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Student’s name: Larry A Christy

This work and its defense approved by:

Committee chair: Marc Cahay, Ph.D.
Committee member: Punit Boolchand, Ph.D.
Committee member: Altan Ferendeci, Ph.D.
Field Emission Properties of Carbon Nanotube Fibers and Sheets for a High Current Electron Source

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By
Larry Christy

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Dr. Marc M. Cahay, Committee Chair
Abstract

Field emission (FE) properties of carbon nanotube (CNT) fibers from Rice University and the University of Cambridge have been studied for use within a high current electron source for a directed energy weapon. Upon reviewing the performance of these two prevalent CNT fibers, cathodes were designed with CNT fibers from the University of Cincinnati Nanoworld Laboratory. Cathodes composed of a single CNT fiber, an array of three CNT fibers, and a nonwoven CNT sheet were investigated for FE properties; the goal was to design a cathode with emission current in excess of 10 mA. Once the design phase was complete, the cathode samples were fabricated, characterized, and then analyzed to determine FE properties. Electrical conductivity of the CNT fibers was characterized with a 4-probe technique. FE characteristics were measured in an ultra-high vacuum chamber at Wright-Patterson Air Force Base. The arrayed CNT fiber and the enhanced nonwoven CNT sheet emitter design demonstrated the most promising FE properties. Future work will include further analysis and cathode design using this nonwoven CNT sheet material to increase peak current performance during electron emission.
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I dedicate this work to my mother, Treva Marie Christy.
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List of Symbols

CNT = Carbon nanotube

CNF = Carbon nanotube fiber

FE = Field emission

FN = Fowler-Nordheim

SWCNT = Single wall carbon nanotube

MWCNT = Multi wall carbon nanotube

I-V = Current-voltage

$E_{\text{ext}}$ = Externally applied electric field

$\varphi$ = Work function

$\beta$ = Field enhancement factor

$A_{\text{eff}}$ = Effective area of electron emission

$m$ = Mass of electron, 9.109 x $10^{-31}$ kg

e = Charge of electron, 1.602 x $10^{-19}$ C

$h$ = Planck constant, 6.626 x $10^{-34}$ m$^2$kg/s
Chapter 1: Introduction

1.1 Motivation

Advanced cathode electron emitter materials are needed to produce the stable, high current electron beams needed for compact, high power, high frequency vacuum electronic devices. Current state of the art thermionic cathodes require high operating temperature, resulting in inefficient power consumption, poor reliability, and diminished lifetime. Addition of thermal management components to handle the high operating temperature leads to additional device complexity and added weight, which is undesirable. New cathode materials are needed for high current density applications including microwave power amplifiers, miniature X-ray sources, micro-machines mass spectrometers and ion propulsion, among others [1, 2, 3].

This project is primarily motivated by the urgent need for cathodes operated in DC mode in a traveling wave tube for the Directed Energy Directorate (Air Force Research Laboratory at Kirtland). Towards that goal, new cold cathode concepts are needed that must operate at temperatures less than 1000 °C, provide total emission current of at least 10 mA at a current density of at least 1 A/cm², and be capable of at least one hour of continuous operation.

To achieve the goal of 10 mA total emission current, cathode design will include the fabrication of an array of Carbon Nanotube Fibers (CNFs), since current individual CNFs can only provide a few mA emission current before failure. This work will provide a proof of concept and options for cathode design to advance the work of S. Fairchild’s group and the Directed Energy Directorate (Air Force Research Laboratory at Kirtland) on the use of CNFs to build cathodes operated in DC mode in a traveling wave tube (TWT) [1].
Carbon nanotubes (CNTs) will be exclusively investigated in this work as CNTs have proven to be excellent field emitters due to their high aspect ratio as well as high electrical and thermal conductivity [4, 5, 6, 7, 8]. Recent research has focused on fabricating CNT sheets, yarns, and fibers in an attempt to transfer their exceptional physical properties from the nanoscale to the macroscale [9, 10, 11]. CNT yarns that are spun from vertically grown CNT arrays have been studied for their use as FE sources [12, 13, 14], and there have been some recent reports on the exceptional FE properties of acid spun CNTFs [11, 15, 16, 17].

In this thesis, the FE properties of CNFs from the groups of Prof. Pasquali at Rice University and Prof. Koziol at the University of Cambridge (UK) will be reviewed. Additionally, CNFs from Professors Schulz and Shanov at the University of Cincinnati will be integrated into several cathode designs and their FE properties are analyzed and compared to the two previously reviewed CNFs.

1.2 Research Aims

The need for advanced cathode electron emitters for various applications is clearly outlined. The goal of this research is to provide a CNT based cathode capable of emitting a maximum current of 10 mA prior to failure. There is immediate need for use of CNFs to build cathodes operated in DC mode in a TWT. Fibers from the University of Cambridge and Rice University will be reviewed for FE performance. This thesis aims to improve upon the properties of these fibers in pursuit of 10 mA peak current prior to failure. Cathode design will revolve around processing CNTs from the University of Cincinnati, characterizing these CNT fibers, diagnosing FE performance, and modeling FE from the CNF based cathodes. This process is outlined in figure 1.1.
1.3 Thesis Outline

The outline of the aims of this thesis, to fulfill the needs described above, is as follows:

**Chapter 2** – Background: overview of CNTs and their material properties. Also, fundamentals of FE process and characterization are presented.

**Chapter 3** – Aim 1: the design and fabrication of cathodes from UC CNT fibers and sheets. The goal is to achieve 10 mA peak current prior to failure.

**Chapter 4** – Aim 2: characterization of cathodes from UC CNT fibers and sheets. FE properties will be analyzed for comparison to the Rice and Cambridge CNFs.

**Chapter 5** – Aim 3: review FE performance of cathodes fabricated from Rice and Cambridge CNT fibers.

**Chapter 6** – Applications and future work for improved CNF cathodes, using CNTs from the University of Cincinnati.
Chapter 2: Background

2.1 Review of Carbon Nanotubes

Section 2.1.1 provides an overview of the significance of CNTs, including their history, structure, and applications. Section 2.1.2 outlines their electrical properties. Section 2.1.3 overviews the form of CNT synthesis used by the University of Cincinnati, namely, chemical vapor deposition (CVD). Section 2.1.1 reviews the fundamentals of FE, including a history of FE theoretical studies with a focus on the Fowler-Nordheim (FN) model. Finally, section 2.1.2 described the FE properties of CNT arrays.

2.1.1 Introduction

Sumio Iijima rediscovered CNTs in 1991 using transmission electron microscope (TEM) studies performed on by-products of C\textsubscript{60} fullerenes synthesized with an electric arc discharge [18]. The novel properties of CNTs have inspired the research and will continue to do so far into the future.

Figure 2.1 TEM images of the first observed multi-walled CNTs reported by Iijima in 1991 [18].
The element carbon is a very common and, by far, the most versatile element which forms the majority of organic compounds [19]. Carbon consists of 6 electrons, two of which fill the 1s and 2s orbitals (inner orbitals). The remaining four valence electrons can fill the sp, sp2, or sp3 hybrid orbitals. The electron configuration will determine the formation of one of three allotropes, fullerenes (sp2), graphite (sp2), or diamond (sp3). Solid carbon can form any one of the three allotropes, shown in figure 2.2 [20]. Diamond is the crystalline form of carbon resulting from sp3 bonding, resulting in sp3 orbitals separated by an angle of 109.5°; sp3 hybridization yields the tetrahedral bonding of each carbon atom with four equidistant neighboring atoms, forming four σ covalent bonds. Graphite consists of hexagonal bonded sheets of carbon with three valence electrons occupying the planar sp2 hybrid orbital. This forms three very strong in-plane σ bonds with the remaining electron forming a weak out-of-plane π bond [20].

Figure 2.2 Various allotropes of carbon [20].
The third carbon allotrope, buckminsterfullerenes or fullerenes, was discovered in 1985 by Rick Smalley et al. [20]. Smalley discovered a spherical fullerene (C_{60} fullerene) consists of 60 carbon atoms bonded together in the shape of both hexagons and pentagons likened to a soccer ball. CNTs are elongated fullerenes forming extremely high aspect ratio tubes, capped at each end with the hemisphere of a fullerene. CNTs have similar sp2 bonding (with 2 σ and 2 π bonds) to graphite. The number and nature of the bonds determine the geometry and properties of the carbon allotropes [20].

CNT structures can be described and understood as rolled graphene sheets. The large aspect ratio makes the CNT a nearly ideal one-dimensional (1-D) object, and is expected to have unique properties. In particular, a CNT exhibits high electrical conductivity, thermal conductivity, and mechanical strength along its axis. CNTs can be separated into two categories, single walled CNTs and multi-walled CNTs, where single-walled carbon nanotubes (SWCNTs) consist of a single rolled graphene sheet and multi-walled carbon nanotubes (MWCNTs) have multiple SWCNTs nested inside of one another. Depending on the arrangement of the carbon atoms, SWCNTs can be metallic or semiconducting [21, 22]. Furthermore, the CNT has high mechanical stability and chemical inertness due to strong C-C bonds. The tensile strength of SWCNTs can be as high as 20 times that of steel; measurements of ~45 GPa have been reported [23, 24]. The tensile strength is ~150 GPa for defect free MWCNTs [25, 9].

