Individual Carbon Nanotube Probes And Field Emitters
Fabrication And T

Guangyu Chai
University of Central Florida

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INDIVIDUAL CARBON NANOTUBE PROBES AND FIELD EMITTERS

FABRICATION AND THEIR PROPERTIES

by

GUANGYU CHAI
B.S. Peking University, 1999
M.S. University of Central Florida, 2003

A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Physics
in the College of Arts and Sciences
at the University of Central Florida
Orlando, Florida

Fall Term
2004
ABSTRACT

Since the discovery of carbon nanotubes (CNT) in 1999, they have attracted much attention due to their unique mechanical and electrical properties and potential applications. Yet their nanosize makes the study of individual CNTs easier said than done.

In our laboratory, carbon fibers with nanotube cores have been synthesized with conventional chemical vapor deposition (CVD) method. The single multiwall carbon nanotube (MWNT) sticks out as a tip of the carbon fiber. In order to pick up the individual CNT tips, focused ion beam (FIB) technique is applied to cut and adhere the samples. The carbon fiber with nanotube tip was first adhered on a micro-manipulator with the FIB welding function. Afterwards, by applying the FIB milling function, the fiber was cut from the base. This enables us to handle the individual CNT tips conveniently. By the same method, we can attach the nanotube tip on any geometry of solid samples such as conventional atomic force microscopy (AFM) silicon tips. The procedures developed for the FIB assisted individual CNT tip fabrication will be described in detail.

Because of their excellent electrical and stable chemical properties, individual CNTs are potential candidates as electron guns for electron based microscopes to produce highly coherent electron beams. Due to the flexibility of the FIB fabrication, the individual CNT tips can be easily fabricated on a sharpened clean tungsten wire for field emission (FE) experimentation.

Another promising application for individual CNT tips is as AFM probes. The high aspect ratio and mechanical resilience make individual CNTs ideal for scanning probe microscopy (SPM) tips. Atomic force microscopy with nanotube tips allows us to image relatively deep features of the sample surface at near nanometer resolution.
Characterization of AFM with individual CNT tips and field emission properties of single CNT emitters will be studied and presented.
To my parents, Ciduo Chai and Menglan Tang, for their endless patience, encouragement, and love.
ACKNOWLEDGMENTS

Special thanks to my advisor, Dr. Lee Chow, who guided and encouraged me through all the work. I would like to thank my committee members, Dr. Johnson, Dr. Brownstein, Dr. Bindell and Dr. An. I would like to express gratitude to Dr. Dan Zhou for his advice and encouragement. I would also like to thank Mr. Zia Ur Rahman and Alex M. Schwitter at University of Central Florida (UCF) Materials Characterization Facility (MCF), who shared their knowledge and enthusiasm with me. In addition, I would like to thank Dr. Winningham, Mr. Kezheng Chen, Dr. Vanfleet and Dr. Walters in UCF physics department for their assistance, advice and support. Finally, I would like to thank my friends for giving me the love, understanding, and support that made it possible for me to accomplish my graduate studies.
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<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>CCVD</td>
<td>Catalytical chemical vapor deposition</td>
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<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive spectrometer for x-ray quanta</td>
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<tr>
<td>EFM</td>
<td>Electric force microscopy</td>
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<tr>
<td>FE</td>
<td>Field emission</td>
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<tr>
<td>FEED</td>
<td>Field emission energy distribution</td>
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<td>FEM</td>
<td>Field emission microscopy</td>
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<td>FIB</td>
<td>Focused ion beam</td>
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<tr>
<td>FN</td>
<td>Fowler-Nordheim</td>
</tr>
<tr>
<td>LMIS</td>
<td>Liquid metal ion sources</td>
</tr>
<tr>
<td>MCF</td>
<td>Material characterization facility</td>
</tr>
<tr>
<td>MFM</td>
<td>Magnetic force microscopy</td>
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<tr>
<td>MWNT</td>
<td>Multi-wall carbon nanotube</td>
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<tr>
<td>PECVD</td>
<td>Plasma-enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SPM</td>
<td>Scanning probe microscopy</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<td>--------------</td>
<td>-------------------------------------</td>
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<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-wall carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>UCF</td>
<td>University of Central Florida</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
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</table>
CHAPTER ONE: INTRODUCTION

