWCNTs outnumbered the formation of CNFs by a factor of roughly 29 over the entire substrate. In agreement with this trend, Moshkalyov and coworkers reported on the growth of CNFs with relatively thick (6 nm)
films of Ni catalyst and the growth of long MWCNTs with very thin (>1 nm) films of Ni catalyst upon exposure to the binary gas mixture of H\textsubscript{2}-CH\textsubscript{4} (4:1) at 900 K [71].

Other authors have extended work in this area in order to understand the conditions required to reliably grow SWCNTs [72,73,74]. Li and coworkers [72] prepared catalyst nanoparticles of diameter between 3 to 14 nm by thermal decomposition of metal carbonyl complexes. They reported that no SWCNTs grew at any of the catalyst nanoparticles that were larger than 8.5 nm. Consistent with these results, Li and coworkers [74] found that nanoparticles less than 2 nm were more active in forming SWCNTs while particles larger than 7 nm did not form SWCNTs. Cheung et al. [73] prepared discrete catalyst nanoparticles with diameters 3, 9, and 13 nm and showed growth of SWCNTs from the 3 nm nanoparticles, double-walled carbon nanotubes (DWCNTs) from the 9 nm nanoparticles, and MWCNTs from the 13 nm nanoparticles. As in the cases of arc discharge and laser ablation techniques, binary catalyst mixtures have also been shown to improve the yield of SWCNT [19]. Alvarez and coworkers [75] reported a synergistic relationship between Co and Mo when being used to catalyze the growth of SWCNTs. With only Co being used as the catalyst at 973 K under flow of CO, the end product yield was 1.8% (weight of carbon per total catalyst weight) and consisted of a mixture of MWCNTs and SWCNTs with selectivity of SWCNTs of only 7%. Under the same conditions when the Co was substituted with Mo, there was almost no carbon growth (end product yield of 0.6%) and there were no SWCNTs. When Co and Mo were combined in a 1:1 ratio, the overall yield was roughly the same at 1.7% while the selectivity to SWCNTs increased substantially to 62.5%. Subsequent increases in Mo content compared to the Co content further increased the
SWCNT selectivity up to 96% at a Co-Mo mixture of 1:4. Using X-ray absorption spectroscopy, they found that Co is gradually reduced to a metal from an initial oxide state while the Mo transformed into its carbine after growth. They claimed that Mo acts to stabilize the Co$^{+2}$ ions which, in turn, increased the SWCNT selectivity. Other groups noticed similar synergistic effects of Mo with Fe or Co catalysts [20, 76, 77] where selectivity towards SWCNT growth was greatly increased.

Interestingly, much of the work done [24, 78, 79, 80, 81, 82] has used carbon source gases (e.g. acetylene, benzene, ethanol) that were shown to be vastly less thermodynamically stable [63] than those used by Bazzana [68] and others [64, 65, 66, 67]. The use of thermodynamically stable carbon source gases stems from the idea that the more thermodynamically stable a carbon source gas is, the less prone it is to pyrolytic decomposition at elevated temperatures. Pyrolytic decomposition results in undesirable deposition of amorphous carbon which acts to poison the catalyst particles. As mentioned earlier, higher carbon growth temperatures are thought to form CNTs with less defects and well-graphitized shells [23]. By choosing less thermodynamically stable carbon source gases, the temperature at which carbon growth occurs must be lowered in order to prevent pyrolytic decomposition of the source gas. This in turn would lead to defects in the CNTs. For example, Lee and coworkers [24] showed bamboo-shaped carbon nanotubes grown from iron catalyst under flow of acetylene in the range 1023-1223 K and Piedigrosso and coworkers [81] reported spiral carbon nanotubes from cobalt catalyst under flow of acetylene in the range 823-1073 K. None of these authors reported any cracking of the acetylene even at these high temperatures. It is possible that the kinetics of the catalytic decomposition of acetylene is faster than that of it cracking. Mo
and coworkers [83] discovered using quadruple mass spectroscopy that upon spaghetti-like growth of CNT at 873 K under flow of a mixture of acetylene and hydrogen (10 cm³/s and 100 cm³/s (STP) respectively), the acetylene did not indeed crack. Indeed, it had been originally reported by Baker and Harris [84] that unsaturated hydrocarbons (e.g. acetylene), while being less thermodynamically stable at elevated temperatures, exhibited much higher reaction kinetics (higher yields and higher deposition rates) than saturated hydrocarbons. In addition, they observed that saturated carbon gases (e.g. methane and carbon monoxide) tended to produce highly graphitized filaments with fewer walls compared with unsaturated gases. Many groups interested in growing SWCNTs tend to use the saturated carbon gases [20,85,86] whereas those interested in growing MWCNTs tend to use the unsaturated carbon gases [24,78,79,80,81,82]. By choosing the appropriate carbon source gases for the types of CNTs desired and carefully controlling the residence time of the carbon source gases on the catalyst, it is possible to grow CNTs regardless of the thermodynamic stability of the gases used.

2.1.2.2 Vertical Alignment Methods

Vertical alignment of CNTs on the substrate is of one of the most important qualities for FEDs. Non-vertically aligned CNTs tend to have a shielding effect on the voltage field which, in turn, substantially decreases the emitted current [87]. The three ways to allow for vertical alignment are densely-packed growth, templated growth, and PECVD.

Growing CNTs in a densely-packed way forces all of the CNTs to grow vertically due to van der Waals interaction between the tubes. In order to facilitate this type of growth, it is important to prepare the substrate surface with a dense area of active catalyst
particles. Most typically [88,89], the catalyst and surface are prepared by a sol-gel process and the carbon source gas used is acetylene, which was previously described to have very high deposition kinetics compared to the saturated carbon source gases [84]. The sol-gel technique involves mixing tetraethoxysilane (TEOS) with 1.5M iron nitrate and ethyl alcohol in a 10:15:10 ratio by volume [89]. After magnetic stirring, concentrated HF (0.4 volumes) was added to the solution followed by additional stirring. The mixture was then dropped onto a quartz plate to form a 30-50 µm thick film which subsequently turned into a gel. The film was dried overnight at 353 K and was followed by calcination at 723 K for 10 hours under vacuum. Following that, the substrate was reduced at 773 K for 5 hours in a flow of H₂/N₂ (9:91) at 180 Torr (reference standard not provided). Finally, a mixture of acetylene and nitrogen (9:91) replaced the reducing gases at 873 K and 180 Torr. After 48 hours exposure to the carbon source gas, MWCNTs with height 2000 µm were formed over the entire substrate. This marked a significant increase from Li and coworkers [88] who had grown 100 µm tall MWCNTs after 5 hrs exposure to acetylene at 973 K at 110 cm³/min (reference standard not provided). Li et al. [88] claimed that longer periods led to deposition of amorphous carbon and bending of the MWCNTs arrays. While the differences in temperature could have accounted for some of the differences between the two groups’ results, Pan et al. [89] attributes their results to their refined sol-gel technique where Li and coworkers [88] had formed a sol-gel from TEOS, 0.1M iron nitrate, and ethyl alcohol in a 10:11.4:10.4 ratio. Since the sol-gel technique prepares the substrate surface and catalyst for carbon growth, any alteration to this technique can lead to large differences in the results as was demonstrated by Pan and coworkers [89]. In order to try to apply this technique for FE
studies, Fan and coworkers [90] synthesized “towers” of densely packed nanotubes by use of a shadow mask. This allowed for the fabrication of arrays of “towers” on the substrate, each “tower” acting like a single emitter. Rather than using the sol-gel technique, they opted to electrochemically etch Si wafers to form a nanoporous layer of silicon on the substrate wafer. Shadow masks with varying pattern-dimensions were used and 5 nm Fe films were deposited through the shadow mask by e-beam evaporation. Upon exposure to 1000 cm$^3$/s (STP) ethylene for 15-60 minutes at 973 K, the MWCNT “Towers” were formed with heights between 30 and 240 µm. They reported that porous Si wafers offered better availability of the ethylene gas to the catalyst particle than standard Si wafers since Fe is known to typically grow with base-growth mechanism on silicon substrates [18]. They also noted that the porous Si possibly had improved surface interaction with the Fe catalyst since the nanoparticles were much smaller than those on the normal Si substrates. Additionally, when the aspect ratio of the MWCNTs exceeded 5, they fell onto the non-porous Si substrate, whereas on the porous substrate, they continued to grow vertically. The authors attributed this to an indication of weaker interactions at the interfaces between the nanotubes and flat silicon surface compared to the porous silicon.

A second strategy for obtaining vertically aligned CNTs is through the use of templates. The most commonly used ones for the purpose of growing vertically aligned CNTs alumina templates [91,92,93]. Porous alumina templates typically contain vertical nanopores which can range in diameter from a few to hundreds of nanometers and in length from a few microns to several hundred microns. These pores are created by electrochemical anodization of aluminum and the parameters can be varied to control the
diameter, length, and density of the pores. Huczko [94] has published a review of template-based synthesis of nanomaterials and it can be consulted for additional information regarding template preparation and parameters. The idea behind using porous templates is that the carbon nanotubes would grow within the pores so that all of their dimensions match that of the alumina template. The first known implementation of this strategy was done by Kyotani and coworkers in 1995 [91]. They grew carbon tubes (i.e. tubes of amorphous carbon as opposed to CNT which are composed of graphitic carbon) within two alumina templates, one with 230 nm pores and the other with 30 nm pores. Under pyrolytic decomposition of propylene (2.5% in N₂) at 1073 K with a flow rate of 200 cm³/s (STP), pyrolytic carbon deposited on the side walls of the alumina template. Upon washing in 46% HF solution, the alumina dissolved and the carbon tubes remained. Che and coworkers [92] prepared carbon tubes using 200 nm pore templates under both pyrolytic decomposition (1173 K) and catalytic decomposition (818 K) with either ethylene (9.92% in He) or pyrene as the carbon source gases and Ni (9.4% Ni resinate solution), Fe(NO₃)₂, or Co(NO₃)₂ as the catalyst sources. Upon dissolution of the template with concentrated HF, they noted the carbon tubes were not highly ordered, that is, they lacked graphitization. However, upon heating at 773 K for 36 hours, the Ni-catalyzed carbon tubes became more graphitic as shown by electron diffraction and TEM. Further improvements to the quality of carbon tubes grown within alumina templates were made by Li and coworkers [93]. They fabricated a hexagonal close-packed nanochannel alumina template with 32 nm pores and a 6 µm height by anodizing an aluminum sheet in 0.3 M oxalic acid solution at 288 K under a constant voltage of 40 V. Cobalt catalyst was then electrochemically deposited into the bottom of the template
pores, although the amount deposited was not noted by the authors. Finally, they exposed the substrate to 4-5 hours of 100 cm$^3$/s (STP) CO flow at 873 K followed by 2 hours of 10% acetylene in nitrogen at 923 K and the same flow rate. The authors claimed that the CO treatment was to reduce the cobalt catalyst, however this seems unlikely. Typical reducing agents are H$_2$ or NH$_3$ [19] where the hydrogen species reacts with oxide groups to reduce metal oxides. One possibility is that the purity of their CO was less than research grade (99.998%). The authors did not publish the purity grade of their CO gas, however, a common impurity in CO is hydrogen [68]. This trace amount may have been enough to keep the cobalt catalyst in a reduced form. Since the temperature of their experiment was relatively low, it is possible that the CO did not decompose to form carbon tubes due to its reaction kinetics being sufficiently slow at that temperature [84]. Nevertheless, they obtained well-graphitized, highly-ordered carbon nanotube arrays with diameter 47 ± 2.5 nm and lengths 6 µm shown by TEM and SEM.

With the advent of PECVD, the use of templates for vertically aligned growth has diminished. Moreover, the need to prepare sol-gel surfaces for close-packed growth was eliminated as well. PECVD accomplishes vertical alignment by making use of strong voltage fields in the direction perpendicular to the substrate by holding the substrate at an electrical ground state and negatively biasing (400-600V typical) the gas inlet which is typically placed above the substrate [19]. PECVD exists in different configurations, hot filament, microwave, dc, inductively coupled, and rf, however they all operate on the same principles. Conrads and Schmidt [95] presented a review on the different configurations of plasma systems and it can be consulted for further study. Chen and coworkers [96] grew vertical arrays of CNFs from diamond-polished Ni (100) wafers by
PECVD with the aid of a carbonized tungsten filament as heating source. The source gases used were high purity (99.999%) nitrogen and methane (99.9%) with a methane concentration of 2.0 vol% and a total flow rate of 70 cm$^3$/s (STP). In order to prepare the substrate surface for growth, a negative bias of 315 V was applied for 5 minutes in addition to the substrate being held at 1173-1223 K in the presence of the source gases. This was reported to upset the substrate surface to produce catalyst particles in the presence of strong plasma which served to prohibit carbon growth due to its etching quality. Subsequently, the negative bias was decreased to 270 V while the substrate temperature was decreased to 1073 K to facilitate growth of CNFs at a rate of 20 µm/h. The resulting CNFs had varying diameters in the range of 50-500 nm with a uniform density distribution across the entire substrate of approximately $10^8$ cm$^{-2}$. No explanation was made for such a wide distribution, although it is most likely due to a random distribution of Ni particles created during the initial high negative bias and high temperature step prior to carbon growth since the diameter of the catalyst particle is known to generally determine that of the carbon filament grown from it [12,15]. Chen and coworkers later refined their process by switching to a polycrystalline Ni substrate, altering the initial plasma step, changing the carbon source gas to acetylene, and increasing the flow rate to 300 cm$^3$/s (STP) [97]. The initial plasma step, negative bias of 550 V, was significantly higher than their previous work and the growth temperature was decreased to a range between 973-1073 K. The resulting CNFs had a smaller over diameter range of 30-100 nm. Again, this wide distribution could be attributed to their method of preparing the catalyst particles. They reported bundle-like growth where there were dense patches of CNFs ($10^9-10^{10}$ cm$^{-2}$) surrounded by small patches of void. This
growth pattern was attributed by the authors to be due to the polycrystalline nature of the substrate which seems likely due to the fact that the growth of carbon filaments is very sensitive to the nature of the catalyst and the substrate supporting it [12]. By switching from methane to acetylene, they were able to decrease the temperature of the carbon growth process by taking advantage of acetylene’s faster kinetics [84] as is important when trying to make electronic devices whose substrates cannot handle high temperatures.