Hamada proposed describing the helical arrangement, chirality, of the structure carbon pentagons within the CNTs by referencing corresponding lattice points of a graphene sheet [26]. The structure of single-walled CNT is specified by a chirality vector (C_h) connecting two points on the two-dimensional graphene sheet. SWCNTs can be described by a pair of integers (n, m) that define their chiral vector. Figure 2.3 illustrates the chirality vector for a graphene sheet [27].
Figure 2.3 The unrolled lattice of a CNT, likened to a single graphene sheet [27].

The chirality vector, $C_h$, is defined as

$$C_h = na_1 + ma_2$$

(1)

where $a_1$ and $a_2$ are the unit vectors of the hexagonal lattice. The unit vectors $a_1$ and $a_2$ are defined as

$$a_1 = \frac{\sqrt{3}a}{2} + \frac{a}{2}y$$

and

$$a_2 = \frac{\sqrt{3}a}{2}x - \frac{a}{2}y$$

(2)

where the C-C bond length or lattice constant, $a$, is assumed to be approximately 1.42 Å. The actual bond length is slightly different due to the curvature of the CNT [20]. This assumption takes the premise that the lattice constant of graphite (graphene) is 1.41 Å, while the lattice constant for a buckyball ($C_{60}$) is 1.44 Å. The chiral angle, $\theta$, can then be expressed as
\[
\cos \theta = \frac{2n+m}{2\sqrt{n^2+m^2+nm}}
\]  

(3)

There are countless ways in which one can figuratively ‘roll’ graphene into a SWCNTs. SWCNTs can be ‘zigzag’ if \( m=0 \), ‘armchair’ if \( n=m \), and ‘chiral’ if \( n \neq m \) and \( m \neq 0 \). The chiral angle for a zigzag tube and armchair tube are \( 0^\circ \) and \( 30^\circ \), respectively [27]. The types of chirality are illustrated in figure 2.4. The diameter of a SWCNT can be calculated from the integers \( n \) and \( m \) [28].

\[
D = \frac{|c_h|}{\pi} = \frac{a\sqrt{3(n^2+m^2+nm)}}{\pi}
\]  

(4)

Figure 2.4 Types of CNTs: (a) armchair, (b) zigzag, and (c) chiral [27].

The diameter of SWCNTs is limited by the energy required to maintain the tubular shape. The smallest possible CNTs are theoretically the \( (5, 0) \) zigzag CNT with a diameter of 0.39 nm, the \( (3, 3) \) armchair CNT with a diameter of 0.41 nm, and the \( (4, 2) \) chiral CNT with a diameter of
SWCNT diameters typically fall in range of 1 – 1.5 nm. MWCNTs can range in diameter from 1 nm to over a hundred nanometers. The distance between concentric nanotubes is directly related to the van der Waals bond or π bond that maintains the relatively weak bond between graphene sheets in graphite. Stressed by the curvature of CNTs, a separation distance of 0.34 nm is present between concentric nanotubes [30]. This π bond creates a distance of 0.335 nm between graphene layers [19]. Much like the layers of graphene within graphite, the nanotubes within MWCNTs are weakly bound to one another.

2.1.2 Electrical Properties of Carbon Nanotubes

The electric structure of a SWCNT can be predicted by the chiral vector (Ch). As the structure of SWCNTs are similar to sheets of graphene, the chiral vector can determine whether the SWCNT will be either metallic or semiconducting in nature. The SWCNT will be considered metallic if \( n = m \) (armchair) or if \( |n - m| = 3i \), where \( i \) is a nonzero integer. All other SWCNTs are considered to be semiconducting with an energy gap that is inversely proportional to the diameter of the CNT [31]. The energy gap can be approximated by the diameter, \( d \) of the SWCNT,

\[
E_g = \frac{\|t|a_{c-c}\}}{d}, \text{where } a_{c-c} = \frac{a}{\sqrt{3}}
\]  

where \( a_{c-c} \) is the distance between nearest carbon atoms within a graphene sheet and \( t \) is the nearest tight binding overlap energy; \( t \sim 3.13 \text{ eV} \) for graphite and \( \sim 2.5 \text{ eV} \) for graphene. The energy gap can range from 0 to 1 eV [27]. In MWCNTs, about one third of the nested tubes will be metallic which dominate the electrical properties of the entire tube. As such, most MWCNTs tend behave as metallic conductors. At low bias, most electric conduction occurs in the outermost tube of
MWCNTs with some interaction in the interior tubes; the properties of the outermost tube seem to dominate the electrical properties [32].

The one-dimensional structure of CNTs afford unique electron transport along the length of the tube (ballistic transport). On the macroscopic scale (1 micrometer or more), the conductivity is dependent on the material. Classical transport theory can be used to understand the electrical properties. CNTs are considered to fall within the mesoscopic scale (between 1 and 100 nanometers), and such quantum transport theory must be applied to understand electron transport [27]. There are three characteristic lengths which are employed under the quantum transport theory. The relationship between these three lengths determines the transport regime to which CNTs operate. The mean free path, $L_m$, is the average length that an electron travels before it is scattered. The Fermi wavelength, $\lambda_F$, is the de Broglie wavelength of an electron at the Fermi level. The phase-relaxation length, $L_\phi$, is the length over which an electron retains its coherence as a wave [27]. On the macroscopic scale, Ohm’s law can be used to calculate conductivity. When the length, $L$, of material is much greater than $L_\phi$, which is in turn much greater than $L_m$ (macroscopic scale), electrons behave classically (particle-like). During diffusive motion, elastic scattering occurs because the wave function is localized ($L_m \ll L_\phi \ll L$); resistance increases as $L$ becomes large, becoming an insulator. Ballistic transport occurs when an electron conducts with no phase or momentum relaxation ($L \ll L_m, L_\phi$) [27].

2.1.3 Synthesis of Carbon Nanotubes

Iijima discovered CNTs during the arc discharge synthesis of fullerenes. This discovery, coupled with a method of producing CNTs lead to the boom in CNT related research. Along with arc discharge, there are two other CNT fabrication methods: laser ablation synthesis and thermal synthesis. Chemical vapor deposition, a thermal synthesis method, will be discussed in further
A thermal CVD system, as shown in figure 2.5, consists of a furnace, feedstock gasses, and an exhaust output. Resistive heaters allow the furnace to operate at a temperature of roughly 780-820° C [33]. A substrate deposited with Fe, Ni, Co, or an alloy of the three transition metals (catalysts) on the surface is placed in the furnace. An annealing step is then performed in an inert atmosphere (i.e. argon) to form nanocatalyst islands from the deposited thin films of the above mentioned catalyst metals. A carbon precursor gas such as methane (CH₄), acetylene (C₂H₂), or ethylene (C₂H₄) is flowed across the catalyst coated substrate [34]. The gas reacts with the catalyst particles to produce CNTs.

Figure 2.5 Diagram of a water-vapor assisted CVD Furnace: consists of gas inlets, resistive heating elements, sample holder, and exhaust [35].
2.2 Fundamentals of Field Emission (FE)

Section 2.2.1 reviews the fundamentals of the FE process from a historical perspective, including a description of the widely used Fowler-Nordheim (FN) model. Section 2.2.2 describes some fundamental aspects of FE from CNT arrays.

2.2.1 Introduction

Four years after Iijima discovered CNTs, de Heer demonstrated FE from CNTs [36]. Heer fabricated a small electron gun from a MWCNT film that was capable of producing a current density of 100 μA/cm$^2$ at 200 V, increasing to more than 100 mA/cm$^2$ at 700 V. The FN model for the tunneling of electrons through a metal-vacuum potential barrier was used to validate the measured FE currents. The FN model describes the current due to electrons tunneling through a metal-vacuum potential barrier at 0 K [37]. In the absence of an externally applied bias, the metal-vacuum potential is depicted in figure 2.6.

![Figure 2.6 Potential barrier for a metal. The Fermi level, $\mu$, is the highest occupied electron level in the conduction band. The work function, $\varphi$, is the difference in energy between the Fermi level and a field-free vacuum near the surface [38].](image)

Figure 2.6 Potential barrier for a metal. The Fermi level, $\mu$, is the highest occupied electron level in the conduction band. The work function, $\varphi$, is the difference in energy between the Fermi level and a field-free vacuum near the surface [38].
There are three ways electrons can be emitted from a material; namely FE, thermionic emission, and photoemission. Both thermionic and photoemission require electrons to obtain sufficient energy to overcome the potential barrier. Thermionic emission occurs when the material is heated such that the electrons acquire enough kinetic energy, $E_T$, which is greater than the barrier ($E_T \geq \varphi + \mu$). Photoemission occurs when incident light (photons) has energies exceeding the work function, such that electrons in the conduction band may overcome the potential barrier ($E_p = h\nu \geq \varphi$) \[38\]. During FE, electrons are transmitted through the potential barrier. This is known as quantum tunneling, where electrons have a chance to tunnel across a potential barrier when an electric field is applied. A simplified potential barrier is presented in figure 2.7a, the barrier height becomes $\varphi + \mu - E_x$, where $E_x$ is the kinetic energy of the electrons. The applied electric field, $F$, reduces the barrier width to $(\varphi + \mu - E_x)/qFx$, where $q$ is the charge of an electron, ($e = 1.6 \times 10^{-19} C$).