1.1 Research Objectives

After the discovery of carbon nanotubes,\textsuperscript{1} the processes of studying their properties began quickly thereafter. The biggest obstacle of CNTs research is the fact that they are below the resolution of optical microscope. The small size of CNTs makes it difficult to study their mechanical, electrical and other physical properties. The size aspect is part of the reason that people first studied the average CNT properties from CNT thin films. Later on, with the fancy equipment design, people started to study the properties of in situ individual CNTs from CNT thin films. Problems such as screen effects from the neighboring nanotubes can not be resolved completely. In addition it is unusable in actual applications.

This dissertation attempts to study the physical properties of individual CNTs, without other neighboring CNTs. As a result, no screen effect is involved and the result is more persuasive. For this purpose, a method based on FIB technique is established to fabricate individual CNT tips.

Recently in our condensed matter nanomaterial research lab, a novel individual CNT probe sample was synthesized based on catalytic chemical vapor deposition (CCVD) method.\textsuperscript{2} This new configuration includes a single MWNT as the core of a micron size carbon fiber. The MWNT sticks out as the tip of the fiber. The main advantage is that instead of manipulating the nano-size CNT under electron microscope, we can manipulate the micron size carbon fiber with individual CNT tip under optical microscopes.
Even though the problem of manipulating nano-size CNT is simplified by the micron size carbon fiber, the handling of the micron size fiber is still far from simple. A reliable and controllable way of cutting and handling the micron size fiber with nanotube tip is still needed to be brought to light for future study of the physical properties of individual CNTs.

One of the major contributions of this research is to establish a new method based on FIB technique to fabricate individual CNT tips. This makes the mechanical and electrical properties test for individual CNT tips possible. Individual CNTs were first fabricated on clean tungsten wires and mounted on home made platform designed for FE test. FE properties such as threshold voltage, field enhancement factor were measured and excellent results were obtained. Other promising applications such as scanning probe microscopy tips are also explored. Individual CNT tips are fabricated on conventional AFM cantilevers. AFM cantilevers with CNT tips were then used for standard sample scanning. The results showed that CNT tips have superior advantages of long life time in rough sample topography characterization when compared with conventional silicon tips.

1.2 Dissertation Outline

The material for this dissertation is presented in five chapters: introduction, literature review, experimental methodology, results and discussions, and conclusions. The mechanism of FIB and the description of AFM function for individual CNT mechanical test are brought up in the first chapter. Field emission theory is also introduced in this chapter.
Chapter 2 will describe the background information. It will first describe the major CNT preparation methods. The FE properties of CNT thin films and single CNTs will be discussed. The potential applications of individual CNTs as SPM tips will follow.

Chapter 3 will explain the detail experimental procedures applied in this dissertation. First, a novel individual CNT sample developed by our group based on CCVD method is described. Second, an FIB based pick up process of individual CNT tip is discussed. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations are shown. Then the FE setup for FE test is described. Finally the FIB assisted AFM with individual CNT scanning tip fabrication is given.

Chapter 4 will describe results obtained using the experimental procedures described in chapter 3. First, FE properties of tungsten will be measured as reference. Some theoretical simplification will be discussed. Then FE I-V characters from individual CNT tips will be presented and calculations from the obtained data will be carried out. The field enhancement factor of individual CNT will be calculated and compared with some computational prediction. Finally, the unique properties and characteristics of AFM with CNT tips will be presented. AFM with new conventional silicon tip are also tested for comparison.

Chapter 5 will presented some important conclusions based on the results of the research. Some potential improvement of the research will be discussed and the research foreseen will be discussed.
1.3 Focused Ion Beam Technology

FIB technology has been well developed in the recent two decades. Liquid metal ion sources (LMIS) work as the ion generator; electric and magnetic fields are used to accelerate and focus the ion beams. Compared with electron based microscopy such as SEM and TEM, the main difference is that the beam is ion made instead of electron made. Ions have much larger masses compared with electrons and will have more momentum when accelerated with same voltage difference for identical charge magnitude.