The strain point of display glass, 939 K, (e.g. manufactured by Corning) is much lower than the standard carbon growth temperatures (> 973 K) used in the early work with PECVD-based growth of vertically aligned CNTs. In an effort to bring field emission displays comprised of vertically aligned CNTs closer to reality, Ren and coworkers [98] demonstrated the ability to fabricate such a sample at a sufficiently low temperature using display glass as a substrate. For catalyst preparation, they sputtered 40 nm of nickel onto the display glass. Interestingly, the authors failed to reveal the exact temperature of their carbon growth and only reported that temperatures less than 939 K were used. Nonetheless, they showed several results that further solidified the knowledge gained from the traditional thermal CVD methodology. When ammonia was not present or used prior to carbon growth, no CNTs grew and only some amorphous carbon was found on the substrate surface. The ammonia acts as a reducing agent for the metal and enables the catalyst to decompose the carbon source gas [19]. Second, they reported that as the Ni thin film decreased in thickness, the diameters of the CNTs decreased as well. This has been reported elsewhere for thermal CVD growth procedures [69,70]. The authors reported that as the CNT diameter decreased below 50 nm, they lost their vertical
alignment although no explanation was given to explain this. Most other groups studying PECVD have not studied small-diameter CNT growth [96,97,99,100] and as such, understanding on this phenomenon is minimal. The CNTs were shown to stand individually [98,100], unlike the wavy bundled fashion typically found in dense-packed growth suggesting that Van der Waals forces play less of a role in PECVD-based growth for vertical alignment of the CNTs. It is possible that the thinner CNTs have such an extreme aspect ratio compared to thicker CNTs that they tend to fall over due to the lack of a wide base to support the relatively high center of mass. While the authors attributed the breakup of the Ni thin film to the plasma bombardment, it is very likely that the Ni thin film broke up due to the elevated temperatures that the substrate was subjected to during the plasma bombardment as was shown by Bower and coworkers [69] and other groups [64,101]. Finally, the SEM micrographs of the resultant CNTs where shown to contain many structural defects that are typically associated with growth at low temperatures [23].

Huang and coworkers [99] reported large differences in the growth of carbon nanotubes by PECVD for Ni, Co, and Fe catalysts. Catalyst films with thickness 10, 17, 24, 30, and 35 nm were deposited onto titanium substrates by magnetron sputtering. The substrates were exposed to a mixture of acetylene and ammonia (40:160) with a total flow rate of 200 cm³/s (STP) for 10 minutes at a pressure of 10-20 Torr (reference standard not provided). No value for the negative bias applied to the substrate was given. Additionally, the growth temperature was not provided. The authors reported that Ni resulted in well-graphitized, vertically aligned, and straight CNTs without any noticeable amorphous carbon deposits on the tubes. Both Fe and Co resulted in bamboo-like growth
where Fe samples had crooked growth more or less normal to the substrate while Co samples had crooked growth in bundles. In all film thicknesses tested, Ni resulted in the largest CNTs (both diameter and length) whereas Co formed the smallest CNTs. The conditions used in their PECVD experiments seemed to favor growth kinetics for Ni catalyst, much like previous work done in thermal CVD experiments [66].

In order to show the benefits of PECVD over ordinary thermal CVD, Bower and coworkers [102] grew CNTs catalyzed by Co supported on Si substrates where the negative bias voltage was applied to only half of the growth period. Upon sputtering of 2 nm thin film of Co catalyst onto the Si substrates, the sample was heated to 1098 K in flowing hydrogen at a pressure of 20 Torr (reference standard not provided). Next, the hydrogen was replaced by a mixture of ammonia and acetylene (typically 70-90% ammonia) with a flow rate of 200 cm³/s (STP) and the 1kW microwave plasma was turned on. For the first half of the experiment, the plasma was not engaged and the growth was very wavy in structure. However, all of the nanotubes became vertically aligned and straight for the second half of the experiment when the plasma was engaged. With this experiment, the authors were able to demonstrate the effects of the plasma and its ability to vertically align CNTs during growth. A second experiment showed how the growth was always perpendicular to the substrate no matter how the substrate was oriented within the chamber (horizontally, vertically, diagonally) or if the substrate was irregularly shaped (radial, or wavy substrate surface). The authors attributed this characteristic to a self-bias potential established on the substrate surface that is immersed in the high frequency plasma where the field line is terminated perpendicular to the
surface [103]. Electrostatic forces would align the CNTs with the field direction since this is the most energetically favorable orientation.

2.1.2.3 Lithographic Patterning

The ability to pattern a substrate so that targeted growth is facilitated is the second most important aspect required for FEDs. In the case where a thin-film of catalyst is deposited onto the substrate prior to CNT growth, without any patterning method, catalyst is deposited equally across the entire substrate and subsequent CNT growth leads to complete coverage of the substrate. Fan and coworkers [90] demonstrated that use of a shadow mask fabricated by UV lithographic techniques allowed for discrete “towers” of CNTs to be formed. During the deposition of the thin-film of Fe catalyst, a shadow mask was situated between the Fe evaporation source and the substrate. This procedure forced the Fe to be deposited only through the holes patterned in the shadow mask, producing arrays of squares of Fe thin-film on the substrate surface. Upon exposure to the carbon source gases, discrete “towers” of CNTs where grown on the substrate. When attempting to create a FED, it is desirable to grow CNTs in an array with repeatable precision. When FEIs are too close together, they shield each other from the field enhancement effect causing the emitted current to drastically decrease [87]. Since UV lithography is limited in its resolution due to the wavelength of the UV light, it is not possible to create arrays of individual CNTs. However, electron-beam lithography (EBL) has been shown to have adequate resolving power to pattern the catalyst in such a way that individual CNTs can be grown in arrays or any other desirable pattern [85,104,105]. Ren and coworkers [104] demonstrated the use of EBL to pattern the vertically-aligned growth of 150 nm diameter carbon filaments. P-type boron doped silicon substrates were coated
with 5% 100MW polymethylmethacralate (PMMA) with a top coat of 2% 950MW PMMA. A pattern consisting of ~ 100 nm dots separated by either 1 µm or 2 µm depending on the sample was formulated and transferred to the substrate via EBL. The patterned resist was subsequently developed in a solution of methyl isobutyl ketone (MIBK) and isopropyl alcohol (3:1) to remove the dots that had been patterned by the e-beam. Next, 15 nm of Ni was deposited by e-beam evaporation and the pattern of Ni remained on the substrate upon lift-off of the resist layer. Carbon growth was facilitated by PECVD and the authors showed arrays of vertically aligned carbon filaments of varying heights (0.1-5.0 µm). The authors did not explain the variance of the heights of their carbon filaments although it most likely that much of the catalyst had formed silicides as there were no barrier layers deposited on the Si substrates. The typical transition metal catalysts used for CNT growth, Ni, Fe, Co all readily form silicides with Si at the typical carbon growth temperatures [19]. The most common barriers used to protect against the formation of silicides are SiO₂ and Titanium Nitride [19].

Ensuring that the patterned catalyst thin-film breaks up into single catalyst nanoparticles is paramount to guarantee growth of a single CNT at each site. Merkulov and coworkers [105] investigated critical diameters for deposited catalyst thin-films above which; the catalyst would break up into multiple nanoparticles and below which; the catalyst would break up into a single catalyst nanoparticle. The same patterning technique as noted in [104] was used, although the authors deposited a buffer layer consisting of 10 nm of Ti prior to deposition of the Ni catalyst in order to prevent the formation of Ni silicides. Upon PECVD at 973 K, the authors reported bamboo-structured CNF with diameters approximately 100 nm. By varying the dot diameters of
the EBL pattern, they were able to study how the Ni film broke up under thermal stress. They discovered that dots smaller than 350 nm in diameter produced a single catalyst nanoparticles while dots larger than 350 nm produced multiple catalyst nanoparticles. The authors also mentioned that this critical diameter could differ based on the choice of buffer layer, substrate, and catalyst type and thickness, although no such experiments were demonstrated.

While most EBL has been restricted to 100 nm patterning due to equipment capabilities [104,105], Javey and Dai [85] were able to demonstrate 20 nm resolution patterning with their state of the art EBL setup which enabled them to successfully show patterned growth of SWCNTs by thermal CVD. As mentioned previously, the ability to grow SWCNTs by CVD requires the catalyst particle to be very small [72,73]. By depositing very thin-films of catalyst metal between 2-20 Å, the authors were able to create catalyst particles less than 7 nm in diameter. In order to facilitate patterned growth of SWCNTs, a similar technique to previous work done for the patterned growth of CNFs [104,105] was used. Unfortunately with the catalyst film being so thin, even dots as small as 20 nm broke up into several catalyst nanoparticles. By evaporating the catalyst by e-beam evaporation at a 5-10° angle away from the substrate normal, a shadow masking effect occurred due to the walls of the resist wells. This allowed less atoms of the catalyst to deposit on the substrate and enabled the possibility of creating single catalyst nanoparticles with a diameter roughly 2 nm at each site upon careful annealing. The authors explain this behavior by the Einstein relation where clustering of atoms takes place within a radius similar to their mean diffusion distance. According to the authors, annealing at too high of a temperature led to complete evaporation of the catalyst while
annealing at too low of a temperature led to incomplete aggregation of the catalyst resulting in multiple nanoparticles at each site. While the annealing temperature used (1048 K for Pt catalyst) was far below the boiling point of the bulk metal, as nanoparticles become less than 10 nm in diameter, they can evaporate more readily due to the “Kelvin effect” [106].

2.2 Carbon Nanotube Field emission Device Characterization

Electrical characterization by applying known voltages and measuring current readings is commonplace in electronics research and enables the ability to benchmark devices, to better understand device operability, and to tune and improve device performance. FEDs are usually tested in a vacuum environment to minimize electron scattering between the cathode and anode [107]. In addition, high-voltage sources and low-current measurement devices with very low electrical noise are required for the electrical testing. Beyond these broad general setup requirements, the specifics are left to the individual research groups. Without specific standards, differences in the equipment setup, equipment used, and experimental assumptions between research groups can make cross-comparisons cumbersome and difficult. Therefore, it is important to consider all of the experimental details while qualifying and quantifying the performance of devices.

2.2.1 Field emission Characterization: Equipment

In general, FE testing requires a vacuum chamber with electrical feedthroughs and a device to supply high voltage (0-1000V) and measure low currents (pA resolution). The equipment used by various research groups differs in the abilities to obtain ultra high vacuum (UHV) and noise-minimal measurements. Deviations in both of these
characteristics have been shown in the literature to either affect the device’s performance [11] or the ability to compare device turn-on voltages [11,97,108,109], a standard electrical device benchmark.

Many research groups perform electrical characterization of their FEDs within high-vacuum environments between $10^{-5}$-to-$10^{-8}$ Torr [36,39,110,111] rather than ultra-high vacuum environments [11,35] due to the expense of ultra-high vacuum specific chambers and their associated equipment. Bonard and coworkers [112] reported enhanced current stability and device lifetime as the vacuum increased beyond $10^{-8}$ Torr. Devices were tested at pressures of $10^{-3}$, $10^{-8}$, and $10^{-10}$ Torr and voltage was sourced by a Keithley 237 source-measure unit which has capabilities of sourcing up to 1000 V and measuring to pA current sensitivity. Both current stability and device lifetime were reported to increase with increasing vacuum. In addition, emitted current also increased by a factor of 3 with increasing vacuum from $10^{-3}$ to $10^{-10}$ Torr. Current degradation half-times, the time it took for the emitted current to drop to one half of the original value while applied voltage was held constant, were shown to increase substantially with increasing vacuum. At $10^{-3}$ Torr, $10^{-8}$ Torr, and $10^{-10}$ Torr, the current degradation half-times were 9.2 hours, 210 hours, and 961 hours, respectively. Fransen reported even higher current degradation half-times of better than 1400 hours at a vacuum pressure better than $3\times10^{-9}$ Torr [113]. Since the research groups that typically use only high-vacuum testing environments are not concerned with long-term device lifetime, there was no need for ultra-high vacuum environments. However, with FEDs being researched for implementation into commercial or consumer products, there needs to be continuing studies on the effect of vacuum pressure with respect to device performance.
One of the typical benchmarks that has been reported in the literature for electrical characterization comparisons between FEDs is the turn-on voltage. Turn-on voltage for FEDs is simply the voltage required by the device to emit a current that is greater than the electrical noise-floor. As electronics become more miniaturized and low-power requirements have increased, turn-on voltage can give insight into whether or not a device is capable of fulfilling these needs. Unfortunately, since this benchmark is dependent on the noise-floor, research groups using different equipment in different environments also have different noise levels which may or may not be taken into consideration during their comparisons of their device against others. Some groups have modified the definition of turn-on voltage to include a specified measured current, however, there is no agreement on the current value to be specified.

For example, Bonard and coworkers [124] defined turn-on voltage to be the voltage required by the device to produce an emission current density of $10 \mu A/cm^2$ while Mu and coworkers [108] specified an emission current of $2 \mu A$ and Chen and coworkers [97] specified a broad emission current range of microamperes. Without knowing the effective current emitting area, a specification that was not reported by the authors, it is not possible to compare the devices. Unfortunately, in the literature, authors have cited others’ work as a comparison to their devices without ensuring the same definition for turn-on voltage. Bonard and coworkers [112] compared their results of $2.6 V/\mu m$ at $10 \mu A/cm^2$ to that of Amaratunga and Silva [114] who obtained $4 V/\mu m$ at $10^{-3} mA/cm^2$. Bonard and coworkers only looked at the turn-on voltage value and did not take into account the current that the voltage corresponded to and reported that their device had 65% of the turn-on voltage of Amaratunga’s and Silva’s device. Since their
device required less voltage at a higher current, their device is indeed much improved over that of Amaratunga and Silva; in fact, much more so than they had reported. Since emission current does not increase linearly with increased voltage, values cannot be accurately extrapolated and comparisons between turn-on voltages are not practical unless the same definition of turn-on voltages are used between the research groups.