**Figure 2.7** (a) Simplified potential barrier near the metal/vacuum interface after application of an external electric field [38], (b) potential barrier which includes Schottky lowering by the image force potential [39].
Realistically, there is an image force potential (for an electron outside of the metal) that lowers the potential barrier at \( x = 0 \). This is referred to as Schottky barrier lowering and is included in figure 2.7b as the term \( \frac{e^2}{4x} \). The potential barrier then becomes \( E_x = -\frac{e^2}{4x} - eFx \)

The current density due to FE is typically calculated using FN equation 6 [39] which is strictly valid at 0 K but is often employed to interpret FE data at room temperature. The FN result for the field emitted current density \( J \) is:

\[
J = \frac{aF^2}{t^2(y)\varphi} e^{-\frac{b\varphi^2}{F}v(y)}
\]

where \( J \) is in \( \text{A/cm}^2 \), \( a \) and \( b \) are constants equal to \( 1.54 \times 10^{-6} \text{ eV A/\sqrt{V}} \left( \frac{e^3}{8\pi e h} \right) \) and \( 6.83 \times 10^7 \text{ eV}^{-3/2} \text{V/cm} \left( \frac{8\pi\sqrt{2m}}{3eh} \right) \), respectively. The following functions \( t(y) \) and \( v(y) \) are dependent on the applied external electric field and work function of the emitting material \( y = \frac{\sqrt{eF\varphi}}{\varphi} \).

\[
t(y) = v(y) - \left( \frac{2y}{3} \right) dv/dy
\]

\[
v(y) = \sqrt{\frac{1+\sqrt{1-y^2}}{2}} \left( E(k^2) - \frac{y^2K(k^2)}{1+\sqrt{1-y^2}} \right)
\]

where

\[
E(k^2) = \int_0^{\pi/2} \sqrt{1-k^2\sin^2\alpha} \, d\alpha, \quad K(k^2) = \int_0^{\pi/2} \frac{d\alpha}{\sqrt{1-k^2\sin^2\alpha}}, \quad k^2 = \frac{2\sqrt{1-y^2}}{1+\sqrt{1-y^2}}
\]
F is the applied electric field (V/cm), and ϕ is the work function (eV). For typical material parameters and external electric field values, the function t(y) is close to and so often set equal to 1. The Nordheim function, ν(y), can vary significantly with y which varies with F [40].

The sharp tip of each CNT enhances the electric field locally as the electric field lines are concentrated at the CNT tip. A field enhancement scale factor, β, is used to account for this effect. The field enhancement factor leads to an increase of the local electric field at the CNT tip compared to the value V/d corresponding to the average electric field between an anode and cathode separated by a distance d with a potential difference V between them. As a result, the local electric at the CNT tip is found as follows:

\[ F = \frac{V}{d} \rightarrow F_{\text{local}} = \frac{\beta V}{d} \]  

(10)

Field enhancement factors for CNTs have been reported from ~1000 - 8000 to as high as 26,000 [41]. If FN FE is taking place, the emitted current should be well fitted by an expression of the form [42, 43]

\[ I (A) = A_{\text{eff}} \frac{1.54 \times 10^{-6}}{\phi} \beta^2 E_{\text{ext}}^2 e^{-\frac{6.83 \times 10^7 \phi^{3/2}}{\beta E_{\text{ext}}}} \]  

(11)

where \( A_{\text{eff}} \) is the effective area (in cm\(^2\)) of the emitting fiber, \( \phi \) is the work function (in eV) of the emitting surface, \( \beta \) is the field enhancement factor and \( E_{\text{ext}} \) is the externally applied electric field (in V/cm), i.e., \( E_{\text{ext}} = \frac{V}{d} \), where V is the applied bias (in Volts) between anode and cathode (assumed to be same as between tip of the fiber and the anode since the potential drop along the fiber is negligible) and d is the distance (in cm) between the anode and the base of the CNT fiber.
cathode. As a result, if FN FE prevails, equation (11) predicts that the FE data should obey the following relation [44]:

\[
\ln \left( \frac{I}{E_{ext}^2} \right) = \ln(a) - \frac{b}{E_{ext}}
\]  

(12)

where \( a \) and \( b \) are given by

\[
a = 1.54 \times 10^{-6} \frac{A_{eff} \beta^2}{\varphi},
\]  

(13)

and

\[
b = 6.83 \times 10^7 \left( \frac{\varphi^{3/2}}{\beta} \right).
\]  

(14)

FN field emission occurs when equation (12) is linear while \( \ln(I/E_{ext}^2) \) is plotted as a function of \( 1/E_{ext} \). This plot is referred to as a Fowler-Nordheim plot and is used to demonstrate field emission as opposed to thermionic emission. Once the work function of the CNT emitter is known, the field enhancement factor (\( \beta \)) can be calculated; bare CNTs are assumed to have a work function of 4.8 eV [45]. The slope of the FN plot (-b), given in equation (12), is used to determine \( \beta \). Knowing the electric field enhancement factor, the effective area participating in FE can then be calculated.

### 2.2.2 Field Emission from CNT arrays

Because of their relatively low work function and their high aspect ratio, CNTs are strong contenders as field emitters. The small diameter of the MWCNTs (10’s of nanometers) focus the
electric field at the tips of the CNTs is referred to as the electric field enhancement factor, mentioned in the previous section. Notably, the current density, total current, emission efficiency, and turn-on field are important metrics to determine the performance quality of a CNT cathode emitter.

**Figure 2.8** Reduced local electric field in a CNT array as neighboring CNT emitters are closer to one another [46].

Current density from individual CNTs can be as high as $10^7$ A/cm$^2$ [47], however CNT fibers have much lower current densities, due to screening effects [48]. As the CNTs are placed closer together the field enhancement factor is reduced because of a reduced field locally to the individual CNT. This screening effect was simulated by Nilsson and he found that screening effect can be minimized if the separation distance between CNTs is more than twice their height [46]. Figure 2.8 depicts the screening effect as three CNT emitters are positioned closer to each other. Smith found that an optimized FE occurs in a three-dimensional array when the tube separation is
three times the CNT height [49]. Heer estimated that only 0.1% of the total CNTs in an array are emitting, since only a fraction of the CNTs are sharp enough [36]. The traveling wave tubes described in the problem statement of this work require a 10 mA peak current prior to failure. In the following chapters, CNFs from Rice University and the University of Cambridge will be overviewed with regards to their relevance to the TWT specifications. Additionally, the design of UC based CNT cathodes will be performed, fabricated, and tested for comparison to the aforementioned CNFs.
Chapter 3: CNT Emitting Cathode Design and Fabrication

3.1 Proposed CNT Cathode Designs

Section 3.1.1 provides an overview of the CNT fiber cathode design process and proposed designs for several cathodes to be tested. Specifically, section 3.1.2 outlines the design and rational for a single CNT fiber emitter. Section 3.1.3 outlines the design and rational for a cathode array of three CNT fibers. Section 3.1.4 outlines the design and rational for an emitter, using a CNT nonwoven sheet fiber. Section 3.1.5 outlines the design and rational for an emitter, using an enhanced CNT nonwoven sheet fiber. Section 3.2 outlines the CNT cathode fabrication process. The CNT fibers used to fabricate the cathodes in this chapter were provided courteous by Dr. Shanov and Dr. Schulz (UC Nanoworld Laboratories).

3.1.1 Introduction

The CNT fiber cathodes will be prepared by hand. Design begins with sketching a template for cathode construction; AutoCAD was used in this work. Design considerations include mounting the CNF to a conductive base (to act as an electrical contact during field emission), controlling the length of the CNT fiber, controlling the alignment of the fiber, and controlling the tip morphology. These considerations are addressed by designing the template with two rectangular outlines in place of copper sheets. These rectangular footprints are separated by 2 mm, with a guide line for the CNT fiber that runs orthogonal to this 2 mm gap. Finally a line will be added to direct a laser, which will be used to cut the CNT fibers to length. This laser guideline will be placed bisectionally to the CNT fiber within the 2 mm gap, cutting the length of the CNT to 1 mm. This process will yield two cathodes with 1 mm long CNF emitters.
3.1.2 Single CNT Fiber Emitter

The cathode comprised of a single CNT fiber will establish a baseline comparison for field emission performance. Construction of the cathode will follow the template design presented in figure 3.1. The CNF will be placed along the blue line in contact with the two copper pads. A CO$_2$ laser will then be used to cut the CNF along the green line, forming two 1 mm long emitters. This cut will be performed orthogonally to the CNT fiber, allowing for a flat edge on the emitting surface. The FE properties of this emitter will be measured and compared to prominent CNT fibers.

![Figure 3.1 AutoCAD template for the single CNT fiber cathode.](image)

3.1.3 Array of Three CNT Fibers

The cathode comprised of a three CNT fiber array should increase the peak emission current prior to failure. It is expected that the screening effect will limit electron field emission, resulting in a peak current less than three times that of the single fiber. Construction of the cathode will follow the template design presented in figure 3.2. The CNT fibers will be placed along the blue lines in contact with the two copper pads. As Nilsson found, the optimized separation distance between CNTs is twice the height [46]. However, due to experimental constraints the CNFs are...
places 1 mm apart, a distance equal to the CNF height. The electron collecting anode was known to have a 3 mm diameter, too small to separate the CNFs by the optimized 2 mm distance. Therefore, a distance of 1 mm was chosen to allow testing with the array of 3 CNT fibers. A CO\textsubscript{2} laser will then be used to cut the CNFs along the green line, forming two 1 mm long (3 CNF) arrayed emitters. This cut will be performed orthogonally to the CNT fiber, allowing for a flat edge on the emitting surface. The FE properties of this emitter will be measured and compared to the single CNT fiber.