There are two basic functions of FIB: spattering and ion induced deposition. These two main functions allow the FIB to work as a micro machine shop. Micro or nano fabrication of samples can be done in sub micron scale by spattering off or depositing materials to the sample surface with FIB. This technique is highly valuable in industry and academic area. Many of experimental and industrial works are greatly simplified with the help of FIB, some can not even been done without it.

1.3.1 FIB instrument

FIB technology is based on the application of field emission ion sources called liquid metal ion sources, which can generate an extremely intense beam of ions. The beam can be focused to less than 10 nm with current densities in the focusing spot several A/cm². The main components of the LMIS include a metal ion source reservoir, a sharp tungsten tip and extracting electrode. The metal source is coated on the W tip and heated to its melting temperature. A high positive voltage is applied between the emitter and the extracting electrode. Under the action of the surface tension and the electrostatic forces simultaneously, the liquid metal thin layer forms
to a conical shape. The conical tip is very sharp; the radius of the apex is believed to be only about 5 nm. As a result, highly intense electric field is built up around the liquid metal tip. The metal atoms vaporization from the liquid phase is greatly enhanced because the surface potential barrier is dramatically reduced by the high surface field. Right after the atoms escape from the surface, they are ionized and then accelerated by the same electric field and form the ion beam. Although there are many ion sources available, Ga ions are currently the most popular ones in use.

Figure 2 shows a schematic diagram of the two lens ion column through which the ions travel after being extracted from the LMIS. The ions are drawn through an acceptance aperture that limits the ion current that will eventually reach the sample, and a beam-defining aperture that serves to collimate the beam. Included in the column are two electrostatic lenses, a condenser lens, and an objective lens, which focus the beam and accelerate the ions to a kinetic energy of 30 keV. A spot size of less than 10 nm is readily attainable in recent FIB machines. The focused beam is scanned over the sample surface using an octupole deflector.
Figure 1  A schematic diagram of LMIS

Figure 2  A schematic diagram of an FIB ion focusing column
1.3.2 Sputtering and deposition

The liquid metal ion source is the basis of FIB systems. They use many kinds of metal ions which can be focused into a spot less than 10 nm in diameter with current densities as high as 10A/cm². The two main features of the FIB tool that are most useful are the capability to remove material from the sample by sputtering and to deposit materials to the sample by ion induced reactions at sub-micron dimensions. As a result, the FIB technique is widely used for cross-section cut, TEM sample preparation, and IC circuit design modification.9, 10, 11

The sputtering process responsible for the effect occurs when the incident beam transfers sufficient momentum to surface and near-surface atoms for them to escape through a cascade of collisions. Figure 3 shows the schematic diagram of the FIB sputtering. The sputtering yield is the number of sputtered atoms per incident ion. Both the ion beam current and the sputtering yield dominate the removal time of the materials. In the presence of reactive gasses, the yield can be increased due to chemical reactions initiated by the ion beam. A serious and deleterious complication to milling is redeposition. As material is sputtered away, some of it redeposit in the volume that is being sputtered.
Figure 3  FIB sputtering
Figure 4  FIB CVD deposition

1. Ion beam. 2. Gas deliver vessel. 3. Sample. 4. Deposited metal. 5. Metal containing gas.
In addition to material removal, FIB systems have the capability to deposit material by ion beam assisted chemical vapor deposition. FIB induced deposition of metals was first reported 1984. Metal containing gas compound is first induced by fine vessels into the surface region where the deposition is to be made. The ion beam is used to decompose the gas. The metal is deposited at desired area with sub-micron precision and the decomposed gas pumped away. Some of the materials that have been deposited by FIB CVD include, SiO₂, Al, Pt, W, Cu, and Au.

1.3.3 Applications of FIB technique

As summarized below, FIB can be used as a micro-machine to fabricate features on a sample with sub-micrometer scale by removal of material. In the semiconductor industry, FIB is a power tool for failure analysis to cut and image cross-sections of a suspected faulty part of a circuit. It can be also used for creating electrical or mechanical connections, repairing both optical and x-ray mask clear defects and repairing and modifying integrated circuits. Another useful application of FIB is in the preparation of samples for use in the TEM and STEM.