2.2.2 Field emission Characterization: Field Amplification Factor

Field emission devices (FEDs) are also benchmarked against each other based on their field amplification factors [10,11,19,87,112]. The field amplification factor can be found from the Fowler-Nordheim equation when the values for the applied voltage, measured current, distance between anode and cathode, and emitting area are known. The work function of the emitter is typically unknown, but takes on an assumed value depending on the research group. This assumption makes the calculation of the field amplification factor cumbersome, since the work function of the emitter is strongly related to its geometry which can change in the event of resistive heating of the tip due to the Nottingham effect caused by the difference in energy between emitted and replacement electrons at the tip [115].

In order to calculate the field amplification factor, most research groups have assumed a constant work function of roughly 5 eV for their CNT films [111,112,125] or 4.6 eV [10] which corresponds to that of bulk graphite. Bonard and coworkers [112] reported that this assumption was justified for estimation purposes by comparing its fit to a geometrically-based calculation of the field amplification factor. The geometrically-based calculation was originally demonstrated by Dyke and Dolan [107] and consists of fitting the emitter surface with an equipotential surface surrounding an isolated sphere-
on-orthogonal cone. The field amplification factor is calculated as the potential gradient at the apex of the equipotential surface divided by the electric field that would normally be present if the emitter were a planar cathode.

Xu and coworkers [116] reported on the work functions of single MWCNT emitters. The authors measured the work functions in situ within a TEM in a standard diode setup where the CNT emitter was adhered to a tungsten tip electrode by Van der Waals forces and the counter-electrode was gold by utilizing the principle of contact potential difference. Upon excitation into a mechanical resonance state by applying an alternating electrical field across both electrodes as was previously demonstrated by Poncharal and coworkers [117], a direct current voltage, $V_{DC}$ was added to the alternative voltage. Since the work function of bulk gold is known, the work function of the MWCNT tip would be determined by the $V_{DC}$ where the amplitude of the mechanical vibration was made to be zero. The authors showed that depending on the state of the tip, be it opened, closed, or capped with amorphous carbon, and the geometry of the emitter, the actual work function differed in the range of 4.51 – 4.78 eV.

While Xu and coworkers’ conclusion of the necessity of in situ work function measurements differ from the views of Bonard and coworkers, it is important to note that the key difference between the presented literatures was the use of arrays of field emitters by Bonard et al. [112] versus the use of single emitters by Xu et al. [116]. When creating a Fowler-Nordheim fit, the data collected is based on the entire device, not individual emitters. It is quite possible that the variances in work function between the tips and throughout the measurement are averaged out when many emitters are evaluated, whereas the variance in work function is maximized when evaluating a single emitter at a time.
calculation using the Fowler-Nordheim equation for the case of single emitters where the work function varies from 4.51 to 5 shows a difference of 16.7% for the calculation of the field enhancement factor which could, in fact, be non-negligible for devices using single emitters. For film emitters, it is important to realize that the field amplification factor includes the geometry of the film as a whole in addition to the geometry of the tip. While the in situ method may give an accurate field amplification factor due to the geometry of the tip, this accuracy will be masked by the electrostatic interactions between neighboring emitters which can only be minimized by optimization of inter-emitter distance [87].

2.2.3 Field emission Characterization: Fowler-Nordheim Fitting

In order to demonstrate that a device undergoes field emission, its electrical characterization is subjected to a Fowler-Nordheim fitting. As mentioned earlier, this fitting requires measured current and applied voltage data. The natural log of the product between current and squared inverse voltage is plotted against the inverse voltage. In an ideal F-N device, the slope would be negative and linear; however, the literature has shown that most results are non-ideal. While many research groups have ignored this and simply drawn a straight line through their somewhat conforming points [10,97,108,111,125,118], other groups have tried to explain the deviations [110,112].

The major cause for deviation from F-N theory is due to the incorporation of arrays of emitters. The F-N theory was originally created to describe the field emission phenomena of a single metallic emitter [29]. Qualitatively, F-N theory has been shown to be of reasonable fit to experimental data of arrayed-emitters as shown by the authors who simply draw the F-N slope through their data. As mentioned previously, Collins and Zettl [110] reported different emission behaviors in the presence of low electrical fields
and high electrical fields. They considered space-charge buildup in order to explain the knee in their F-N plot since, at high-current densities; space charge reduces the actual electric field at the emitter tip causing a sharp breakpoint often seen as a “knee” in F-N plots (Figure 6). However, they later discounted this hypothesis since space-charge buildup leads to a non-linear saturation whereas their experimental data showed a linear progression following the knee. They also considered the model of Latham and Wilson [119], where the electronic properties of the insulating layer beneath the emitters dominate the I-V characteristics of the emission as opposed to the emitters themselves. The Latham and Wilson (L-W) model predicts very sharp turn-on events which were observed by the authors. The sharp turn-on events are predicted by the L-W model due to the fact that some electrons have to tunnel through the insulator to reach vacuum at the

Figure 6: Example of I-V curve showing a knee in the F-N plot [110]
onset of field emission from metallic tips. The tunneling current though the insulator can lead to a local dielectric breakdown which leads to a current “avalanche”. Further, the L-W model has the same functional form as the F-N model. Linearity in the F-N plot allows for the application of both L-W and F-N models. Unfortunately, neither model could predict the high-electrical field behavior that was observed. Also, the authors were able to show dramatic differences between individual emitters. This difference is not possible under the L-W model where emission is governed by interactions with the insulating material and only weakly dependent on the actual emitters. The authors concluded that inter-emitter interactions were most likely the cause of the field emission behavior they observed causing the well-defined breaking point or knee in the I-V characterization.

Bonard and coworkers [112] have also reported on deviations from F-N theory. They attributed these deviations to either the semi-metallic character of the emitter or space-charge effects. Space-charge effects can be caused by a screening of the applied electrical field by the emitted electrons in the tip vicinity. It had been reported elsewhere by two groups, Barbour et al. [120] and Theophilou et al. [121] that this phenomenon does not begin until fields greater than 6-7 V/nm are applied resulting in a monotonic diminution of the F-N slope. Bonard and coworkers, however, reported non-monotonic changes beyond 4 V/nm suggesting that space-charge effects were not the cause of the deviations from the F-N model, in agreement with the conclusion of Collins and Zettl [110]. While, in general, MWCNTs are considered to have metallic properties [19], upon closer examination, de Heer and coworkers [122] found through field emission microscopy that the spatial charge distribution of the emitting states of each tube was
non-homogenous. This finding suggested that the electrons are emitted from electronic states localized at the tip rather than delocalized conduction-band electrons as would occur in metals. Scanning tunneling spectroscopy measurements and theoretical local density of states calculations were reported by Carroll and coworkers [123]. Their findings showed that the local density of states at the tip presented sharp band states that were superposed on the graphitic density of states. The sharp band states correlate to the presence of pentagonal defects at the tip of the CNT. While it is possible for these extra energy bands could cause the deviations from F-N theory, there has not been enough work in this area to be able to make any conclusions. Depending on the position of the localized states with respect to the Fermi level, the emission characteristics of the CNT tips can differ. However, it is uncertain as to the extent of the change in emission characteristics due to these localized states. Additionally, the effects of an embedded metal nanoparticle within the CNT tips, as common in all CVD growth methods, on the emission characteristics has not been sufficiently studied.

2.2.4 Tuning the Field Emission Properties

With EBL being a much more practiced technique, it is possible to take advantage of its patterning capabilities to optimize the patterned growth of CNTs to minimize shielding effects from adjacent emitters while still allowing for the densest array possible. It has been reported in the literature that optimal spacing between adjacent emitters depends on the height of the emitters [87,109,124,125]. Nilsson and coworkers [87] predicted the optimal spacing between adjacent emitters was twice the height of the emitter. The authors performed electrostatic calculations of the electric field penetration between parallel standing tubes assuming tubes of 1 μm length, 2 nm diameters, and
constant work function, and utilized F-N theory to calculate the effect on emission current. While the authors did not publish their simulation methodology, they did show plots of field enhancement and current density as functions of the distance between the emitters in support of their two to one spacing hypothesis. Groning and coworkers [109] independently reported similar findings from theoretical electrostatic calculations.

Experimentally, Nilsson and coworkers compared three films of vertically aligned CNTs grown by micro contact printing of ethanolic inks [126] of 10, 40, and 60 mM Fe(NO$_3$)$_3$ · 9H$_2$O under a mixture of acetylene and nitrogen (1:5) at 993 K. Qualitatively, the resulting films were reported to be of low, medium, and high densities. The authors found the medium-density film to perform the best and explained that the high density film was hampered by electrostatic screening effects due to the proximity of the neighboring tubes while the low density film had too few emitters. These conditions were supported by their theoretical electrostatic calculations. Bonard and coworkers [124] showed similar qualitative results using the same experimental procedure. They found that their medium-density CNT film consisting of CNTs with height roughly 3 µm and inter-emitter distance of roughly 2 µm allowed for high field amplification along with a high enough emitter density to produce homogeneous emission (lack of “dark spots” due to electrostatic shielding) at low applied electrical fields. Suh and coworkers [125] reported optimal array spacing equivalent to the height of the emitters. Vertically aligned CNTs were grown by the alumina template method and the array spacing and CNT diameter was adjusted by the anodizing technique. Substrates with intertube distances of 104 nm were designed to grow carbon nanotubes with diameter 38 nm while substrates with intertube distances of 65 nm were designed to grow carbon nanotubes
with diameter 19 nm. The authors reported a maximum in the field amplification for the 104 nm sample when the CNTs were of height approximately 100 nm. For the 65 nm sample, the maximum in the field amplification occurred when the heights of the CNTs were approximately 65 nm. A wide range of optimal CNT height to inter-electrode distance ratios (0.67 - 2) shows that much work still has to be done in terms of optimization of packing density of CNT film emitters. Further investigation is necessary to gain a more complete understanding of the compromise between electrostatic shielding and high aspect ratio emitters.
3.0 EXPERIMENTAL

In order to grow arrays of various tubular allotropes of carbon using chemical vapor deposition, a thermogravimetric reactor was used. The thermogravimetric reactor was equipped with a precise feed gas delivery system which was used to deliver an accurate mixture of gases to the reactor. An inline gas chromatograph was used to verify the composition of the reactant gases and product gases during the experiment. Silicide barrier films of SiO2 were grown on silicon substrates by thermal oxidation. For deposition of thin-films of the nickel catalyst, a glass bell-jar thermal evaporator was used. Subsequent evaluation and analysis was done with optical profilometry, atomic force microscopy, x-ray spectroscopy, and scanning electron microscopy. Preliminary electrical characterization was performed in a high-vacuum chamber with an external source-measure unit.

3.1 Thermogravimetric Reactor System

The thermogravimetric reactor system can be broken down into two major subsections: the feed-gas delivery system and the thermogravimetric reactor (Figure 7). The feed-gas delivery system was metered both manually and digitally and served to mix and deliver the feed-gases with varying controlled amounts of water vapor to the thermogravimetric reactor. The thermogravimetric reactor was composed of a fused quartz reactor tube where the substrate was hung from a Cahn balance through a Pyrex® extension tube. All of the valves in the feed-gas delivery system were solenoid valves controlled by a switchboard. The feed-gas lines were either stainless steel grade 316 or...
flexible Teflon® lines inside a stainless steel grade 316 over-braid. The lines were all connected using Swagelok® fittings of stainless steel grade 316.

Figure 7: Schematic of the Thermogravimetric reactor system
Adapted from [68]

3.1.1 Feed-gas Delivery System

Seven gases were used during the investigation. While there were provisions for the use of argon gas as an inert species, helium and nitrogen were used exclusively as the inert species for safety, dilution, and cooling purposes. The helium gas was purchased from Medtech in the ultra-high purity grade with a minimum purity of 99.999%. Dry nitrogen was also purchased from Medtech with a minimum purity of 99.99%. Methane,
carbon dioxide, carbon monoxide, hydrogen, and water were used as reactant gases. The former four were purchased from Medtech, while the water was supplied by a custom built water saturator. The purity of these four gases purchased from Medtech were all classified as ultra-high purity and had the minimum purity of 99.99% for methane, 99.99% for carbon dioxide, 99.97% for carbon monoxide, and 99.999% for hydrogen. Prior to mixing with the other gases, the carbon monoxide was passed through a “carbonyl destruction chamber” composed of a quartz tube packed with quartz wool and heated typically to 623 K. The pretreatment was necessary to decompose any iron carbonyl that may have been present in the gas. There were provisions for both analog and digital regulation of the gases. Analog regulation of the gases was conducted by feeding the gases to Brooks Model 8944 mass flow regulators. Each regulator outputted to a manometer comprised of precision bore capillary tubes (1 mm ID, 0.90 m length) with Meriam high vacuum manometer fluid. These manometers were used to obtain calibration curves of flow rate in cm³/s versus pressure drop in centimeters of Meriam fluid (Appendix A). The calibration curves were corrected for Standard Temperature and Pressure and could be used to establish appropriate gas phase flow composition. Digital regulation of the gases was provided by Brooks model 5850E digital mass flow controllers with the Brooks model 0154E external display with rated accuracy of ± 0.3 cm³/s. For calibration of the digital mass flow controllers, the manual mass flow controllers were used.