![Figure 3.2 AutoCAD template for the arrayed CNT fiber cathode.](image)

### 3.1.4 CNT Nonwoven Sheet Emitter

The emitter comprised of a single CNT nonwoven sheet was conceived to allow for high current capacity and thermal management when emitting. As there is more mass to this emitter, the resistance along the emitter will be reduced and more current will be able to conduct within the CNT sheet. The added mass will also allow for better heat management, reducing damage from high temperature and allowing for an emitter with a longer lifetime. As the CNT sheet is still very thin (~20 μm), the field enhancement factor is still expected to be very high, allowing for good
field emission performance. Construction of the cathode will follow the template design presented in figure 3.3. The 1mm wide CNT sheet will be placed within the blue lines in contact with the two copper pads. A CO\textsubscript{2} laser will then be used to cut the CNFs along the green line, forming two 1 mm long CNT sheet emitters. This cut will be performed orthogonally to the CNT fiber, allowing for a flat edge on the emitting surface. The FE properties of this emitter will be measured and compared to the single CNT fiber.

![Figure 3.3 AutoCAD template for the CNT nonwoven sheet cathode.](image)

### 3.1.5 Enhanced CNT Nonwoven Sheet Emitter

The emitter comprised of an enhanced single CNT nonwoven sheet; this design was conceived to allow for high current capacity and thermal management when emitting. The CNT sheet was ‘enhanced’ by cutting a triangular tip with the laser. This triangular tip should focus the electric field. As a result, the local field will increase and subsequently so will the field enhancement factor. Since the field enhancement factor is greater, so too will the peak emission current be greater. Again, there is more mass to this emitter. The resistance along the emitter length will be reduced and more current will be able to conduct within the CNT sheet. The added mass
will also allow for better heat management, reducing damage from high temperature and allowing for an emitter with a longer lifetime. Construction of the cathode will follow the template design presented in figure 3.4. The 1 mm wide CNT sheet will be placed within the blue lines in contact with the two copper pads. A CO₂ laser will then be used to cut the CNFs along the green line (at a 60° angle to the fiber), forming two 1 mm long CNT sheet emitters. This cut will be performed orthogonally to the CNT fiber, allowing for a flat edge on the emitting surface. The FE properties of this emitter will be measured and compared to the single CNT fiber.

![AutoCAD template for the ‘enhanced’ CNT nonwoven sheet cathode.](image)

**Figure 3.4** AutoCAD template for the ‘enhanced’ CNT nonwoven sheet cathode.

### 3.2 Fabrication of CNT Cathodes

The CNT fibers and bulk CNT powder were provided by the Nanoworld Laboratories at the University of Cincinnati. The CNT fiber was prepared by spinning vertically aligned carbon nanotubes (VACNTs) from a silicon substrate with a coating of Al₂O₃ (10 nm)/2 nm iron alloy (catalyst). CNT synthesis was conducted at 750 °C and was assisted by a water vapor feed. The water vapor was generated by passing argon gas through a bubbler containing water. The VACNTs were synthesized in a First Nano ET 3000 CVD reactor (figure 3.5).
The carbon nanotube fiber was spun directly from 4–6 mm long aligned carbon nanotube arrays (figure 3.6). The fibers were prepared using a semi-automated spinning machine (figure 3.7) [50]. The fibers were reported to have a diameter of roughly 20 – 40 um.

**Figure 3.5** First Nano ET 3000 CVD reactor, located at the UC Nanoworld Laboratory (courtesy of Dr. Shanov, University of Cincinnati).

**Figure 3.6** Formation of spun CNT fibers: (a) and (b) show the initial formation of the fiber, (c) SEM image of the CNT fiber, (d) microscopic image of the CNT fiber, (e) CNT fiber collection [50].
Figure 3.7 Semi-automated spinning machine, located at the Nanoworld Laboratory [50].

The CNT nonwoven sheet was prepared by vacuum filtration, based on Liang’s work at Florida State University [51]. The process includes preparation of a highly dispersed CNT solution and then filtration of the CNT dispersion onto a filter membrane. The CNT dispersion is prepared by mixing CNTs with DI water and a select surfactant. 1–2 mm long MWCNT powder was used in the prepared CNT sheets. The mixture of CNTs, DI water, and surfactant was dispersed to create a uniform suspension. A 10 gsm (g/m²) sheet was prepared with 40 mg of CNT powder, dispersed with 80 mL of DI water along with 50 μl of surfactant. Probe sonication (figure 3.8a) was then performed for 45 minutes. Sheet formation was completed onto a Teflon coated fiberglass filter membrane using a Millipore vacuum filtration system (figure 3.8b); the completed CNT sheet was 70 mm in diameter and roughly 20 μm thick (figure 3.8c).
The CNT emitting cathodes were fabricated by hand. The templates were first printed and cut out of paper, using the designs discussed in the previous sections. The templates were cut out and double sided tape was placed over the copper pad footprints. 0.5 mm thick cooper pads were cut to size (6 mm x 12 mm) with a shear cutter. The copper pads where then pressed upon the double sided tape, ensuring that the pads would remain straight within the template outlines. The CNT fiber(s) and CNT sheet(s) were cut to approximately 3/4 inch with scissors. Following the guidelines, the CNT fiber(s) or CNT sheet was placed upon the two copper pads and held into place on each end with the double sided tape. Next, silver paste (Ted Pella silver paint) was used to permanently attach the CNT fibers and nonwoven sheets to the copper substrate; the silver paste also promotes electrical conduction between the copper base and CNT emitter. Next, the CNT emitters were cut to size with an automated Universal Laser Systems VLS3.50 laser mill. The VLS3.50 is equipped with a CO₂ laser in the infrared spectrum (10.6 µm wavelength) with a maximum power rating of 50W. Following the aforementioned AutoCAD designed template, laser cutting was performed with an estimated 3 W of power and a cutting rate of 1 cm/s. All of the
samples were completed on one 100 mm diameter paper template (figure 3.9). The completed single CNT fiber cathode can be found in figure 3.10.

**Figure 3.9** Completed CNT emitting cathode samples, CNT emitters silver pasted to the copper base.

**Figure 3.10** 20um Carbon Nanotube thread silver pasted to 0.5mm thick copper strips (6mm wide).
The completed CNT cathodes were then optically measured, with a Keyence VHS-2000 digital microscope (figure 3.11), to determine relevant feature sizes. The single CNT fiber emitter is shown in figure 3.12, after laser cutting. It is clear in this 100x image that one half of the sample has been bent during handling. Zooming in to 300x, the length of the CNF emitter is measured to be 881.03 µm (figure 3.13). Figure 3.14 shows the average diameter of the single CNF emitter to be 31.83 µm. Finally, the emitting surface is presented in figure 3.15. The laser cutting did not provide a perfected flat emitting surface, but instead there are two ~10 µm bundles of CNT protruding from the surface. This will result in less uniform emission, with more electron emission at these ‘sharp’ tips.

Figure 3.11 Keyence VHS-2000 digital microscope, located at the University of Cincinnati.
Figure 3.12 Single CNT fiber emitter at 100x magnification.

Figure 3.13 Single CNT fiber emitter at 300x magnification, length = 881.03 µm.
Figure 3.14 Single CNT fiber emitter at 500x magnification, diameter = 31.83 µm.

Figure 3.15 Emitting surface for the single CNT fiber emitter at 500x magnification.
The array of three CNT fibers was then examined under the microscope. Figure 3.16 shows two of the three arrayed CNF emitters after being cut to size with the CO\textsubscript{2} laser. The emitting surface of the middle arrayed CNF is presented in figure 3.17. Although the surface morphology is more flat, it is clear that the cut was not performed perfectly perpendicular to the fiber length. There also appears to be some splaying of the emitting surface CNTs; this is likely due to the laser power being too high or perhaps just the result of the spun fibers coming unfurled. This will result in less uniform emission, with more emission occurring at the tip portion of the fiber.

Figure 3.16 Arrayed CNT fiber emitter at 100x magnification, showing 2 of 3 fibers in microscope window.
Likewise, the CNT nonwoven sheet emitter was then examined under the microscope. Figure 3.18 shows the CNT sheet emitter after being cut to size with the CO$_2$ laser. The square shaped emitter is presented in figure 3.19. The CO$_2$ laser cut straight edges into the emitter surface, although it appears that some edge damage occurred due to too much laser power. Using the image in figure 3.19, the length of the emitter was measured to be 1130 $\mu$m, the width was measured to be 894 $\mu$m, and the thickness of the CNT sheet is ~20 $\mu$m.
Figure 3.18 Completed CNT nonwoven sheet emitter at 100x magnification.