1.4 Atomic Force Microscopy

1.4.1 Introduction to AFM

The scanning probe microscopy (SPM) was first invented in 1986. The most popular one is the atomic force microscope (AFM). AFM images show significant information about
sample surface topography with superior resolution. AFM can examine features from atomic scale\textsuperscript{15} up to sizes larger than 100 $\mu$m. Compared with electron based microscopy, AFM also has many great advantages.

AFM sample preparation is extremely simple. Actually, the sample needs nearly no preparation. Samples can be observed at one atmosphere. As a result no dehydration of the sample is needed. AFM can even observe specimen in a liquid environment\textsuperscript{16}, which has incomparable advantages in biology science. AFM obtains images via the interaction force between the scanning tip and the sample surface. There is no charging problem as the electron based microscopy has. So the sample is not required to be conductive and no metallic coating of the sample is required. The atomic vertical resolution of AFM presents superior surface contrast as respect to scanning electron microscopy. The high vertical range also allows AFM to examine relatively rough sample surfaces. A schematic diagram of an AFM is shown in figure 5.
Figure 5  Schematic diagram of AFM working stage.
The atomic resolution of AFM is contributed by a number of key issues such as extremely sharp scanning tips with high aspect ratios, a very sensitive photodetector, and a precise piezo scanner.

AFM obtains images by sensing the force between a scanning tip and the sample surface. Commercial tips are made by silicon or silicon nitride. The sharpness of the tips dominates the AFM image qualities. The fine curvature of the apex allows AFM to detect atoms and molecules. The high aspect ratio gives AFM the ability to image relatively deep surface features. A laser beam shines on the cantilever and reflects back to the photodetector (figure 5). The flexible cantilever will tilt and bend according to the sample topography when the tip is scanning on the sample surface. In response, the reflected beam will also scan on the photodetector. The images are recorded electronically. The photodetector, the piezo scanner, and the scanning tip form a feedback loop. It not only lets the AFM measure the tip-sample interaction force, but also maintains the force at a low, almost constant level. Low level interaction force will protect both the sample and the sharp tip.

There are several image modes of operation of the AFM. They are developed based on different types of force sensing method.

Contact mode: The contact mode is the most straightforward AFM mode. It measures the topography by sliding the tip across the sample surface. The tip is always in contact with the surface during scanning. With the help of the feedback loop, the deflection of the cantilever is kept constant. Image contrast depends on the interaction force. It can be also easily used in liquids. Since the tip is continuously touching the sample surface, the sample surface, especially for soft specimens, can be damaged.
Figure 6  Schematic graph and FIB image of an AFM tip
(a) The schematic diagram of an AFM scanning tip: r is the radius of the tip curvature and L/W is the aspect ratio. (b) FIB image of a commercial AFM cantilever with a pyramid Si tip.
Noncontact mode: An additional AC signal is applied to drive the cantilever to vibrate with its resonant frequency. When the vibrating cantilever is trying to approach the sample surface, the van der Waals force between the tip and the sample surface will cause a frequency shift of the oscillating cantilever. The van der Waals force is determined by the tip-surface separations. The AFM image formation is carried out by keeping a constant frequency shift of the cantilever resonant frequency.\textsuperscript{19} Again this mechanism is achieved by the feedback loop mentioned in the contact mode. During the scanning, the tip never touches the sample surface. As a result, there is no sample damage to any kind of specimens. In the noncontact mode, the tip-sample interaction force is very small. Thus, the life time of the sharp tip is much longer. The greatest disadvantage is that the noncontact mode is not suitable for scanning samples in liquid environment.