Following the gas flow regulation, regardless of which method was utilized, the gases were mixed and dried in a 304L-HDF 316 stainless steel cylinder (300 cm³) filled 33% with 5A molecular sieves and 67% with Drierite®. The mixed gases were then
passed either to the reactor or to vented to the atmosphere during a change of reactor feed gas conditions. The gases could be fed into the reactor either dry or saturated with water. An ensemble of three-way solenoid valves allowed for passage through the water saturator or a complete bypass of the water saturator into the reactor.

3.1.2 Water Saturators

The water saturator system consisted of five 500 mL Kimax® flasks hooked in-series and submerged in a 40 L glass container (Figure 8). The feed gases were fed to the water saturator system through a 6.35 mm OD preheated copper line. Thermolyne insulated heating tapes capable of outputting up to 209 Watts were used to heat the lines to beyond 373 K. A 750 Watt heating coil/mixer from Fisher was used to heat the water

![Figure 8: Schematic of the Water Saturator where only three of the flasks have been represented. Adapted from [68]](image_url)
bath while ensuring temperature uniformity throughout the water bath. The temperature was controlled by an Omega CN9000A controller to within 0.1 K of the set point and Type-K Chrome-alumel thermocouples from Omega were used to monitor the temperatures. The gas stream was fed to each flash through fritted Kimax® glass gas-dispersion tubes while interflask passage utilized 3/8” OD Tygon tubing. The fifth flask was filled with 0.5 mm diameter glass beads to prevent small droplets from being entrained with the saturated gas stream. Additionally, a Chrome-alumel type K thermocouple from Omega was inserted into the fifth flask to record the temperature of the saturated gases in order to calculate the amount of water that was added to the gases. The partial pressure of water called for in the experimental design was set by the equilibrium vapor pressure at the bath’s temperature. Finally, the saturated feed gas stream entered the reactor through heated feed lines to prevent condensation of the water within the lines. As mentioned previously, the water saturator system could be bypassed by three-way solenoid valves to deliver dry feed gas to the reactor if desired.

3.1.3 Thermogravimetric Reactor

As mentioned previously, the reactor tube contained two sections: a heated fused quartz tube and a cooler Pyrex® extension tube (Figure 9). The Pyrex® extension tube was used to connect the quartz tube that was typically 900 K to the Cahn balance that was typically at room temperature. This fixture was mounted vertically on anti-vibration frames supported by three pneumatic pistons from Vibraplane. The bottom of the fused quartz section was tapered and connected to a 316 stainless steel Swagelok® union tee with a Vycor® fitting. Fused quartz raschig rings 0.8 cm in length and 0.8 cm in diameter were used to partially fill the fused quartz tube to a height of 0.24 m from the bottom.
The rings served to provide a preheating zone for the reaction gases and to keep the gases well intermixed. A temperature profile of the reactor was previously made [68] showing the isothermal zone (± 1 K) between 2.5 – 6.5 cm above the packing (Appendix B). The isothermal zone temperature was monitored by type K thermocouples from Omega which

Figure 9: Schematic of Reactor Tube Adapted from [68]
was passed through the stainless steel union tee at the bottom of the reactor through the raschig rings and protected from the feed gas stream by Omegatite 450 alumina non-permeable tubes from Omega. Heating of the reactor was facilitated by ATS 3210 furnaces which consisted of 4 half-cylinder resistive heating elements capable of delivering temperatures as high as 1373 K. The 4 heating elements were situated into 2 zones, an upper and lower region, each zone controlled by a Eurotherm Type 2404 controller programmer.

All samples were suspended from the Cahn balance into the reactor by two Nichrome hang-down wires in series. The first wire served as an extension wire from the arm of the Cahn balance to the end of the Pyrex® extension tube while the second wire served as a further extension into the isothermal zone within the fused quartz tube. The Pyrex® extension tube had a restrictive orifice with a diameter of 0.953 cm. Helium gas was sent through the Cahn balance and flowed downwards to this restriction where it was vented. This helium “curtain” prevented the feed gas from entering the Cahn balance protecting the sensitive electronics therein.

3.1.4 Gas Chromatograph

A Hewlett Packard model 5890 series II gas chromatograph (GC) was used to analyze the reaction gas composition both at the entrance and exit of the reactor. Withdrawn gases were transported to the GC by way of heated lines into an insulated sample box. The sample box contained a heated aluminum block in direct contact with a network of 0.31 cm OD stainless steel grade 316 lines and stainless steel grade 316 toggle valves from Swagelok. This manifold was pumped down to below $5 \times 10^{-3}$ Torr by a rotary vacuum pump. A mercury manometer in conjunction with a MacLeod gauge was
used to measure the vacuum. A sampling valve connected the manifold directly to the GC and once engaged, a gas sample of 0.1 cm³ was injected into the carrier gas stream within the GC. The carrier gas used was a mixture of 91.5% helium and balance hydrogen from Medtech. This mixture was specifically chosen to allow for maximum sensitivity towards the detection of the five reaction gases when using the thermoconductivity detector. The particular column used was 1/8” diameter, 12’ long stainless steel grade 316, and packed with Porapak Q.

3.2 Thermal Oxidation Furnace and Optical Profilometer Analysis

Growth of an oxide layer on silicon substrates was facilitated by a Bruce Furnace 7355B. The furnace has the capability to process wafers up to 6” in diameter for oxidation and nitride growth. The Bruce Furnace 7355B was used to oxidize 3” p-type silicon wafers to form a barrier layer against the catalyst metals deposited in subsequent processes. This step was required due to the fact that nickel readily forms silicides with silicon at elevated temperatures unless a barrier layer is present on top of the silicon. The thermal oxide growth was accomplished in a wet O₂ process where the O₂ was bubbled through a flask containing deionized water held at 373 K. Oxidation occurred at 1373 K under flow of wet oxygen at 1250 cm³/min (STP) for 20 minutes.

Optical profilometry – non contact film thickness determination was performed using a NanoSpec 200 with a white light optical spectrometer. This technique allows for quick thickness measurements across entire wafers and utilizes the attenuation in the reflected light off of the substrate compared to a control substrate without the thin-film. The NanoSpec 200 was used to obtain the thickness of the thermal oxide layer grown on the silicon wafers.
3.2 Thin-film Apparatus

Thin-film deposition was performed using a Denton Vacuum DC Magnetron sputterer model DV 502A with the optional thermal-evaporation bell-jar attachment (Figure 10). The sputterer was used to deposit ultra-high purity chromium thin-films onto non-conductive substrates to decrease the charging of the substrate under the electron beam during in scanning electron microscopy. Prior to deposition, the chamber was evacuated to $7 \times 10^{-7}$ Torr with a turbomolecular pump. Liquid nitrogen was used to further increase the vacuum to $2 \times 10^{-7}$ Torr. The plasma was subsequently ignited under a pressure of $5 \times 10^{-3}$ Torr of research grade argon and a 10 Å thin-film of chromium measured by a quartz crystal microbalance was deposited onto the substrate. For deposition of high purity nickel, the sputterer was exchanged with an optional thermal-evaporation bell-jar attachment. The nickel sample, typically a thin wire, was carefully cut to the appropriate length ± 350 µm and was mounted onto a tungsten basket which was placed 20 cm above the substrate between two electrodes. Upon evacuation of the

![Figure 10: Schematic of Thin-film Evaporation Apparatus](image)

The nickel wire in the tungsten basket, the glass bell jar with a volume of 0.026 m³, the vacuum at 7×10⁻⁷ Torr, the automatic shutter, and the substrate are shown. The DC power supply is set to 0 - 60 A.
bell-jar to $7 \times 10^{-7}$ Torr, the nickel wire sample was evaporated under application of 10-12 amps provided across the tungsten basket.

### 3.4 AFM Analysis

Atomic Force Microscopy was performed using a Digital Instruments Dimension 3000 scanning probe microscope (SPM) installed within an acoustical anti-vibrational chamber equipped with a NanoScope IIIa SPM controller. The AFM was operated in Tapping Mode at all times using an n-antimony-doped silicon tip with ultimate tip radius of 8 nm and resonance frequency between 303 – 350 kHz. In order to correct for tilting of the sample, the inclination was digitally corrected by application of a first-order plane-fit mathematical function in both the x and y directions. The AFM was used to obtain surface roughness of the native substrate as well as the substrate after deposition of the nickel thin-film.

### 3.5 XPS Analysis

X-ray Photoelectron Spectroscopy was performed using a refurbished Phi model non-monochromated 300 Watt dual-source (aluminum, 1486.8 eV and magnesium, 1253.6 eV) for Kα x-rays with a hemispherical analyzer with spot analysis diameter, 1.1 mm in a custom-built ultra-high vacuum system operated at $2.3 \times 10^{-9}$ Torr and room temperature. The angle between the incident x-ray and the electron take-off was 54° and the electron take-off angle was 90° relative to the substrate surface. XPS was used to characterize nickel thin-film thicknesses because they were too thin to be measured reliably with an AFM. By comparing substrates with and without the thin-film, a value of the signal attenuation for the silicon 2p peak was calculated by comparing intensity
peak areas. The signal attenuation in addition to several parameters were entered into the National Institute of Standards and Technology (NIST) Electron Effective-Attenuation-Length Database software which subsequently calculated the thin-film thickness. The parameter were outlined and supplied by the user’s guide for the software. Due to transport approximations, surface roughness, surface excitations, and surface refraction, the inherent error in the thickness calculations was approximately 10%.

3.6 SEM Analysis

Scanning electron microscopy was performed using a Hitachi model S-4700 CFE SEM. This technique was used to characterize the formation of catalyst nanoparticles as well as the carbon nanofibers or nanotubes. For the most part, samples were simply inserted into the SEM chamber for observation without any special pretreatment. For studies where the substrate was particularly troublesome in terms of charging effects, a thin layer of chromium was sputtered onto the substrate prior to observation in the SEM. Typically, a working distance of 5 mm was used as this was the minimum working distance allowed for access to the full range of accelerating voltages. An accelerating voltage of 2 keV and a beam current intensity of 10 µA were used for general observation. However, at higher magnification, due to excitation of the carbon nanotubes under the electron beam, a range of accelerating voltages from 1 – 10 keV and beam currents from 10 – 20 µA were necessary to observe the sample. For studies to determine the heights of the nanotubes, a custom substrate holder was used to hold the substrate parallel to the electron beam direction.
3.7 **Electron-beam Lithography**

E-beam lithography (EBL) was investigated to determine its viability in patterning substrates to allow for arrayed-growth of carbon nanotubes. This process was performed using a Zeiss Supra 25 SEM equipped with the J.C. Nabyte ver. 9 lithography and pattern generation system. Two different molecular weights of poly(methyl methacrylate) (PMMA), 495k and 950k were sourced from Microchem and used in a bi-layer process where the 495k served as the bottom layer and the 950k served as the top layer. Since the lower molecular weight polymer dissolves faster than the higher molecular weight polymer [127], this specific bi-layer setup allows for high-resolution lithographic patterning while enabling easier lift-off due to the exposed surface area of the PMMA adjacent to the deposited metal (Figure 11). Upon exposure to the EBL patterning, the exposed areas were developed in a 1:3 mixture of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA). Subsequently, a thin-film of metal, gold-palladium for characterization of the pattern or nickel for patterned catalyst was deposited with the patterned PMMA bi-layer acting as a mask. Finally, the substrate was subjected to the lift-off process where the excess PMMA was stripped off of the sample by acetone leaving only the patterned metal thin-film on the substrate surface.
3.8 Electrical Characterization

Electrical characterization was performed within a ~ 125 in³ vacuum chamber (Figure 12) evacuated to $4 \times 10^{-7}$ Torr with a Balzers TPU-060 turbomolecular pump. The pressure was measured by a Kurt J. Lesker KJL-912163 convection gauge equipped with a digital readout for pressures between $1 \times 10^{-3}$ - $1 \times 10^{-3}$ Torr and a Granville-Phillips Series 260 Controller with Ion gauge for pressures between $1 \times 10^{-9}$ - $1 \times 10^{-3}$ Torr. A Keithley 237 source-measure unit was used to provide voltages up to 1000V and to measure current down to pA resolution. The background electrical noise of the system was typically 400 pA. A Mitutoyo micromanipulator accurate to ± 2 µm was used to
Figure 12: Schematic of Field emission Test Chamber with a sharpened 304 Stainless Steel Pin Anode adjustable with a 3-axis Micromanipulator to adjust the position and distance of the steel pin anode from the device under test (DUT).

The DUT was placed on the aluminum cathode which was electrically isolated from the chamber with a polytetrafluoroethylene (PTFE) dovetail and a borosilicate glass cylinder. Alternatively, a parallel-plate aluminum diode setup was fabricated and used (Figure 13).

Figure 13: Schematic of Field emission Test Chamber with Aluminum Parallel Plate Diode Setup with inter-electrode separation of 100 µm
This specific test setup bypassed the micromanipulator and was designed to allow for testing with a fixed inter-electrode distance of 100 µm. In both setups, voltage was swept in a linear staircase algorithm and following each run, the measured current was recorded. Current-Voltage (I-V) curves as well as F-N plots were subsequently constructed.

3.9 Methodology

*In situ* methods to fabricate carbon nanotube based field emission devices have shown great promise in terms of reproducibility when compared to *ex situ* methods. In order to take advantage of these advantages, most researchers have focused on utilizing chemical vapor deposition techniques [24,78,79,80,81,82]. Unfortunately, the experimental parameters found in the literature vary greatly making it difficult to understand the system in such a way as to be able to improve the resulting devices. By using carbon feed gas that is known to be less thermodynamically stable than the five gases, H$_2$, CH$_4$, CO, CO$_2$, and H$_2$O, the possibility of pyrolytic decomposition of the gases increases. With pyrolytic decomposition poisoning the experiment, it is difficult to formulate any conclusions pertaining to growth mechanism and the result is generally CNTs with amorphous carbon defects or overgrowth. Use of five gases can be troublesome as there are many possible mixtures that could be formulated. However, by defining intensive parameters based on thermodynamic principles: gas phase carbon activity, O/H ratio, temperature, and total pressure of reaction, it is possible to specify five gas mixtures that are not simply random combinations (Appendix C).