Figure 3.19 Completed CNT nonwoven sheet emitter at 200x magnification. L = 1130 μm, W = 894 μm.
Finally, the enhanced CNT nonwoven sheet emitter was examined under the microscope. Figure 3.20 shows the enhanced CNT sheet emitter after being cut to size with the CO$_2$ laser. The triangular tipped emitter is presented in figure 3.22. The CO$_2$ laser power was clearly too high during the cutting of the CNT sheet tip. The edges are damaged and too much material has been removed from the emitter surface which lead to a tip that was not perfectly sharpened. Additionally, there was too much silver paste used in the fabrication of this sample which bled into the CNT sheet emitter surface. Using the image in figure 3.21, the length of the emitter was measured to be 1083 μm, the width was measured to be 962 μm, and the thickness of the CNT sheet is ~20 μm. Even though the laser power setting was not ideal, the angle at the emission tip is close to the designed 120°, the measure angle at the tip was determined to be 119.91° (figure 3.22).

![Figure 3.20 Enhanced CNT nonwoven sheet emitter at 100x magnification.](image)
Figure 3.21 Enhanced CNT nonwoven sheet emitter at 200x magnification. L = 1083 μm, W = 962 μm.

Figure 3.22 Completed CNT nonwoven sheet emitter tip at 500x magnification. θ = 199.91°.
Chapter 4: Field Emission Performance of CNT Emitting Cathodes

4.1 Introduction

Section 4.2 provides an overview of the FE characterization procedure. Section 4.3 outlines the results of these FE trials, followed by FN modeling and analysis in section 4.4. Concluding, section 4.5 will overview the FE properties and performance of the four designed cathodes. The field emission testing was performed at the Material Directorate (AFRL) at Wright-Patterson Air Force Based in Dayton, Ohio. The experiments were carried out under supervision of Dr. Steven Fairchild, along with the assistance of Gregg Gruen and Tyson Back.

4.2 Field Emission Testing Chamber

FE testing of the CNT fibers were carried out in an ultrahigh vacuum chamber with a base pressure $\sim 10^{-7}$ Pa (figure 4.1). A copper anode probe tip (3 mm diameter, figure 4.2a) was aligned with the CNT fiber cathodes using two cameras incident to windows on the chamber (figure 4.2b). The CNT emitting cathodes were mounted to a stainless steel sample holder with silver paint. The first camera was used to accurately determine the anode-cathode gap distance, $d$. The gap was adjusted with integrated stepper motors capable of 2.5 $\mu$m per step. Once the gap distance was set, the voltage on the anode was increased at a rate of 1 V per 10 s to the maximum of 1000V (forward sweep). After holding the potential fixed at 1000V for 2 minutes, it was decreased to 300 V (reverse sweep) at the same rate as for the forward sweep. A Keithley 6517A source meter was used in these experiments. Data was recorded at each voltage setting with LabView control. Once a complete sweep (forward and reverse) was carried out, the gap distance $d$ was then reduced and the data acquisition process was repeated.
Figure 4.1 Ultrahigh vacuum chamber equipped for field emission data acquisition, picture courtesy of Gregg Gruen.

Figure 4.2 (a) Copper anode with example CNT emitter (courtesy of Steven Fairchild) and (b) chamber window of the FE chamber.
4.3 Results of Field Emission Characterization

The first sample tested was the single CNT fiber emitting cathode. Figure 4.3 plots the FE data of this single CNT fiber, for both forward and reverse sweeps at different values of the gap distance \( d \). At a gap distance of 2 mm, there is only a peak current of 0.0382 mA. The maximum emitted current increases to 0.402 mA with a gap distance of 1.5 mm and a drop to 0.378 mA at 1 mm. The size of the hysteresis loops in the FE data increases as the gap decreases; this is due to an increase in a change in the morphology of the fiber. Some of the sharper features (like the two surface protrusions mentioned in section 4.2) contributing to FE for the large gap distance were destroyed at the larger applied fields, leaving CNTs with lower field enhancement factor. Consequently, an increase in the threshold field will be observed for the remaining CNTs in subsequent sweeps. This destruction can be due to self-heating effects or intense ion back bombardment leading to shorter CNTs hence larger FE threshold. At a gap distance of 1 mm, there are two sudden drop in the emission current around \( E_{ext} = 0.8 \, \text{V/µm} \) and \( E_{ext} = 0.9 \, \text{V/µm} \). Again, this is attributed to self-heating effects leading to a sudden failure to emit for some of the CNTs forming the fiber. Figure 4.4 shows the tip of the CNT fiber after failure; CNTs at the tip becomes spread out due to due to Coulomb charge repulsion forces during electron emission.
Figure 4.3 Field emission data for the single CNT emitting cathode at gap distances of 2 mm, 1.5 mm, and 1 mm.

Figure 4.4 Failed CNT fiber tip after field emission testing.
The array of three CNT fibers was then tested. Figure 4.5 plots the FE data of the arrayed CNT fiber emitting cathode, for both forward and reverse sweeps at different values of the gap distance \(d\). At a gap distance of 2 mm, there is an improved peak current of 0.76 mA. Max current increases to 1.05 mA with a gap distance of 1.5 mm and to a very respectable 2.11 mA at 1 mm. Again, the size of the hysteresis loops in the FE data increases as the gap decreases; this is due to an increase in a change in the morphology of the fiber. It is apparent that even at a gap distance of 2 mm, the current is large enough to cause self-heating effects and thus partial destruction of CNTs forming the fiber. At a gap distance of 1.5 mm: while the emission current follows well the 2 mm curve, emission is worse above \(E_{\text{ext}} = 0.45 \text{ V/}\mu\text{m}\). At a gap distance of 1.5 mm, there is a sudden drop in the emission current around \(E_{\text{ext}} = 0.56 \text{ V/}\mu\text{m}\). Then at \(d = 1 \text{ mm}\), there is a drop at \(E_{\text{ext}} = 0.93 \text{ V/}\mu\text{m}\). Again, this is attributed to self-heating effects leading to a sudden failure to emit for some of the CNTs forming the fiber. Although the 1:1 ratio of the emitter height to separation distance is not optimal, it was sufficient for creating a large enough of a field enhancement factor to improve upon the FE performance of the single CNT fiber.

The arrayed cathode yielded a peak current greater than five times that of the single CNT fiber. This was unexpected, as the screening effect should have limited the peak current to less than 3x improvement over the single CNT fiber. As previously tested single fibers have produced peak currents of \(~1\text{mA}\) prior to failure, it is likely that this single CNT fiber failed prematurely. A larger data set is required to provide more indicative individual fiber performance. One theory is that the CO\(_2\) laser leaves behind amorphous carbon on the emitting surface; when the amorphous layer is blown off, catastrophic failure occurs.
Figure 4.5 Field emission data for the arrayed CNT emitting cathode at gap distances of 2 mm, 1.5 mm, and 1 mm.

The CNT nonwoven sheet emitting cathode was then tested. Figure 4.6 plots the FE data of the nonwoven emitter, for both forward and reverse sweeps at different values of the gap distance $d$. At a gap distance of 1 mm, there was only 0.005 mA peak emission current. The maximum emitted current increases to 0.077 mA with a gap distance of 0.75 mm and 0.249 mA at 0.5 mm. The hysteresis loops in the FE is much smaller compared to that of the spun CNT fiber, indicating little damage to the CNTs within the nonwoven emitter. There is, however, still a change in morphology of the CNT emitter as the FE curve (at a gap distance of 0.5mm) does not follow the 0.75 mm gap distance curve. It is possible that stray CNTs at the emitting surface become damaged during emission, where CNTs with lower field enhancements factors now contribute to field emission (of lower peak current). As the CNTs are randomly oriented with the CNT
nonwoven sheet the overall field enhancement factor of the emitter is reduced to that of the spun CNT fibers. Additionally, the flat emission surface results in a lower local electric field incident upon the emitter. These physical characteristics of the CNT nonwoven emitter result in a much lower emission efficiency and peak current; however, the CNT nonwoven does appear to be more robust with no signs of failure at 1000V.

![Graph showing field emission data for the CNT nonwoven sheet emitting cathode at gap distances of 1 mm, 0.75 mm, and 0.5 mm.](image)

**Figure 4.6** Field emission data for the CNT nonwoven sheet emitting cathode at gap distances of 1 mm, 0.75 mm, and 0.5 mm.

Finally, the ‘enhanced’ CNT nonwoven sheet emitting cathode was tested. Figure 4.7 plots the FE data of the enhanced nonwoven emitter, for both forward and reverse sweeps at different values of the gap distance $d$. At a gap distance of 1 mm, there was a 0.665 mA peak emission
current. The maximum emitted current increases to 1.228 mA at a gap distance of 0.75 mm. Once again self-heating produced damage is evident; hysteresis increases with smaller gap distances and there is a sudden drop in the emission current around \( E_{\text{ext}} = 1.25 \, \text{V/µm} \). Compared to the flat cut CNT nonwoven sheet, the enhanced CNT nonwoven provided an increase in peak current by nearly fivefold. Since the enhanced CNT nonwoven had a triangular tip, localized heating at the tip caused failure due to self-heating damages. Conversely, the enhanced CNT nonwoven sheet (0.665 mA at 1 V/µm) performed similarly to the single CNT fiber (0.337 mA at 1 V/µm). Further investigation is required to determine which CNT material is more resistant to self-heating damages.