Tapping Mode (Intermittent contact Mode): This mechanism is similar to the nancontact mode. An AC signal drives the cantilever to oscillate with its resonant frequency. But in the tapping mode, when the cantilever is vibrating, the tip touches the sample surface occasionally. A damping of the oscillation amplitude occurred in the cantilever vibration. It is brought by the contact force the same as in the contact mode. This is the most popular imaging mode because: it eliminates the shear forces occurred in contact mode which can damage the sample surface and decrease image resolution. Since the tip-sample interaction force is smaller, the life time of the tip is increased. Compared with the noncontact mode, it has much better lateral resolution as well as similarly good vertical sensitivity. It can be also used in the liquid environment.\textsuperscript{20}
Figure 7  Tip-sample force curve based on tip-sample separation.
1.4.2 CNT applications as AFM scanning tips

The scanning tip is the heart of the AFM. It is the part closest to the testing sample and all the information originally come from the tip-sample interaction forces. As a result, the high quality of scanning tips such as a sharp tip radius and a high aspect ratio become essential to the AFM image resolution. The nanosized radius of the CNT tip curvature easily gives AFM nanometer resolution. And the high aspect ratio of CNT allows AFM to image relatively deep surface features. The flexibility of the CNT body makes it easier to survive after scanning rigid sample surface, which enhances the life time of the CNT tip.

In this dissertation, FIB technique is applied to fabricate individual CNT tips onto conventional AFM cantilever with Si tips. Digital instruments multi-mode SPM is used to test our nanotube probes on standard AFM calibration samples. In order to increase the life time of our CNT tip while in the same time get better image resolution, the tapping mode is applied as imaging methods for AFM with individual CNT probes. Competitive results are obtained and will be shown in chapter four.
1.5 Introduction to the field emission theory

1.5.1 Fowler- Nordheim relationship

Field emission is the phenomenon described as the emission of electrons from solid or liquid phase into vacuum due to the effect of the high surface electric field. The difference between the field emission and the thermal emission is the energy of the emitting electrons. In the case of thermal emission, only the electrons with sufficient energy can overcome the surface potential and become free electrons. While for field emission, the surface potential is bent in the action of high electric field and the barrier become extremely thin. According to quantum mechanics, electrons can be regarded as wave packages. There is a finite chance for electrons to tunnel through the barrier and become free electrons. The field emission theory was first developed by Fowler and Nordheim. Based on wave mechanics, they derived the relationship of the field emitting current and the local electric field. Today, it becomes the well known theoretical basis to explain the field emission phenomenon.

In 1924, de Broglie showed that electrons can be treated as a wave packet as well as a particle. The probability of an electron at any particular position x can be described as $|ψ(x)|^2$. $ψ$ is the wave function of the electron. Inside the metal it is a propagating function on the x axis. In the surface potential barrier region, it becomes an attenuated function and $|ψ(x)|^2$ drops down very quickly. If the potential barrier is thin enough, $|ψ(x)|^2$ may not become zero when reaching the vacuum region. This means that there is a finite chance for electrons to tunnel through the
surface barrier, even though the electron energy is still small compared with the surface potential. The mechanism is illustrated in figure 8.

For one dimensional case in the x direction the Schrödinger equation, which the wave function $\psi$ obeys, inside the metal is

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} W \psi = 0$$

(1)

and the Schrödinger equation outside the conducting material and within the triangular potential barrier is

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} \left[ W - (\phi + E_F) + Fex \right] \psi = 0$$

(2)

where $W$ is the normal kinetic energy of the electron and $F$ is the electric field.

By substituting

$$y = \left( \frac{\phi + E_F - W}{eF} + x \right) \left( \frac{8\pi^2 m}{\hbar^2} eF \right)^{1/3}$$

Equation (2) is simplified to

$$\frac{d^2 \psi}{d^2 y} + y \psi = 0$$

(3)
Figure 8  Schematic diagram of surface potential barrier under external electric field.

$E_F$ and $\phi$ are the Fermi energy and the work function of the metal respectively.
The solution of the equation (3) is the $1/3$ order of Bessel function.