Much of this work has been done previously [67,68] and involved the use of ternary non-equilibrium phase diagrams. By mapping carbon, hydrogen, and oxygen,
along with the five gases and theoretical phase equilibria on the ternary non-equilibrium phase diagram, it is possible to narrow the range of possible mixtures of carbon feed gas that facilitate carbon deposition (Figure 14). The pentagonal area formed by the five gases represents the possible mixtures of these five gases. The solid line represents the phase equilibrium between gaseous carbon and graphite (a gas phase carbon activity of 1), the dotted line represents the phase equilibrium between reduced nickel and oxidized nickel, and the dashed line represents the phase equilibrium between reduced nickel and nickel carbide. Previous investigations [66,68] have shown the region of interest for growth of CNTs is the nickel carbides and graphite region above the dashed line. By

![Figure 14: Non-equilibrium ternary phase diagram of Ni at 900 K and 1 atm in the C-H-O system Adapted from [68]](image_url)
specifying the gas phase carbon activity to be a fixed value and O/H ratio to be constant, a specific range of mixtures of the five gases can be formulated numerically (Appendix C) and demonstrated graphically (Figure 15). It was found previously by Bazzana [68] that a gas phase carbon activity of 20 and O/H ratio of 0.1 at 900 K and 1 atm produced spaghetti-like MWCNTs on fused quartz substrates with 10.6 nm Ni nanoparticles. When the O/H ratio increased to 0.5 and the Ni nanoparticles decreased to 6.8 nm while all other parameters remained the same, the selectivity towards straight MWCNT with much fewer structural defects increased dramatically. With further optimizations in the reaction parameters, it is possible to obtain pristine samples of low defect, straight, high aspect ratio MWCNTs.

![Figure 15: Non-equilibrium ternary phase diagram of Ni at 900 K and 1 atm in the C-H-O system representing a specific mixture of the five gases with a fixed $\alpha_c$ and O/H ratio. Adapted from [68]](image-url)
RESULTS AND DISCUSSION

Upon thermal oxidation of the 3 in. silicon wafer to an oxide-layer thickness of 350 ± 4 nm, the wafer was cut into square substrates with side dimensions 8 ± 2 mm. Nickel was deposited onto the substrate and catalyst nano-particles were formed after an annealing step. Multi-wall carbon nanotubes were grown from the catalyst nanoparticles upon exposure to a gas reactant mixture. Optimizations in the amount of nickel deposited as well as the composition of the feed gas were investigated (Appendix D). In addition, electron-beam lithography and electrical characterization techniques were explored.

4.1 Formation of Nickel Nano-particles

The thickness of the thin-films of nickel that were evaporated onto the silicon substrates was controlled by the mass of the nickel wire evaporated and two values, 1.8 mg and 0.5 mg were used. While values less than 0.5 mg were tested, the results were not repeatable. Evaporation of 1.8 ± 0.01 mg of nickel wire hung within a tungsten basket resulted in a thin-film thickness of 1.50 ± 0.01 nm as measured by XPS (Table 1). A similar evaporation procedure was performed for 0.5 ± 0.01 mg of nickel wire. Due to the difficulty in placing the nickel wire within the tungsten basket, the wire was instead hung from underneath the tungsten basket and resulted in a thin-film thickness of 0.60 ± 0.01 nm as measured by XPS (Table 1). In order to ensure that the thin-films were uniform, their RMS roughness was studied using AFM. The substrate without any nickel thin-film showed an RMS roughness of 0.15 ± 0.01 nm, while the substrate with the nickel thin-film showed an RMS roughness of 0.17 ± 0.02 nm. The lack of a significant
difference between the RMS roughness measurements suggests that the nickel thin-film was conformal to the substrate and of uniform thickness.

<table>
<thead>
<tr>
<th>Mass of Ni (mg)</th>
<th>Orientation of Ni in W basket</th>
<th>Thin-film thickness (nm) (±10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 ± 0.01</td>
<td></td>
<td>0.22 – 0.26</td>
</tr>
<tr>
<td>0.5 ± 0.01</td>
<td></td>
<td>0.39 – 0.41</td>
</tr>
<tr>
<td>0.5 ± 0.01</td>
<td></td>
<td>0.59 – 0.61</td>
</tr>
<tr>
<td>1.8 ± 0.01</td>
<td></td>
<td>1.49 – 1.51</td>
</tr>
</tbody>
</table>

Table 1: Thin-film analysis by XPS upon evaporation of various masses and orientations of Ni wire within a W basket. Thin-film thicknesses were taken from three areas on each sample and the resulting values are represented as a range.

When the nickel thin-films were annealed at 1173 K under flowing hydrogen gas, \( v = 20 \text{ cm}^3/\text{s} \) (STP: 1 bar, 273 K) for 5 minutes, the thin-films broke up and became nano-particles with diameters less than 18 nm. The reducing environment caused by the flow of hydrogen gas was used to ensure that the nickel catalyst did not oxidize. The break-up of the thin-film into nano-particles has been reported in the literature [64,69] and is hypothesized to occur due to the differences between the coefficients of thermal expansion between the nickel and the silicon dioxide (e.g. the coefficient of linear thermal expansion at 293 K, \( \alpha \), for nickel and silicon dioxide is \( 13 \times 10^{-6} \text{ K}^{-1} \) and \( 5.9 \times 10^{-7} \text{ K}^{-1} \) respectively) as well as the enhanced surface mobility and cohesive forces due to the elevated temperatures being above the Tammann temperature of the nickel atoms, 863 K.
The nano-particles were measured from SEM images both manually (Figure 16) and by using an automated method provided by Scion imaging software (Figure 17). These methods are based on those demonstrated by Bazzana [68] who demonstrated by AFM the existence of nickel nanoparticles with diameters comparable to those calculated by the Scion imaging software. While it was not possible to verify the existence of nanoparticles less than 10 nm in diameter by AFM due to the tip-effect dominating the topographic data, it was hypothesized that nanoparticles less than 10 nm in diameter existed as light colored dots in SEM micrographs based on the work of Bazzana and the lack of contrary evidence. The Scion imaging software relied on the overall topographical contrast.
Figure 17: SEM images of Ni Nano-particles formed from the annealing of 1.5 nm thin-film under hydrogen flow: $v = 20 \text{ cm}^3/\text{s}$ (STP: 1 bar, 273 K) for 5 minutes. The overall topographical contrast was sufficient for the Scion software; automated characterization was performed on these samples contrast within the SEM micrographs. Samples with catalyst nano-particles formed from an initial thin-film thickness of 1.5 nm were easily measured accurately by the software, while samples with an initial thin-film thickness of 0.6 nm did not provide sufficient topographical contrast for the software to detect and had to be measured manually. The most populated diameter of the nickel nano-particles of the substrates with 0.6 nm thin-films when 92 nano-particles were surveyed over two SEM micrographs with areas approximately 0.05 $\mu\text{m}^2$ was $6.1 \pm 1$ nm. Since these nano-particles were sized close to the limits of the resolving power of the SEM, the percent error in estimating the diameters was relatively large due to the edges of the nano-particles not being well-
pronounced. There are several characteristics that govern the overall image quality of the SEM micrographs: Lateral resolution, substrate charging, and the mean free path of secondary electrons relating to the substrate material. With a working distance of 5 mm and accelerating voltage of 2 keV, the lateral resolution of the SEM was limited to approximately 3.0 nm [128]. The nickel was supported by silica and since silica is an excellent insulator, it readily charges when exposed to the electron beam causing distortions in the micrographs’ contrast. Finally, the diameters of the nano-particles were similar to the mean free path of secondary electrons within the nickel [129] which can cause a lack of edge definition. Substrates with 1.5 nm thin-films of nickel showed the most populated diameter of the nickel nano-particle to be $10.2 \pm 1$ nm when 447 nano-

![Diameter of Ni Particles vs Population](image)

**Figure 18:** Population distribution for the Diameters of Ni Nano-particles after annealing at 1173 K in flowing hydrogen at 20 cm$^3$/s (STP) for 5 min. The black curve represents substrates with 0.6 nm thin-films while the grey curve represents substrates with 1.5 nm thin-films.
particles were surveyed over four SEM micrographs with areas approximately 0.05 µm² (Figure 18). The broadness of the distribution for the 1.5 nm thin-films suggests that some sintering effects had taken place during the annealing process.

4.2 Formation of Spaghetti-like MWCNTs

Samples with an initial thin-film thickness of 1.5 nm resulted in the growth of spaghetti-like MWCNTs upon processing with the following conditions for 90 minutes: \( \hat{\alpha}_c = 20 \), \( O/H = 0.1 \), \( T = 900 \text{ K} \), \( P = 1 \text{ atm} \), \( v = 20 \text{ cm}^3/\text{s (STP)} \) (Figure 19). The diameters of the spaghetti-like MWCNTs were found to be uniform at 19 ± 2 nm. The population density of the spaghetti-like MWCNTs was on the order of \( 2 \times 10^9 \) per cm². The growth

Figure 19: SEM image of Spaghetti-like MWCNT growth from 1.5 nm Ni thin-film after annealing in hydrogen at 1173 K and 90 minutes of the following conditions: \( \hat{\alpha}_c = 20 \), \( O/H = 0.1 \), \( T = 900 \text{ K} \), \( P = 1 \text{ atm} \), \( v = 20 \text{ cm}^3/\text{s (STP)} \)
direction of each tube seemed to be random and the tube structure was full of kinks and acute angular turns.

4.3 Formation of Both Spaghetti-like MWCNTs and Straight MWCNTs

In an effort to decrease the growth of the spaghetti-like MWCNTs in favor of MWCNTs with a straight morphology, the O/H ratio was increased as was shown in the work of Bazzana [68]. Substrates with nickel thin-film thickness of 1.5 nm were annealed in hydrogen at 1173 K and subsequently processed for 90 minutes with the following conditions: $\hat{a}_c = 20$, $O/H = 0.5$, $T = 900$ K, $P = 1$ atm, $v = 20$ cm$^3$/s (STP) (Figure 20). The growth (both length and population density) of the spaghetti-like

![SEM image showing both Spaghetti-like MWCNT growth and relatively straight MWCNT growth from 1.5 nm Ni thin-film after annealing in hydrogen at 1173 K and 90 minutes of the following conditions: $\hat{a}_c = 20$, $O/H = 0.5$, $T = 900$ K, $P = 1$ atm, $v = 20$ cm$^3$/s (STP)](image_url)
MWCNT was reduced by the increase of O/H ratio to 0.5, however, their diameters remained roughly the same at 19 ± 2 nm. The population density of the spaghetti-like MWCNTs was roughly halved compared to growth at O/H ratio of 0.1 and was on the order of 1×10^9 per cm². Relatively long and straight MWCNTs with a thin diameter of 10 ± 2 nm were also grown at the 0.5 O/H ratio condition alongside the spaghetti-like MWCNTs. The population density of the straight MWCNTs was comparatively sparse - on the order of 3×10^8 per cm².

4.4 Formation of Straight Uniform-diameter MWCNTs

In order to increase the yield of the growth of straight MWCNTs, the amount of nickel deposited onto the substrate prior to processing in the five gases was decreased. This experimental change was based on the generally accepted notion that the diameter of the carbon nanotubes is determined by the diameter of the catalyst nano-particles [15,68] which is controlled by the thickness of the thin-film [69,70]. Samples were prepared with a 0.6 nm thick thin-film of nickel and were annealed in hydrogen at 1173 K. Subsequently, the samples were processed at the following reaction conditions: \( \hat{\alpha}_c = 20 \), \( O/H = 0.5 \), \( T = 900 \text{ K} \), \( P = 1 \text{ atm} \), \( \nu = 20 \text{ cm}^3/\text{s (STP)} \) (Figure 21). The resulting growth was comprised of straight MWCNTs with a very uniform diameter 7 ± 2 nm (Figure 22). The deviation noted here was based on uncertainty due to the image quality limitations of the SEM rather than a range of observed diameters as noted for the previous experiments. At magnifications above 100kx, the MWCNTs were observed to be excited by the electron-beam of the SEM into movement in all directions with the base of the nanotube stationary. The population density of the resultant straight MWCNTs was estimated to be
in the order of $1 \times 10^9$ per cm$^2$. Spaghetti-like MWCNTs were almost entirely absent when these growth parameters were used. In all cases, less than 3 spaghetti-like MWCNTs were observed across an area of 0.5 cm$^2$ translating to a population density of at most, $1.5 \times 10^0$ per cm$^2$. Most samples that underwent these growth parameters were entirely devoid of spaghetti-like MWCNTs. These specific growth parameters were run several times on silicon samples from the same wafer to ensure that the selective growth of straight MWCNTs was repeatable (Figure 23). The growth density was fairly uniform across the entire substrate without any occurrences of patches or bundles of carbon.
nanotubes. However, it is important to note that the angles at which the MWCNTs appeared to grow from the substrate varied substantially. Since the e-beam of the SEM was observed to excite the MWCNTs to rotate about their connection to the substrate, it is difficult to conclude if their growth angle was due to the growth process or the SEM observation. Additional experiments with the same parameters but at a lower O/H ratio of 0.1 showed almost no growth on the substrate with only a few (> 10) straight MWCNTs on the entire substrate.

Figure 22: High-resolution SEM image of Straight MWCNTs with diameter 7 ± 2 nm. The blurriness in the image is due to the excitation of the MWCNTs under the electron-beam of the SEM.
4.5 Electron-beam Lithography

Patterned deposition of gold-palladium onto the substrate was performed using the EBL technique. Since metals that oxidize readily, such as nickel, can cause charging effects when observed with SEM, it was important to choose an appropriate metal to be used for the purpose of optimizing the EBL parameters. Gold-palladium does not oxidize rapidly and served as the metal thin-film used to characterize the patterning process with SEM. In order to ensure a single catalyst nanoparticle would form from the patterned metal thin-film site, it is important to make the well-diameter as small as possible. The Zeiss Supra 25 was found to be limited to feature-sizes larger than 80 nm using the standard soft-bake PMMA bi-layer procedure. In order to allow for successful 40 nm resolution patterning, the PMMA bi-layer had to be hard-baked onto the substrate (Figure 24). As a direct consequence of the PMMA hard-baking, wells with a diameter of 43 nm
Figure 24: Electron-beam lithographic patterning of Gold-Palladium with 43 nm diameter wells with a pitch of 180 ± 10 nm were formed; however, the resist layer could not be removed and thus, the sample could not be further used.