![Field Emission: Enhanced CNT Nonwoven Sheet](image)

**Figure 4.7** Field emission data for the enhanced CNT nonwoven sheet emitting cathode at gap distances of 1 mm and 0.75 mm.
4.4 Fowler-Nordheim Modeling and Analysis

Referencing equation 11, the FE data of the CNT fiber (when plotted as $\ln(I/E_{ext}^2)$ vs $I/E_{ext}$) should fall on the same straight line if FN emission prevails. Figure 4.8 shows the $\ln(I/E_{ext}^2)$ vs $1/E_{ext}$ FN plot for the single CNT fiber at a gap distance of 1 mm. In this plot, the forward and backward sweeps do not overlap as only the linear regime of emission was considered (failure within the fiber is not reported within the FN plot). The effective area (emission area) $A_{eff}$ and field enhancement $\beta$ can be extracted from the FN plot using equations 13 and 14. For the forward sweep of the single CNT fiber emitting cathode, $\beta$ was calculated to be 6,152 and $A_{eff}$ was found to be $1.295 \times 10^{-6}$ cm$^2$. For the backward sweep of the single CNT fiber emitting cathode, $\beta$ was calculated to be 7,448 and $A_{eff}$ was found to be $1.185 \times 10^{-7}$ cm$^2$.

![FN Plot: Single CNT Fiber, 1 mm gap](image)

**Figure 4.8** Fowler-Nordheim plot for the single CNT fiber emitting cathode, separation distance = 1 mm.
It is difficult to draw meaningful conclusions from this trial as the fiber failed several times throughout the experiment. It was expected that the field enhancement factor would decrease during the backward sweep due to self-heating damages, but $\beta$ was calculated to be $\sim$17% greater than in the forward sweep. The effective area is reduced, as expected, in the backward sweep. High electric field incident upon the fiber caused irreversible damage; the damaged fiber therefore has fewer emission sites and a $\sim$10x reduction in emission area ($A_{eff}$).

Next, the array of three CNT fibers was analyzed to determine $\beta$ and $A_{eff}$. Figure 4.9 shows the $\ln(I/E_{ext}^2)$ vs $1/E_{ext}$ FN plot for the arrayed CNFs at a gap distance of 1 mm. It is apparent that there are different linear regimes in both the forward and backward sweep. These linear regimes indicate that field emission is occurring due to the influence of an applied electric field. The transition(s) in slope observed in this plot can be attributed to a change in emission area [15], a change in work function [52], and/or current saturation caused by thermal effects [53]. The effective area (emission area) $A_{eff}$ and field enhancement $\beta$ for each of the slopes can be extracted from the FN plot using equations 13 and 14. For the forward sweep of the arrayed CNT fiber emitting cathode, $\beta_1$ was calculated to be 17,182 and $A_{eff1}$ was found to be $2.159 \times 10^{-11}$ cm$^2$; $\beta_2$ was calculated to be 10,616 and $A_{eff2}$ was found to be $4.519 \times 10^{-9}$ cm$^2$. For the backward sweep of the single CNT fiber emitting cathode, $\beta_1$ was calculated to be 12,700 and $A_{eff1}$ was found to be $1.589 \times 10^{-11}$ cm$^2$; $\beta_2$ was calculated to be 8,224 and $A_{eff2}$ was found to be $3.557 \times 10^{-9}$ cm$^2$. 
Figure 4.9 Fowler-Nordheim plot for the arrayed CNT fiber emitting cathode, separation distance = 1 mm. There are two regions, noted as ‘1’ and ‘2’, which indicate the slope variations within the FN plot.

In both the forward and backward sweep, there is a transition in the slope of the FN plot. A transition occurs at ~0.000167 cm/V for the forward sweep and at ~0.000142 cm/V for the backward sweep. As expected the field enhancement factor decreases during the backward sweep due to self-heating damages, $\beta_1$ was calculated to be ~26% smaller than in the forward sweep; $\beta_2$ was calculated to be ~23% smaller than in the forward sweep. The effective area increases at the transition from region 1 to region 2. The increased electric field promotes more emission sites and consequently the effective area. In the backward sweep, the effective area decreases due to fiber damages from self-heating.

The CNT nonwoven sheet was then analyzed to determine $\beta$ and $A_{eff}$. Figure 4.10 shows the $\ln(I/E_{ext}^2)$ vs $1/E_{ext}$ FN plot for the CNT sheet emitter at a gap distance of 0.5 mm. The
effective area (emission area) $A_{eff}$ and field enhancement $\beta$ for each of the slopes can be extracted from the FN plot using equations 13 and 14. For the forward sweep of the CNT nonwoven sheet emitting cathode, $\beta$ was calculated to be 9,107 and $A_{eff}$ was found to be $1.068 \times 10^{-12}$ cm$^2$. For the backward sweep of the single CNT nonwoven sheet emitting cathode, $\beta$ was calculated to be 10,226 and $A_{eff}$ was found to be $2.579 \times 10^{-13}$ cm$^2$.

![FN Plot: CNT Nonwoven Sheet, 0.5 mm gap](image)

**Figure 4.10** Fowler-Nordheim plot for the CNT nonwoven sheet emitting cathode, separation distance $= 0.5$ mm.

The field enhancement factor seems to increase during the backward sweep in comparison to the forward sweep; $\beta$ increased by $\sim 11\%$ over that in the forward sweep. This increase is likely due to desorption of amorphous carbon at the emission sites, which builds up during the laser milling process. The effective area decreases by roughly fourfold during the backward sweep. This
can be attributed to some CNT fiber damages from self-heating, but likely the cause is simply that a fewer portion of high $\beta$ CNTs are emitting in the backward sweep opposed to many low $\beta$ CNTs emitting in the forward sweep.

Finally, the enhanced CNT nonwoven sheet was analyzed to determine $\beta$ and $A_{eff}$. Figure 4.11 shows the $\ln(I/E_{ext}^2)$ vs $1/E_{ext}$ FN plot for the CNT sheet emitter at a gap distance of 0.75 mm. It is apparent that there are different linear regimes in both the forward and backward sweep. The effective area (emission area) $A_{eff}$ and field enhancement $\beta$ for each of the slopes can be extracted from the FN plot using equations 13 and 14. For the forward sweep of the arrayed CNT fiber emitting cathode, $\beta_1$ was calculated to be 16,265 and $A_{eff1}$ was found to be $3.076 \times 10^{-12}$ cm$^2$; $\beta_2$ was calculated to be 12,432 and $A_{eff2}$ was found to be $2.478 \times 10^{-11}$ cm$^2$. For the backward sweep of the single CNT fiber emitting cathode, $\beta_1$ was calculated to be 19,993 and $A_{eff1}$ was found to be $1.529 \times 10^{-13}$ cm$^2$; $\beta_2$ was calculated to be 10,969 and $A_{eff2}$ was found to be $1.128 \times 10^{-11}$ cm$^2$.

In both the forward and backward sweep, there is a transition in the slope of the FN plot; occurring at ~0.00012 cm/V for the forward sweep and at ~0.000114 cm/V for the backward sweep. The field enhancement factor increases during the backward sweep in region 1. This increase is likely due to desorption of amorphous carbon at the emission sites, which builds up during the laser milling process. $\beta_1$ was calculated to be ~19% greater in the backward sweep than in the forward sweep. However, $\beta_2$ is reduced by ~12% in the backward sweep. The effective area increases at the transition from region 1 to region 2. As the field enhancement factor is reduced from region 1 to region 2, there is a higher portion of CNTs, with low $\beta$, emitting and thus an increase in the number of emission sites. $A_{eff}$ is reduced by roughly half in the backward sweep;
this is caused by the self-heating damages to the CNT sheet which ultimately causes the emitter to fail. This can be observed in the failure of the CNT sheet emitter in figure 4.7.

![FN Plot: Enhanced CNT Nonwoven Sheet, 0.75 mm gap](image)

**Figure 4.11** Fowler-Nordheim plot for the enhanced CNT nonwoven sheet emitting cathode, separation distance = 0.75 mm.

### 4.5 Conclusions

In this chapter the fabricated CNT emitting cathodes were characterized and analyzes for field emission properties. As the cathode-anode gap is decreased there is an increased hysteresis in the FE data. This is indicative of a change in the morphology of the fiber due to a progressive destruction of the emitting CNTs on account of self-heating effects. The field emission data shows that the CNT cathodes emit in agreement with FN emission, as the emission data is linear within the FN plot. Analysis of the CNT emitting cathodes was performed, finding that the cathodes have
high field enhancement factors (~6,000 for the single CNT fiber to ~20,000 for the enhanced CNT sheet) and respectable peak current prior to failure (~2 mA for the array of 3 CNT fibers). A summary table with all measured and calculated field emission properties is presented in section 6.1.

The most promising cathodes were the arrayed CNT fiber emitting cathode with 2.11 mA peak current and the enhanced CNT nonwoven sheet emitting cathode with 1.23 mA peak current. Although the goal of 10 mA emission prior to failure was not achieved, these two cathodes performed very respectably. Section 6.2, overviews future work that will expand upon these cathode designs and improve upon them to achieve the 10 mA peak current goal. Achieving higher maximum emitted current should be attainable by reducing the electrical resistivity and increasing the thermal conductivity of the fibers. FE occurs mostly from the tip of the fiber where the density of electric field lines is the largest and the local electric field at the end of the CNTs on the fiber tip is larger than the applied electric field due to the enhancement factor, leading to emission from the tip. As the current through the fiber increases, the emission current eventually saturates (due the limited electric conductivity). This reduction is due the progressive shielding of the applied external field with the onset of space-charge effects on the tip of the fiber.
Chapter 5: Field Emission Properties of Notable CNT Fibers

5.1 Introduction

Section 5.2 provides an overview of the FE properties from Cambridge carbon nanotube fibers. The section is adapted from the work of Dr. Marc Cahay, unpublished. Section 5.3 outlines the field emission properties of Rice carbon nanotube fibers. The section is adapted from the work of Dr. Steven Fairchild. Finally, section 5.4 provides a summary of several CNT field emitters reported in the literature.