4.6 Electrical Characterization

In order to ensure both the pin and parallel plate diode setups operated as designed, preliminary studies on an antimony n-doped silicon Veeco TESP AFM probe with a resistivity of $1 \times 10^{-4} \, \Omega\cdot m$ were performed. A standard parallel plate diode setup with inter-electrode separation of 100 μm was designed and used to test for field emission behavior from the AFM probe. Voltage was swept in a linear staircase with 0.5 V steps and the resulting current was measured, recorded, and plotted (Figure 25). This result was not repeatable and the typical current-voltage response from several other AFM
probes of the same type showed no such current rise with voltage. In fact, the measured current level remained at the noise-level of the system, 50 ± 30 pA, for applied voltages ranging from 0 to 1000 V.

Due to the lack of repeatable field emission performance from the AFM tips and the difficulty in observing the sample during testing due to the visual obstruction inherent in the parallel plate setup, the current-voltage relationship using a 304 stainless-steel pin counter-electrode and the AFM probe was investigated. In order to “zero” the micromanipulator, an initial test was conducted with the pin counter-electrode in contact with the AFM probe. Voltage in the range 0 to 3.5 V was swept in a linear-stepwise fashion through the Keithley 237 Source-Measure unit in 0.5 V steps and the resulting current was measured and recorded (Figure 26). When the micromanipulator was used to
Figure 26: Current-Voltage relationship of an Antimony n-doped Silicon Veeco TESP AFM probe as measured by a Keithley 237 Source-Measure unit upon application of 0 to 3.5V in 0.5V steps relative to electrical contact as given by using the micromanipulator. Lower values of the micromanipulator result in more of the counter-electrode contacting the AFM probe. Deviation bars are within the data points.

raise the pin above the AFM probe surface, the current dropped to the system noise level, 50 ± 30 pA, and remained there even with the application of voltages up to 1000 V.

Substrates with MWCNTs were also tested in both the pin and parallel plate diode setups. Samples with spaghetti-like MWCNTs (Figure 19) or straight MWCNTs (Figure 21) did not produce any measurable current beyond the system noise, 50 ± 30 pA, for all applied voltages from 0 to 1000 V. No field emission behavior was noted even when the micromanipulator equipped diode setup was used to bring the counter-electrode to within 50 ± 10 µm of the samples.
4.7 Discussion

Optimization of the growth parameters to allow for preferential growth of either spaghetti-like MWCNTs or straight MWCNTs was investigated. The two major parameters leading to preferential growth were found to be the nickel nanoparticles’ diameters and the O/H ratio. Electron-beam lithography was investigated as a method to pattern substrates to allow for arrayed growth of carbon nanotubes and was found to be problematic when the feature-size decreased below 100 nm. Electrical characterization using the custom built field emission high vacuum measurement system produced inconsistent results with a standard AFM probe and did not detect any field emission from CVD grown MWCNTs.

4.7.1 Preferential Growth of Multi-walled Carbon Nanotubes

Spaghetti-like MWCNTs where found to grow with 19 nm diameters from substrates with 1.5 nm thin-films of nickel. Since virtually no MWCNTs of this morphology were found on substrates with 0.6 nm thin-films of nickel, it is suggested that the diameter of the nickel nanoparticles played a key role in the preferential growth of either types of MWCNTs. It has been reported in the literature that the catalyst nanoparticles undergo geometrical reconstruction throughout the growth process [15,130]. Furthermore, it has been shown that the morphology of the MWCNT depends on the geometry of the sites on the catalyst nanoparticles where the precipitation of graphitic carbon occurs during the growth procedure [68]. At elevated temperatures, such as the growth temperature of 900 K, the metal nanoparticles’ change in overall size and geometry can be attributed to increased surface mobility, evaporation by the “Kelvin effect”, and size-based melting point depression [106,131].
Since the growth temperature, 900 K, is above the Tamman temperature for nickel, 863 K, this environment promotes the sintering of neighboring nickel nanoparticles due to the increased mobility of the nickel surface atoms. For the samples with spaghetti-like MWCNT, it is possible that the 10.2 nm nickel nanoparticles sinter together to form larger nanoparticles that grow 19 nm diameter carbon nanotubes. However, it was experimentally shown (Figure 19 and Figure 20) that the gas mixture could also effect the resulting morphology of the MWCNTs. When the O/H ratio was increased from 0.1 to 0.5 on substrates with a 1.5 nm thin-film of nickel, both spaghetti-like and straight MWCNTs of their respective diameters (19 and 10 nm) were observed. This experiment was conducted with the rest of the parameters being identical, including the growth temperature, suggesting that the growth morphology is not determined by a single parameter.

While the O/H ratio was not observed to affect the overall diameter of the nickel nanoparticles, it seemed to affect how the graphitic carbon precipitated from the catalyst. More specifically, the O/H ratio was observed to control the growth of straight MWCNTs. For all occurrences of catalyst nanoparticles that were greater than or equal to 19 nm in diameter, spaghetti-like growth occurred at the typical growth parameters of \( \hat{\alpha}_c = 20, \ O/H = 0.1, \ T = 900 \text{ K}, \ P = 1 \text{ atm}, \ \nu = 20 \text{ cm}^3/\text{s (STP)}, \) and an O/H ratio of either 0.1 or 0.5 for a total reaction time of 90 minutes. When catalyst particles of diameter roughly 10 nm or less existed on the substrate, no MWCNTs with the corresponding diameter were observed when the O/H ratio was 0.1. However, when the O/H ratio was increased to 0.5, straight MWCNTs with diameters roughly 10 nm were observed. Furthermore, when the diameters of the nickel nanoparticles were restricted to be mainly
below 10 nm by deposition of 0.6 nm thin-films on the substrate, almost no growth was found at an O/H ratio of 0.1 while straight MWCNTs (1×10⁹ per cm²) were found at an O/H ratio of 0.5. This observation is in agreement with the results that have been reported by Bazzana [68] which showed that increasing O/H ratio from 0.1 to 0.5 hampered the growth of spaghetti-like MWCNTs and favored the growth of straight MWCNTs.

As the catalyst nanoparticles decrease in diameter below 10 nm, the ratio between the surface atoms and bulk atoms increases substantially. Since the surface atoms are not as energetically stable as the bulk atoms, this leads to increased surface mobility as mentioned before as well as the “Kelvin effect” where the surface atoms spontaneously evaporate. The balance between these two effects has been suggested by Moisala and coworkers [106] to be related to the diameter of the catalyst nanoparticles. For catalyst nanoparticles below 5 nm, the authors reported that the “Kelvin effect” was much more prevalent than sintering effects where the catalyst nanoparticles became smaller under elevated temperatures instead of larger. Bazzana [68] suggested that the sintering effects were more prevalent for catalyst nanoparticles above 10 nm. Experiments also demonstrated the possibility for sintering effects in nickel nanoparticles greater than 10 nm (Figure 19). The spaghetti-like MWCNTs that grew from these samples had a relatively larger diameter of 19 nm compared to the 10.2 nm diameter of the nickel nanoparticles prior to carbon growth (Figure 18). It could be further hypothesized that the region between 5-10 nm represents a balance between both sintering and evaporative effects. Experiments (Figure 21) seem to support this hypothesis since the straight MWCNTs grown from substrates with a 0.6 nm thin-film of nickel showed very uniform
diameters of approximately 7 nm without any noticeable population distribution, or deviation from the average nickel nanoparticle size (Figure 18). However, these experiments did not rule out the possibility that the growth kinetics could be enhanced due to the metal catalysts potentially being in the liquid phase which could, in turn, also act to balance out the disappearance of catalyst nanoparticles due to evaporative effects.

Buffat and Borel [131] reported that the melting temperature of gold metal particles smaller than 100 nm was lowered significantly with decreasing diameter. The size-dependent melting temperature relationship for particles was approximated by Friedlander (Equation 4) [132] where it is related to the bulk melting temperature, the densities of the solid phase and liquid phase, and the interfacial energy between the phases as well as the surface energy of the liquid. By inputting the radius of the nanoparticles into the Friedlander expression in addition to the other constants, it is possible to observe the depression of the melting temperature for various metals including nickel below 50 nm (Figure 27). While the bulk melting temperature for nickel is 1726 K, for 10 nm diameter nanoparticles, the melting temperature drops to approximately 1523 K. This temperature is far higher than the growth temperature used in this thesis work, suggesting that the spaghetti-like MWCNTs formed from solid nickel nanoparticles with an increased surface mobility due to the growth temperature. Below

Equation 4: Size-dependent Melting Temperature of particles where $T_c$ is the melting temperature of the particle, $r$ is the radius of the particle, $T_0$ is the bulk melting temperature, $\Delta H_{\text{fusion}}$ is the latent heat of fusion, $\rho_s$ is the density of the solid metal, $\rho_l$ is the density of the liquid metal, $\sigma_{sl}$ is the solid-liquid interfacial energy, and $\sigma_l$ is the surface energy of the liquid.
10 nm, the melting temperature drops much more rapidly such that the nickel nanoparticles below 3 nm may undergo a phase change at temperatures below 973 K.

![Graph showing melting temperature vs. particle diameter](image)

**Figure 27: Estimated melting temperatures of Ni nanoparticles as a function of particle diameter as predicted by the Friedlander expression. Adapted from [106]**

While it was suggested by Moisala and coworkers [106] that the growth kinetics could be enhanced enough to overcome the evaporative effects at very small diameters of nanoparticles due to the particles being in the liquid state; the effects on catalytic activity due to the phase (liquid or solid) of the catalyst has been studied and was shown by Steacie and Elkin [133] to only be a function of temperature when the surface area was constant. Unfortunately, catalytic activity of nanoparticles below 5 nm in both solid and liquid phase has not been studied in great detail and it is unclear if liquid phase catalysts in this range rearrange such that there is an increase in the surface area of the nanoparticle which could enhance growth kinetics enough to overcome the evaporative effects. Carbon nanotube growth with less than 5 nm diameters is typically comprised of
SWCNTs [72,73,74]; however, none were observed on any of the tested substrates in this thesis work under SEM. Other groups with very high resolution SEMs and TEMs have reported SWCNT growth from these nanoparticles diameter and high temperature regimes supporting the hypothesis that growth from catalyst nanoparticles below 5 nm is mediated by a balance between enhanced growth kinetics of liquid metal nanoparticle catalysts and the “Kelvin effect” [20,85,106]. Since the melting temperature of nickel nanoparticles with diameter 4-10 nm is approximated by Friedlander’s equation to be within 1173-1473 K, this suggests that the catalyst nanoparticles in the straight MWCNT growth experiments were all in the solid phase and that their geometry is governed by a balance between the “Kelvin effect” and sintering effects.

Unfortunately, due to the randomized surface break up of the nickel thin-film upon exposure to high temperatures, the population spread of the resulting nickel nanoparticles is too broad to perform accurate melting point measurements through processes such as differential scanning calorimetry (DSC). Additionally, the DSCs available was equipped to accept aluminum crucibles. Since the melting point of aluminum (933 K) is below the temperature required to form the nickel nanoparticles (1173 K), there was no acceptable way to further investigate this phenomena experimentally. To date, no groups have experimentally studied the melting point depression of metal nanoparticles below 10 nm. Without experimental data to compare against the melting point approximations as given by Friedlander, the question of whether the catalyst is a liquid or not at the growth temperature, 900 K, for the range, diameter 4-10 nm, of nickel nanoparticles used to obtain straight MWCNTs cannot be answered.
4.7.2 Electron-beam Lithography

EBL was performed and shown to be capable of creating 43 nm wells with center-to-center spacing of 180 nm. Subsequent lift-off of the PMMA bi-layer was unsuccessful due to the hard baking step needed to obtain this level of resolution. When the standard soft-bake procedure was followed, the upper layer of PMMA collapsed upon deposition of the thin-film of Au-Pa. This caused the wells to be of irregular geometry and diameter. In order to prevent over or under cutting of the resist layer during EBL, the thickness of the PMMA has to be tuned to the capabilities of the equipment. The Supra 25 SEM, when used for EBL, requires the overall resist to be roughly twice as thick as the feature size. For the bi-layer method, the individual PMMA layers have to be quite thin (~ 50 nm) to facilitate this requirement. Unfortunately, as the thickness of the PMMA layer decreases, so does the ease of the lift-off procedure as well as the ability to produce well-defined features due, potentially to a weaker structural integrity of the resist. The hard baking step enhanced the strength of the resist layers to produce well-defined features upon exposure to the e-beam and subsequent development in MIBK/IPA (1:3) (Figure 24), however, it also prevented successful lift-off following the metal deposition step. Most groups that have utilized EBL to pattern substrates have been successful with feature sizes greater than 100 nm [104,105,118]. At such a relatively large feature size, the PMMA layer can be sufficiently thick to be robust enough to not collapse during the EBL process with standard soft-baking methods. With the combination of the use of PMMA bi-layers as well as soft-baking, the lift-off of the resist layer is much easier for feature sizes greater than 100 nm. Javey and Dai [85] have been able to demonstrate successful EBL of 20 nm wells. The authors reported the use of 100
nm thick PMMA, but did not mention which molecular weight of PMMA they used (450k or 975k) or if they used a bi-layer resist method. It is most probable that 975k PMMA was used since, under the standard range of e-beam dosages, the 450k would not resist the e-beam exposure enough to allow for the 20 nm feature sizes. As was mentioned earlier, the resistance to e-beam exposure is related to the molecular weight of the resist with all other variables controlled.

Javey and Dai [85] reported that upon deposition of 1.5 nm of cobalt by electron beam evaporation at an angle of 5-10° relative to the substrate normal (effectively using the PMMA side-walls as "shadow masks") and subsequent resist lift-off and annealing at 1098 K, single 7 ± 2.2 nm diameter Co nanoparticles formed where there were 20 nm wells while multiple (3-5) ~7 nm diameter Co nanoparticles formed where there were 30 nm wells. Since the catalyst nanoparticle diameter range is similar to what was obtained experimentally, 4-10 nm, it is apparent that the ability to form 20 nm wells is critical in ensuring the existence of a single catalyst nanoparticle at each location. Additionally, the use of angled e-beam evaporation to deposit the catalyst metal decreased the total atoms deposited in each well leading to the formation of a single nanoparticle within the 20 nm wells. 30 nm wells failed to form single nanoparticles suggesting that the success of this procedure relies heavily on the quality of the equipment as well as the minimization of common EBL "variables" which include e-beam drift, inaccuracies in the SEM stage movement, beam-blanking errors, backscattering of electrons, outgassing/contamination within the SEM chamber, and dosing errors.
4.7.3 Electrical Characterization

Electrical characterization was performed on various substrates in a high-vacuum environment typically on the order of $10^{-7}$ Torr and room temperature. A Veeco TESP AFM probe fabricated from antimony n-doped silicon with a resistivity of approximately $1 \times 10^{-4} \, \Omega\cdot\text{m}$ was tested in a standard diode setup consisting of two parallel aluminum plates spaced such that the AFM tip would be 100 µm away from the counter-electrode and was found to have a linear F-N slope upon application of a linear voltage staircase sweep suggesting that the current was emitted from the AFM tip through field emission.

It is important to note that similar research done on various field emission tips of similar sharpness to the AFM probe ranging from conductively-doped silicon [36,37] to deposited metal thin-film on silicon [38] and diamond-tipped silicon [39,40,41] showed turn-on voltages approximately two orders of magnitude higher than what was achieved in this experiment (Figure 25). Diamond-tipped oxidatively-sharpened silicon field-emitters were shown to be one of the highest performing field-emitters when compared to all of the standard field-emitters as well as some carbon nanotube emitters [11] suggesting that the initial interpretation of the experimental results where it was thought that the AFM probe had undergone Fowler-Nordheim emission was questionable.

At first, it was hypothesized that the AFM tip mechanically failed due to resistive heating during the current measurement. Optical micrographs of the AFM cantilever and tip showed that there was indeed irreversible damage done to the AFM tip where it had been “blown out” during the electrical characterization, most likely due to resistive heating under applied current (Figure 28). In an effort to test for repeatability, AFM probes of the same type were tested in the same configuration; the measured current was
Figure 28: Optical Micrographs of AFM Tip. On the left is the AFM tip that had “blown” due most likely to resistive heating. The new tip diameter is roughly 4 µm. On the right is a normal AFM tip for comparison with tip extremity out of focus, but specified to 8 nm.

not observed to exceed the level of the system noise for any of the AFM probes. Since the bottom surface of the AFM probes contains tiny burrs from their manufacturing process, it was thought that the electrical contact between the cathode and the AFM probe differed from sample to sample and was insufficient. The test was repeated using conductive silver paste as an interlayer between the cathode and the AFM probe; the measured current never exceeded the level of the system noise suggesting that there was no electrical contact problem between the cathode and the AFM probe. The lack of repeatability as well as an apparent performance increase of two orders of magnitude from the best field-emitters reported in the literature suggested that there was some sort of as yet unidentified experimental error.

Since the use of parallel plates naturally formed a visual obstruction for observation of the sample during the electrical characterization, a second diode setup was constructed. The cathode remained the same while the anode was switched to a 304 stainless steel sharpened pin attached to a micromanipulator. In order to form a “zero” for the micromanipulator, the surface of the AFM probe was electrically characterized.
The point at which the AFM probe was barely electrically continuous with the sharpened pin anode represented the zero-distance separation point between the sample and the anode. The current-voltage relationship of the surface of the AFM probe was measured at varying contact pressures as noted by the micrometer measurements (Figure 26). The curve is typical of Schottky diodes [134] where there is a contact between an n-doped semiconductor (AFM Probe) and a metal (304 Stainless Steel anode). As the contact between the anode and the AFM probe diminished, so did the measured current, although the exponential growth with voltage was still apparent. This result suggested that the initial experiment with the parallel plate diode setup (Figure 25) was in fact not field emission, but a contact between the AFM probe and the anode. Comparing the current measurements (Figure 25 and Figure 26), the results are similar and suggests that if an electrical contact between the AFM probe and the anode in the parallel plate diode setup existed, it was relatively poor. It is likely that the AFM tip had contacted the anode and due to its small dimensions, it resistively heated and catastrophically failed when passing current between the cathode and anode. While testing with the pin-anode diode setup, the AFM probe became electrostatically attached to the anode under applied voltage and had to be physically removed even after the application of voltage was terminated. This phenomenon was repeatable in all trials with this pin-diode setup and further suggests the possibility that the AFM probe was in contact with the anode in the first experiment (Figure 25). When the AFM probe was adhered to the cathode with conductive silver paste, the AFM probe was physically not allowed to become electrostatically attached to the anode so that the cathode and anode could not be electrically bridged by the AFM probe. When the micromanipulator was adjusted so that the pin-anode was removed
from the surface of the AFM probe by several micrometers, upon applied voltage, there were no current measurements observed beyond the system noise. Since, even under application of voltages as high as 1000 V, no current was measured beyond the system noise, this suggests an additional experimental error.

Multi-wall carbon nanotubes have been shown to have excellent field emission properties and relatively low turn-on voltages compared to traditional field-emitters [112]. Since AFM probes do not have as sharp of an aspect ratio as MWCNTs, their field emission properties may have not been noticeable beyond the system noise for the range of voltage tested. Samples with MWCNTs were tested in both diode setups over the voltage range 0-1000 V, however, there was no measurable current beyond the system noise. The literature had shown that various substrates with varying qualities and quantities of MWCNTs had noticeable emitted current at voltages as low as 200 V [112,118] suggesting that the sample under test should have also performed similarly. Based on the reports [11] that mentioned the destruction of MWCNTs upon application of sustained high voltages, the sample under test was subjected to an applied voltage of 1000 V for 4 hours then they were visually checked with an SEM. The population density was found to have been unchanged from the original $1 \times 10^9$ MWCNTs per cm$^2$ suggesting that the sample had not actually received the 1000 V. A $10 \pm 5\%$ M$\Omega$ carbon-film 0.25 W resistor was placed between the anode and cathode in the diode setup and was subjected to voltages between 0 and 1000 V. This resistor value corresponded to the order of magnitude of current that would be expected for a field emission device when subjected to the same applied voltages. Instead of using a linear staircase voltage sweep as was done with the other experiments, individual voltages from 0 to 1000V were
manually set in order to allow for the most accurate responses (Figure 29). Current measurements were taken 5 seconds following the initial application of the voltage. This step was taken to ensure the electrical response had settled to a steady-state value.

Figure 29: Current-Voltage relationship for a 10 MΩ Resistor. The curve follows Ohm’s Law, as represented by the straight line, up until 162 V. Voltmeter confirmed no output voltages greater than 162 V. Deviation bars are within the data points.

Surprisingly, the expected Ohm’s law relationship, which is typically noted by a linear slope I-V curve, was only observed at voltages below 162 V. Beyond 162 V, the current had saturated strongly suggesting that the Keithley 237 Source-Measure unit was compromised. A voltmeter showed that the Keithley 237 Source-Measure unit was incapable of output greater than 162 V. Theoretically, the electrical field is what triggers the field emission effect [29] and by testing at less inter-electrode distances, the voltage required diminishes appropriately for the same field magnitude. When the pin-anode was brought to within 50 ± 10 µm of the MWCNT sample and voltage was applied in the
range 0 – 160 V, no measurable current beyond the system noise level was recorded. Since the MWCNTs (Figure 21) were not specifically vertically-directed on the substrate, it is hypothesized that the varying growth angles of the straight MWCNTs on the substrate caused a shielding effect [87,109,124,125] that strongly diminished the field amplification that typically allows for MWCNTs with superior field emission characteristics.
5.0 CONCLUSIONS

An investigation of the preferential growth of multi-walled carbon nanotubes of both spaghetti-like and straight morphologies in a CVD technique on nickel catalyst nanoparticles with average diameters of 6.1 and 10.2 ± 1 nm was performed using five reactant source gases: methane, carbon dioxide, carbon monoxide, hydrogen, and water at 900 K, 1 atm, and a total flow rate of 20 cm³/s (STP). The nickel nanoparticles were formed from thermally evaporated thin films of thickness 0.6 ± 0.06 nm and 1.5 ± 0.15 nm supported by p-type 001 silicon with a 350 nm diffusion barrier layer of thermal oxide by an annealing process at 1173 K under 20 cm³/s (STP) flow of hydrogen. Spaghetti-like MWCNTs exclusively grew on substrates with 10.2 ± 1 nm nickel nanoparticles at 900 K, 1 atm, total flow rate of 20 cm³/s (STP), gas-phase carbon activity of 20, and O/H ratio of 0.1. An increase of the O/H ratio to 0.5 facilitated growth of both spaghetti-like and straight MWCNTs with all other conditions being the same, albeit the overall growth was greatly hindered with nucleation decreased by at least a factor of two with the spaghetti-like growth outnumbering the straight growth by a factor of about 3. Preferential growth of straight MWCNTs was facilitated by using substrates with 6.1 ± 1 nm nickel nanoparticles at 900 K, 1 atm, total flow rate of 20 cm³/s (STP), gas-phase carbon activity of 20, and O/H ratio of 0.5. At these conditions, the growth of straight MWCNTs outnumbered the growth of spaghetti-like MWCNTs by at least a factor of 10⁸ compared to previous work where the straight MWCNTs were preferred over spaghetti-like MWCNTs by only a factor of 28.6 [68]. It is unclear whether or not the lack of vertical alignment of the straight MWCNTs was due to the growth procedure, the e-beam of the SEM upon observation, or a combination of both. These results suggest that the
optimal parameters for growing straight MWCNTs with this method depend strongly on the nickel nanoparticle diameter and the O/H ratio of the five reactant gases at the stated reaction temperature and pressure supporting the mechanisms as proposed by Bazzana [68].

Preliminary EBL experiments to obtain 20 nm feature sizes were unsuccessful and suggested the need for careful optimization of the resist, the SEM parameters, and overall need for state-of-the-art EBL equipment that can provide the high resolving power needed to facilitate feature sizes in the 20 nm regime. Electrical characterization of candidate devices was hindered due to the lack of availability of voltages above 162 V and the possibility of field-enhancement shielding caused by non-vertically aligned MWCNTs with inappropriate emitter spacing. The current-voltage relationship caused by a Schottky contact is exponential providing a linear slope on a Fowler-Nordheim fit. This fit can be misleading and highlights the importance of taking a baseline contact measurement to ensure that the subsequent measured current-voltage relationship is not from Schottky contact, but from field emission. Finally, a successful field emission device based on carbon nanotube emitters requires straight MWCNTs that are vertically aligned and grown in a pattern such that the emitters are separated by twice their height to minimize electrostatic shielding.
Thermally grown SiO$_2$ was chosen as the diffusion barrier between the nickel catalyst and silicon to prevent the formation of nickel silicides. Electrically, SiO$_2$ is a very good insulator and does not form a good electrical contact between the multi-wall carbon nanotubes and the silicon. In order to form a better electrical contact, a conductive diffusion barrier is favored. Teo and coworkers [118] demonstrated the use of conductive titanium nitride as a diffusion barrier layer against nickel catalyst on silicon substrates. A thin-film of thickness 20 nm of TiN was deposited onto an n-doped Si substrate by rf-magnetron sputtering. This was followed by a sputtering of a 3 nm thin-film of nickel. Upon annealing at 973 K, the surface composition of the sample was examined by Auger electron spectroscopy while the surface was sputtered layer-by-layer by a 2keV Ar+ gun. The authors reported that TiN was successful in preventing the nickel from diffusing into the silicon during the annealing process.

Patterned arrays of MWCNTs are required for field emission applications. In order to grow MWCNTs in a patterned array, nano-scale patterning techniques like electron-beam lithography need to be employed. The literature [85,104,105,118] has shown the ability of EBL to pattern the catalyst successfully leading to patterned arrays of various tubular allotropes of carbon including MWCNTs, SWCNTs, and CNFs. Obtaining a single catalyst nanoparticle at each patterned site requires careful implementation of thin-film deposition techniques as well as state-of-the-art EBL equipment especially for nanoparticles less than 10 nm in diameter [85].

Vertically-aligned MWCNTs are yet another requirement for field emission applications. PECVD has been shown in the literature [97,98,99,102,118] to be the only
viable method to this date to grow vertically-aligned MWCNTs without the need for laborious procedures as required by alumina template methods. While there has not been any work done with using the five-gas mixture as the carbon-source gas in a PECVD, it is possible that this combination would yield vertically-aligned, well-graphitized, straight, high-aspect ratio MWCNTs. A combination of all the above recommendations could possibly lead to the fabrication of a CNTFED with superior electrical characteristics than any other solution available to date.