5.2 Field Emission Performance of University of Cambridge CNFs

At the University of Cambridge carbon nanotube fibers were spun directly from the CVD synthesis zone of a furnace using a liquid source of carbon and iron nanocatalyst [54, 9]. The CNTs are mechanically drawn directly from the gaseous reaction zone, making it was possible to wind up continuous fibers without a limit to the fiber length. The key requirements for continuous spinning are the rapid production of high-purity CNTs to form an aerogel in the furnace hot zone and the forcible removal of the reaction product by continuous wind-up [55]. The CNT fibers were then exposed to a continuous spray of acetone as they were drawn out of the furnace, resulting in immediate condensation into a fiber tens of micrometers in diameter. The diameter of the CNT field emitter as well as the internal CNT alignment were controlled by the rate at which the fiber was extracted from the CVD reactor. The CNTs were single walled with only a few chiralities present, as well as a high degree of graphitic crystallinity (Raman G:D ratio of approximately 15). The CNT fibers were cut with the use of a fiber laser (SPI Lasers, Model G3) operating at 1064 nm with a maximum pulse energy of 1.5 mJ, repetition frequency of 20-500 kHz, pulse duration of 10 ns, and average power of 25 W.
FE characterization from a laser cut CNT fiber 30 µm in diameter was carried out in the same ultrahigh vacuum chamber which will be used to characterize the UC CNFs in this research. A fiber cathode was created by mounting a 5 mm long section of the fiber to a stainless steel sample holder with silver paint. A stainless steel anode probe tip (7 mm diameter) was aligned with the CNT fiber. For d = 1.75 mm at a maximum voltage of 1000 V, the temperature at the tip of the fiber was found to be less than 500°C, indicating that self-heating effects were minimal for that distance d setting.

Figure 5.1a is a plot of the FE data for both forward and reverse sweeps for different values of the gap distance d. The size of the hysteresis loops in the FE data increases as the gap decreases; this is due to an increase in a change in the morphology of the fiber, affecting the FE properties of the emitting CNTs. There is a peak current of ~2.2 mA prior to failure at $E_{\text{ext}} = 0.78$ V/µm for d = 1.25 mm.

Figure 5.1: (a) The increase in the hysteresis in FE data for decreasing value of the fiber tip to anode distance d. For each d value, the top and bottom curves correspond to the forward sweep and reverse sweep
of the cathode to anode applied bias, respectively. (b) FN plot (\( \ln(I/E_{ext}^2) \) versus \( 1/E_{ext} \)) for a 5 mm long and 30 \( \mu \)m diameter laser cut CNT fiber for the forward sweep of the applied bias (courtesy of M. Cahay, unpublished).

Figure 5.1b shows the FN plots corresponding to the samples indicated in figure 5.1a. Specifically, the FN plot for the sample measured at a gap distance of 1.75 mm is shown in figure 5.2 with \( \beta \) in the forward sweep of 12,800 and 13,460 in the backward sweep. It is apparent the current saturation occurs as the applied electric field increases. As the current through the fiber increases, the emission current saturates (due the limited electric conductivity of the fiber, 8600 S/m), and a space-charge limited emission from the tip prevails.

![Figure 5.2](image_url) **Figure 5.2** (a) FN plot of FE data of a CNT fiber for a fiber tip to anode spacing of 1.75mm, showing the forward sweep and (b) reverse sweep of the cathode to anode applied bias. In the linear regime the field enhancement factor (\( \beta \)) in the forward sweep was determined to be 12,800 and in the backward sweep \( \beta \) was determined to be 13,460.
5.3 Field Emission Performance of Rice University CNFs

Although CNT yarns show considerable promise for use as cold cathodes, they suffer from low packing density due to clustering of the CNTs [56] resulting in large spaces between the strands of CNTs comprising the fiber. The densities for these CNT yarns are in the range of 0.2 to 0.8 g/cm$^3$ [56]. The Rice University carbon nanotube fibers are manufactured by a conventional wet spinning technique from bulk-grown single walled nanotubes (SWNTs) dispersed in super acids [16]. The SWNT dispersion is extruded through a small capillary tube resulting in fibers with a density of 1.1 gm/cm$^3$ which is 77% of the theoretical close packing density for 1 nm diameter SWNTs [56]. Sample D, the MWCNT fiber was made with MWNTs (predominantly 1 to 3 walls, length ~5 μm, diameter ~3 nm). The MWNTs were dissolved at 3 wt% in chlorosulfonic acid, spun from a 65 μm spinneret, and coagulated into acetone. The fibers were washed with water (~2 hours) and dried in an oven overnight at 150° C [11]. These fibers were ~90% dense with 10 times the electrical conductivity and 20 times the thermal conductivity of the previous generation wet-spun fibers and their field emission properties were dramatically improved due to their superior morphology [11].

<table>
<thead>
<tr>
<th>Diam. [μm]</th>
<th>Packing Fraction</th>
<th>$S_d$</th>
<th>$\sigma$ [kS m$^{-1}$]</th>
<th>$\kappa$ [W m K$^{-1}$]</th>
<th>$F_{TH}$ [V μm$^{-1}$]</th>
<th>$\beta$</th>
<th>$F_{eff}$ [V μm$^{-1}$]</th>
<th>$I_{max}$ [μA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>90</td>
<td>0.70</td>
<td>0.34</td>
<td>8.3</td>
<td>1.42</td>
<td>4x10$^3$</td>
<td>8x10$^3$</td>
<td>99</td>
</tr>
<tr>
<td>B</td>
<td>70</td>
<td>0.77</td>
<td>0.43</td>
<td>25</td>
<td>9</td>
<td>6x10$^3$</td>
<td>12x10$^3$</td>
<td>194</td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>0.77</td>
<td>0.64</td>
<td>30</td>
<td>23</td>
<td>10x10$^3$</td>
<td>10x10$^3$</td>
<td>259</td>
</tr>
<tr>
<td>D</td>
<td>9</td>
<td>0.90</td>
<td>0.80</td>
<td>570</td>
<td>100</td>
<td>16x10$^3$</td>
<td>8x10$^3$</td>
<td>306</td>
</tr>
</tbody>
</table>

Table 5.1 Properties of CNT fiber samples A- D. Diameter, packing fraction, electrical ($\sigma$) and thermal ($\kappa$) conductivities at 600K, Hermans orientation parameter ($S_d$) as determined by wide angle x-ray diffraction (WAXD), threshold field strength ($F_{TH}$), field enhancement factor ($\beta$), effective field strength ($F_{eff} = \beta F_{max}$) at the fiber tip at 1000 V, and maximum emitted ($I_{max}$) at 1000 V.
Table 5.1 outlines a summary for the Rice fibers tested in the referenced work (based on Steven Fairchild’s work). Figure 5.3 shows the FE data for the samples A-D, followed by the respective FN plots in figure 5.4. The 50 μm diameter SWCNT (C) fiber achieved a max current of 0.259 mA with a field enhancement factor of ~10,000 (1 mm gap distance), while the 9 μm diameter MWCNT fiber achieved a max current of 0.306 mA with a field enhancement factor of ~16,000 (2 mm gap distance). At a gap distance of 1 mm, the MWCNT fiber (D) achieved a max current of 3.7 mA prior to failure with an applied electric field of 0.836 V/μm.

![Graph showing I-V curves for samples A-D. The turn-on voltage is lowest and the emitted current is highest for Sample D.](image)

**Figure 5.3.** I-V curves for samples A- D. The turn-on voltage is lowest and the emitted current is highest for Sample D.
Figure 5.4 Fowler-Nordheim curves and $R^2$ fit values for the I-V curves for samples A, B, C, and D. The voltage range for each curve is from 500-1000 V.

The FE performance is dependent upon the fiber morphology. Increased alignment of the CNTs along the axial length of the fiber results in increased density and therefore increased thermal and electrical conductivity. The Conductivity of sample D was increased by using longer length MWCNTs; this increase is due to more CNT overlap and decreased spacing, which facilitates inter-CNT transport. The fibers with superior morphology were able to withstand current of 3.7 mA before failure, which is the highest value reported for a fiber with a mechanically cut blunt tip. The SWCNT fibers tested with inferior morphology and lower thermal conductivity failed at current levels between 0.5 and 2.5 mA. The Higher thermal conductivity allowed the fiber to sustain higher current levels before experiencing structural damage caused by Joule heating.
5.4 Conclusions

In addition to the Rice and Cambridge CNFs, which have been tested within the same FE chamber at WPAFB, table 5.2 shows the peak current for various CNT fibers reported in the literature [57]. The peak current for the Cambridge CNT fiber was reported to be \( \sim 2.2 \, \text{mA} \) at \( E_{\text{ext}} = 0.78 \, \text{V/µm} \) with a field enhancement factor of 12,800 in the forward sweep and 13,460 in the backward sweep. The peak current for the MWCNT Rice CNT fiber was reported to be \( \sim 3.7 \, \text{mA} \) at \( E_{\text{ext}} = 0.836 \, \text{V/µm} \) with a field enhancement factor of \( \sim 16,000 \). The Cambridge fiber is roughly equivalent to the arrayed CNT fiber cathode (\( \sim 2.11 \, \text{mA} \)), while the enhanced CNT sheet cathode achieves 1.25 mA prior to failure. While all of these emitters achieve 1 mA or more, none of the emitters fulfill the 10 mA peak current objective. The research in this thesis provides a path forward to achieve this goal; chapter 6 outlines several approaches to increase the peak current prior to failure for a CNT based cathode.