Electrical characterization with the aid of an in situ SEM or TEM could reduce the cumbersome testing that occurs in an unaided-eye high-vacuum environment. The use of piezo-electronic stage manipulation within SEMs or high-vacuum AFM/SPMs [135] could also significantly reduce the guesswork that is typically involved when using standard micromanipulators with precision of only ± 2 µm and an order of magnitude worse precision due to mechanical vibrations that enter the test system. A combination of both recommendations would enhance the precision in calculating electric field from applied voltage while also granting the ability to monitor the state of the carbon nanotube throughout the field emission testing in an effort to better understand how the individual shells of the MWCNT behave under field emission conditions.
7.0 REFERENCES


44 http://www.cnanotech.com/products/materials.html

45 http://www.nano-c.com/nanoprod.html

46 http://www.nano-lab.com/carbonnanotubeproducts.html


8.0 APPENDICES
Appendix A
Gas Flow Calibration Charts and Equations
Manual Mass Flow Controllers

The manual mass flow controllers were calibrated by measuring the pressure drop through a precision-bored Pyrex® capillary tube as it changed linearly with gas flow rate over the ranges used. Each calibration point had an error of roughly ± 0.05 cm³/s due to the use of a stopwatch. Both the backup (test) manual mass flow controller and normal (experimental) mass flow controller sets were calibrated and corrected to Standard Temperature and Pressure. In most cases, the output pressure at the gas cylinder was regulated to 20 psi. Some gases required additional flow, so they were regulated to 30 psi.

He (test), STP

\[ y = 4.22352x + 0.04594 \]

\[ R^2 = 0.99951 \]

He Calibration Curve for Backup System
N₂ Calibration Curve for Backup System

H₂ Calibration Curve for Backup System
CO Calibration Curve for Backup System

\[ y = 3.53057x + 0.85430 \]
\[ R^2 = 0.99925 \]

CH\(_4\) Calibration Curve for Backup System

\[ y = 2.69047x - 0.87707 \]
\[ R^2 = 0.99974 \]
**CO₂ (test), STP**

![Graph showing CO₂ calibration curve]

**Equation:**
\[ y = 3.45443x + 0.19895 \]
\[ R^2 = 0.99961 \]

**CO₂ Calibration Curve for Backup System**

**He (experimental), STP - 30 psi**

![Graph showing He calibration curve]

**Equation:**
\[ y = 4.1648x + 2.8201 \]
\[ R^2 = 0.9994 \]

**He Calibration Curve for Experimental System**
$N_2$ (experimental), STP - 20 psi

\[ y = 4.1656x + 0.7135 \]
\[ R^2 = 0.9992 \]

$N_2$ Calibration Curve for Experimental System

$H_2$ (experimental), STP - 20 psi

\[ y = 1.4476x + 0.9234 \]
\[ R^2 = 0.9992 \]

$H_2$ Calibration Curve for Experimental System
CO (experimental), STP - 30 psi

\[ y = 2.88508x + 1.74998 \]
\[ R^2 = 0.99912 \]

CO Calibration Curve for Experimental System

\[ y = 2.2467x + 1.0453 \]
\[ R^2 = 0.9995 \]

CH₄ (experimental), STP- 20 psi

CH₄ Calibration Curve for Experimental System

Note:

CO₂ Calibration Curve for Experimental System is not available due to a fouled Brooks Model 8944 mass flow regulator that could not be successfully refurbished.
Digital Mass Flow Controllers (DMFC)

The digital mass flow controllers were calibrated by measuring the pressure drop through a precision-bored Pyrex® capillary tube as it changed linearly with gas flow rate over the ranges used. Each calibration point had an error of roughly ± 0.05 cm³/s due to the use of a stopwatch. Maximum accuracy of the digital mass flow controllers was made possible by setting each controller’s units to be % of total flow. The DMFCs were calibrated and corrected to Standard Temperature and Pressure. In most cases, the output pressure at the gas cylinder was regulated to 20 psi. Some gases required additional flow, so they were regulated to 30 psi. CO₂ has two calibration curves, one to include a low flow rate regime with an MKS controller unit and the other to include the normal flow rate regime using the standard Brooks model 5850E with model 0154E external display.

![DMFC Calibration Curve for H₂](image)

**H₂ DMFC - 20 psi**

\[ y = 3.60244x - 1.23551 \]

\[ R^2 = 0.99991 \]
DMFC Calibration Curve for CO

CO DMFC - 30 psi

\[ y = 3.78836x - 0.33824 \]

\[ R^2 = 0.99959 \]

DMFC Calibration Curve for CH\(_4\)

CH\(_4\) DMFC - 20 psi

\[ y = 3.38290x + 1.07612 \]

\[ R^2 = 0.99934 \]
**DMFC Calibration Curve for CO₂**

- **Equation:** \( y = 3.85103x - 0.24501 \)
- **R²:** 0.99999

**MKS Calibration Curve for Very Low Flowrate CO₂**

- **Equation:** \( y = 38.45171x - 0.63956 \)
- **R²:** 0.99992
Appendix B
Reactor Temperature Profile
The temperature profile was performed previously by Bazzana [68] with a flow rate of nitrogen of 20 cm³/s (STP) and set so that the isothermal zone was specified between 899 and 900 K. The isothermal zone was found to be at a distance of 2.5 cm beyond the Raschig rings and extended for an additional 3.0 cm.
Appendix C
Gas Phase Carbon Activity and O/H Ratio Equations
The gas phase carbon activity, $\hat{a}_c$, was derived as an arbitrary value of the carbon activity, $a_c$, greater than 1. In the case of graphite, $a_c$ is equal to 1. Since a mixture of five reactant gases were used, a set of independent equilibrium equations forming graphite were required. Thermodynamic activity is defined to be the component mixture fugacity divided by the fugacity of pure component at 1 atm. Since the system is at high temperature and normal pressures, the gas phase can be considered ideal and the carbon activity is expressed as a function of each of the reaction equilibrium constants, the partial pressures of the reactants and products, and the total pressure (1 atm).

$$a_i \equiv \frac{f_i}{f_i^o} = \frac{P_i}{1} \quad (1)$$

$$K_i(T) \equiv \prod (a_i)^{\nu_i} \quad (2)$$

$$2CO \rightleftharpoons C + CO_2 \quad (3) \quad a_c = \frac{K_1(T) \times P_{CO}^2}{P_{CO_2}}$$

$$CH_4 \rightleftharpoons C + 2H_2 \quad (4) \quad a_c = \frac{K_2(T) \times P_{CH_4}}{P_{H_2}^2}$$

$$CO + H_2 \rightleftharpoons C + H_2O \quad (5) \quad a_c = \frac{K_3(T) \times P_{CO} \times P_{H_2}}{P_{H_2O}}$$

A value of carbon activity greater than 1 represents a non-equilibrium formation of carbon gas prior to the formation of carbon in the graphite form. By fixing the gas phase carbon activity to a value greater than 1, equations 3, 4, and 5 can be combined.

$$\hat{a}_c = \frac{K_1(T) \times P_{CO}^2}{P_{CO_2}} = \frac{K_2(T) \times P_{CH_4}}{P_{H_2}^2} = \frac{K_3(T) \times P_{CO} \times P_{H_2}}{P_{H_2O}} \quad (6)$$
The oxygen to hydrogen ratio is simply a ratio between all of the oxygen species and hydrogen species in each of the five gases.

\[
O/H = \frac{P_{CO} + P_{H_2O} + 2P_{CO_2}}{2P_{H_2} + 2P_{H_2O} + 4P_{CH_4}}
\]

(7)

Finally, the Gibb’s phase rule was applied to ensure that the system is fully specified:

\[
F = N + 2 - \pi - R - S
\]

Where \(N\) is the number of components (\(H_2\), \(CH_4\), \(CO\), \(CO_2\), \(H_2O\), and \(C_{gas}\)), \(\pi\) represents the number of phases (gas phase is assumed), \(R\) is the number of independent reactions (there are 3), and \(S\) is the number of independent specifications (\(\alpha_c\) and O/H ratio). Thus, in order to fully specify the thermodynamic system, two intensive variables must be fixed. The most convenient intensive variables are temperature and pressure.

In order for the partial pressures to be found, equations 6 and 7 need to be solved simultaneously. The Newton-Raphson method is typically used to solve systems of equations that can be broken down into a single polynomial. Conveniently, a Microsoft Excel spreadsheet has the computational power to solve for the partial pressures in an iterative procedure and screenshots of this spreadsheet are provided in the following pages.
Microsoft Excel is a powerful spreadsheet tool that can be used to automate calculations. By following the instructions provided on the right side of the spreadsheet, the spreadsheet will provide the DMFC settings to input so that the appropriate flowrate of each gas is delivered to the reactor. The spreadsheet incorporates calibration curves for both the manual manometer and DMFC systems. It also incorporates reaction equilibrium curves for all three independent graphite forming gas phase reactions. These curves are embedded into the equations for each equilibrium constant cell. By inserting the reaction temperature desired, the equilibrium constants will update automatically based on the new temperature. The iterative procedure used is the tool, Solver. Solver allows input of additional constraints like $\bar{a}_c$ and O/H ratio. There are additional embedded equations that will warn the user when to install the MKS unit for the CO$_2$ DMFC. Equilibrium constants were provided from previous work done by Bazzana [68], however, they can alternatively be found in the NIST-JANAF Thermochemical Tables. In order to provide for good interpolation approximations, the equilibrium constant data was fitted to a 6$^{th}$ order polynomial within the range of the data. Finally, saturated steam psychrometric data were also provided from previous work [68] and can alternatively be found in standard chemical engineering thermodynamics textbooks such as Smith, J.M., H.C. VanNess, and M.M Abbott, Introduction to Chemical Engineering Thermodynamics 6$^{th}$ Ed., McGraw Hill, New York, 2001. This data was used to calculate the appropriate water bath temperature to produce the correct partial pressure of water to saturate the feed gas stream according to the experiment parameters.
### Experimental Parameter Solver

**Instructions For Mole Fraction Solver**

1. Type in Desired Temperature in Kelvin
2. Type in P (atm) and Flow Rate (ccps) if experiment calls for an additional
3. The Equilibrium Constants should change to complement the Desired
   Temperature automatically
4. Click “Tools”
5. Click “Solver...”
6. Set Target Cell: “Total” ($B$21) [$B$21] EQual To Value of 1
7. By Changing Cells: “H₂, CO, CH₄, CO₂, H₂O, He” ($B$18-$B$23)
   [$B$18-$B$23]
8. Subject to the Constraints:
   a. “$S, (K)$” [$E$11] [$E$10] 20
   b. “$S, (K)$” [$E$21] [$E$20] 20
   c. “$S, (K)$” [$E$14] [$E$13] 20
   d. “OH” [$E$16] [$E$15] 0.5
   e. “He” [$B$23] [$E$23] 0
9. Click “Solve”

10. In the event of a somewhat incorrect solver guess, keep the proposed
    solution anyways and manually change the offending negative composition
    to a positive more reasonable value such as 0.00. Click “Solve” in Solver
    once again, and it should guess correctly

### Available Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.1879694879</td>
</tr>
<tr>
<td>CO</td>
<td>0.5019798935</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.2279495907</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.4715700963</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.01573962</td>
</tr>
</tbody>
</table>

### Total

|       | 1.00000000   |

### Other Settings

**DMFC Setting**

<table>
<thead>
<tr>
<th>Component</th>
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<tbody>
<tr>
<td>H₂</td>
<td>12.30</td>
</tr>
<tr>
<td>CO</td>
<td>37.63</td>
</tr>
<tr>
<td>CH₄</td>
<td>16.50</td>
</tr>
<tr>
<td>CO₂</td>
<td>54.25</td>
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</table>

**Saturator Bath**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Gauge P (atm)</td>
<td>6.25</td>
</tr>
<tr>
<td>Bath T (°C)</td>
<td>16.7</td>
</tr>
</tbody>
</table>

**Manometer Setting**

<table>
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<tr>
<th>Component</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>H₂</td>
<td>6.4</td>
</tr>
<tr>
<td>CO</td>
<td>10.0</td>
</tr>
<tr>
<td>CH₄</td>
<td>11.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.8</td>
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</table>

**Project Settings In the Design Experiment**

<table>
<thead>
<tr>
<th>Constraint</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S, (K)$</td>
<td>20</td>
</tr>
<tr>
<td>$S, (K)$</td>
<td>20</td>
</tr>
<tr>
<td>$S, (K)$</td>
<td>20</td>
</tr>
</tbody>
</table>

**Run Settings Solver**

- Manual Settings: Solver
- Equilibrium Constants
- Psychrometric
Equilibrium Constants Corresponding to all Three Independent Reactions as a Function of Temperature Fitted to 6th-order Polynomial Equations to allow for good interpolation approximations
Saturated Steam Values where inverse temperature is plotted as a function of the natural logarithm of vapor pressure

\[
\frac{1}{T} = -1.9265441898 \times 10^{-4} \ln(P_{\text{VAP}}) + 3.5745390878 \times 10^{-3}
\]

\[R^2 = 0.99988\]
Appendix D

Summary of Experimental Variables and Results
Various reactor conditions and nickel thin-film thicknesses were studied in order to better understand the conditions that allowed for preferential growth of straight multi-wall carbon nanotubes. In all experiments, the nickel nanoparticles were formed on the substrate after an annealing process where the sample was exposed to flowing hydrogen gas at 20 cm³/s (STP) for 5 min. at a temperature of 1173 K. Additionally, all of the carbon growth processes occurred at 900 K, a gas phase carbon activity of 20, and overall flow rate of 20 cm³/s (STP) for 90 minutes. The only variables that were altered were the O/H ratio and the thickness of the initial nickel thin-films.

<table>
<thead>
<tr>
<th>Mass of Ni (mg)</th>
<th>Thin-film thickness (nm) (±10%)</th>
<th>Nanoparticle Diameter (nm)</th>
<th>O/H Ratio</th>
<th>Resulting MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>1.49 – 1.51</td>
<td>10.2</td>
<td>0.1</td>
<td>Spaghetti</td>
</tr>
<tr>
<td>1.8</td>
<td>1.49 – 1.51</td>
<td>10.2</td>
<td>0.5</td>
<td>Both</td>
</tr>
<tr>
<td>0.5</td>
<td>0.59 – 0.61</td>
<td>6.1</td>
<td>0.5</td>
<td>Straight</td>
</tr>
</tbody>
</table>

**Summary of Experimental Variables and the Resulting Morphology of the Multi-wall Carbon Nanotubes**