<table>
<thead>
<tr>
<th>Field emitter</th>
<th>( I_{\text{max}} ) (mA)</th>
<th>( J_{\text{max}} ) (mA/cm²)</th>
<th>( E_{\text{applied}} ) (V/µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT fibers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chen et al.²⁹</td>
<td>3.01</td>
<td>( 1.1 \times 10^{11} )</td>
<td>0.72</td>
</tr>
<tr>
<td>Kim et al. (Ref. 24)⁸</td>
<td>10.0</td>
<td>3180</td>
<td>…</td>
</tr>
<tr>
<td>Current work</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>Single fiber</td>
<td>1.40</td>
<td>( 1.98 \times 10^{6} )</td>
<td>1.0</td>
</tr>
<tr>
<td>CNT array</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li et al.²⁰⁵</td>
<td>10</td>
<td>( 1.0 \times 10^{9} )</td>
<td>14</td>
</tr>
<tr>
<td>Ryu et al.²⁵</td>
<td>0.7</td>
<td>10</td>
<td>3.3</td>
</tr>
<tr>
<td>CNT films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li et al.²⁰⁶</td>
<td>…</td>
<td>1500</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Calderón-Colón et al. (Ref. 11)⁴</td>
<td>6.5</td>
<td>700</td>
<td>9</td>
</tr>
<tr>
<td>Current work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single-layer triangle</td>
<td>2.10</td>
<td>…</td>
<td>0.66</td>
</tr>
<tr>
<td>2-Layer triangle</td>
<td>3.06</td>
<td>…</td>
<td>0.86</td>
</tr>
<tr>
<td>4-Layer triangle</td>
<td>7.65</td>
<td>…</td>
<td>1.30</td>
</tr>
<tr>
<td>Single-layer straight</td>
<td>0.9</td>
<td>…</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 5.2 Table includes maximum observed current, current density, and applied voltage from the literature as well as results reported here. All experiments were run in dc mode and represent conditions for maximum observable current [57].
Chapter 6: Summary and Future Work

6.1 Summary of Work

The research presented here has provided the groundwork for basics of FE from CNT fibers and to which future CNT emitters can be compared and built upon. This thesis has explored the fundamentals of field emissions and how innovative materials, like CNTs, can be exploited for their unique properties to fulfill the needs of novel applications. The application of focus in this work was a CNT fiber based cathode operated in DC mode for a traveling wave tube (TWT). Specifically, a TWT capable of 10 mA peak current prior to failure for inclusion in a directed energy weapon. Four proposed cathodes were designed, fabricated, and characterized in pursuit to fulfill the needs of this application. The following table (table 6.1) outlines the measured and calculated properties of the four cathodes included in this research. The future of this research will build upon the successes of this research along with improved cathode design, material, and modeling.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Area [cm²]</th>
<th>A_{eff} (F) [cm²]</th>
<th>A_{eff} (B) [cm²]</th>
<th>β (F)</th>
<th>β (B)</th>
<th>I_{max} [mA]</th>
<th>E_{applied} [V/μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single CNF</td>
<td>7.95x10^{-6}</td>
<td>1.30x10^{-6}</td>
<td>1.19x10^{-7}</td>
<td>6152</td>
<td>7449</td>
<td>0.4</td>
<td>0.66</td>
</tr>
<tr>
<td>Arrayed CNFs</td>
<td>2.39x10^{-5}</td>
<td>2.16x10^{-11}, 4.52x10^{-9}</td>
<td>1.59x10^{-11}, 3.56x10^{-9}</td>
<td>17181, 10616</td>
<td>12700, 8224</td>
<td>2.11</td>
<td>0.92</td>
</tr>
<tr>
<td>CNT Sheet</td>
<td>2.26x10^{-4}</td>
<td>1.07x10^{-12}</td>
<td>2.58x10^{-13}</td>
<td>9107</td>
<td>10226</td>
<td>0.25</td>
<td>2</td>
</tr>
<tr>
<td>Enhanced CNT Sheet</td>
<td>7.50x10^{-6}</td>
<td>3.08x10^{-12}, 2.48x10^{-11}</td>
<td>1.53x10^{-13}, 1.13x10^{-11}</td>
<td>16266, 12433</td>
<td>19993, 10969</td>
<td>1.25</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Table 6.1 Summary of measured and calculated properties of the four designed CNT emitting cathodes.

Area = actual measure emission area, F = forward sweep, B = backward sweep.
6.2 Future Work: Improvements to Cathode Design

Both the arrayed CNT fiber cathode and enhanced CNT nonwoven sheet cathode yielded 1 mA or more peak emission current prior to failure. This is within an order of magnitude of the 10 mA peak current objective. Future work would focus on larger arrays of CNT fibers and/or arrays of triangular tipped CNT sheets. The CNT fiber material is fairly aligned and is made from 1-2 mm long CNTs which give it the advantage of high conductivity compared to other dry spun CNT fibers. The conductivity of the CNT fiber material was determined to be ~20,000 S/m, measured by a four-probe, compared to ~8,600 S/m for the Cambridge CNF. Rice fibers are wet spun and values of ~570,000 S/m have been reported [57]. However, the dry spun CNT fibers can be improved by removing the dead space within the fiber by densification. CNT fiber densification can be performed by dipping the CNTs in acetone and will result in a smaller fiber with higher conductivity; in effect the field enhancement will be increased along with electrical and thermal conductivity. By creating a two-dimension array from densified CNT fibers, the peak current should drastically increase. Such arrays would require extremely accurate manufacturing methods to ensure that the CNT fibers have the same diameter and length to ensure repeatability.

Alternatively, the CNT sheet material would allow for a very repeatable cathode. This material is simple to make and can be laser milled to any desired shape and dimension. An array of triangular tipped CNT sheet emitters can be quickly produced and even stacked upon one another to create a two-dimensional array. An improved design would include utilization of a ultra-fast laser (ns or fs) to cut the CNT sheet tip more accurately (sharper), while minimizing buildup of amorphous carbon at the emitting surface of the CNTs. Apart from using a better suited laser mill, material improvement would focus on creating an aligned CNT sheet material to increase the field enhancement factor of the cathode. An aligned CNT sheet material would have higher
electrical conductivity in the direction of field emission current and an inherently higher field enhancement factor over a randomly oriented CNT nonwoven sheet. One such aligned CNT sheet material has been developed at the University of Cincinnati. Like the dry-spun CNT fiber, individual CNTs are pulled from a substrate to form a ribbon/sheet of CNTs. This process can be repeated in layers to form an aligned CNT sheet material of the desired thickness. Figure 6.1 illustrates the aligned CNT sheet manufacturing process [58]. This material can then be densified in a similar manner to the dry spun CNT fibers, with the aim of further improving electrical, thermal, and field emission properties. Again, this material could then be stacked or arranged into an array to increase peak current.

![Figure 6.1 Schematic illustration of the setup (a), CNT sheet preparation from vertically aligned CNT array [58].](image)

A final proposed design improvement is to use a stacking CNT sheet configuration with a thin conductive layer sandwiched between each CNT sheet. The stacking configuration would consist of a dielectric layer stacked upon a metallic layer, stacked upon a dielectric layer, and finally stacked upon the CNT sheet material. This stacking sequence would be repeated until the
desired number of CNT sheets is formed. The principle behind this design is that the conductive metal layers would be coupled to the anode, such that the CNT sheets (connected to the cathode) do not become shielding by the screening effect which reduced the local electric field of the stacked CNT sheet emitters. This design would require careful consideration of a dielectric material with sufficient electric field breakdown properties (such as polyimide) to prevent electron transport from the CNT sheets to the conductive metal layers. The dielectric layers would also need to be designed large enough to prevent field emission at the edges of the CNT sheets to the metal layers. This configuration is essentially creating a capacitor of the emitter sandwich layers; the effect of this charge accumulation on field emission is out of the scope of this current research. As such, separate experimental design, testing, and modeling is required to establish whether or not this proposed design would make a viable electric field emitter. Another simpler approach would be to use the dielectric layers alone to provide a means of controlling the separation distance of the stacked CNT sheet layers.

6.3 CNT Emitting Cathode Applications

Apart from a cathode operated in DC mode for a traveling wave tube, carbon nanotube fibers can be used for various field emission applications. CNF emitters can be integrated into field emission displays (FED) which function like classic CRT displays, but shrunk to size for individual pixels. CNFs can be used to create miniature cold cathode tubes for X-ray applications, as electron sources for scanning electron microscopy or for electron beam lithography applications, as well as microwave power amplifiers, micro-machines mass spectrometers, and ion propulsion.
References