Physically speaking, when $x$ is approaching infinity or $y$ is approaching infinity, the solution should be a wave function propagating to the right. So $\psi$ should have the Hankel function form

$$
\psi = \sqrt{y} H_{1/3}^{(2)} \left( \frac{2}{3} y^{1/3} \right)
$$

The solution of the equation (1) can be simply represented as

$$
\psi = A e^{i \sqrt{8\pi^2 m W}} + B e^{-i \sqrt{8\pi^2 m W}}
$$

The electron wave function is continuous at the metal/vacuum boundary. The two solutions (4) and (5) have to satisfy the boundary condition at the metal/vacuum surface ($x=0$).

$$
\psi\big|_{0^+} = \psi\big|_{0^-}, \quad \frac{d\psi}{dx}\big|_{0^+} = \frac{d\psi}{dx}\big|_{0^-}
$$

The probability for electrons with normal energy $W$ tunneling through the barrier can be calculated as

$$
D(W) = \frac{A^2 - B^2}{A^2}
$$

which is equal to

$$
D(W) = 4 \frac{W(\phi + E_F - W)}{(\phi + E_F)} \left[ -\frac{4}{3} \left( \frac{8\pi^2 m}{\hbar^2} \right)^{1/2} \frac{1}{eF} \right]
$$
This function is then multiplied by the number of electrons arriving at the barrier, given for metals by the Fermi-Dirac distribution function. Integrating with respect to their energy, the total number of electrons tunneling through the barrier and the current they carry can be calculated.

The number of electrons in unit volume in the momentum range $dp_x dp_y dp_z$, is given by the number of cells in the corresponding volume of phase space multiplied by the Fermi-Dirac distribution function:

\[
N(p_x, p_y, p_z) dp_x dp_y dp_z = \frac{2}{h^3} \frac{1}{1 + e^{\frac{E-E_L}{kT}}} dp_x dp_y dp_z
\]

In terms of velocities, $v_x, v_y, v_z$

\[
N(v_x, v_y, v_z) dv_x dv_y dv_z = \frac{2m^3}{h^3} \frac{1}{1 + e^{\frac{E-E_L}{kT}}} dv_x dv_y dv_z
\]

The number of electrons with velocities along the emission direction $x$ in the range between $v_x$ and $v_x + dv_x$

\[
N(v_x) dv_x = \iint dv_y dv_z N(v_x, v_y, v_z) dv_x
\]

\[
= \frac{1}{m} \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} d\varepsilon_{y,z}
\]

\[
N(v_x) dv_x = \frac{4\pi m^2}{h^3} dv_x \int_{-\infty}^{\infty} d\varepsilon_{y,z} \frac{d\varepsilon_{y,z}}{1 + e^{\frac{E_{y,z}-E_f}{kT}}}
\]
The emission current density

\[ dJ = D(W)\nu_x N(\nu_x)dv_x \quad m\nu_x dv_x = dW \]

(10)

\[
J(W)dW = \frac{16m\pi[W(\phi + E_F - W)]^{\frac{1}{2}}kT}{\hbar^3(\phi + E_F)} \ln\left(1 + e^{\frac{E_F - W}{kT}}\right) \exp\left[-\frac{4}{3}\left(\frac{8\pi^2m}{\hbar^2}\right)^{\frac{1}{2}}\left(\phi + E_F - W\right)^{\frac{3}{2}} \right]dW
\]

For field emission \(W < E_F\)

\[ kT \ln\left(1 + e^{\frac{E_F - W}{kT}}\right) \approx E_F - W \]

The integration will result in the Fowler-Nordheim relationship

(11)

\[
J = \int_{-\infty}^{E_F} \frac{16m\pi[W(\phi + E_F - W)]^{\frac{1}{2}}(E_F - W)}{\hbar^3(\phi + E_F)} \exp\left[-\frac{4}{3}\left(\frac{8\pi^2m}{\hbar^2}\right)^{\frac{1}{2}}\left(\phi + E_F - W\right)^{\frac{3}{2}} \right]dW
\]

(12)

\[ J = \frac{e}{2\pi\hbar} \frac{E_F^{\frac{1}{2}}F^2}{(\phi + E_F)\phi^2} \exp\left[-\frac{4}{3}\left(\frac{8\pi^2m}{\hbar^2}\right)^{\frac{1}{2}}\left(\phi^2 \frac{3}{eF}\right) \right] \]
The field emission cross section is weakly dependent on the local electric field $F$. It can be treated as a constant. We can also assume that the relationship of the applied voltage and the local electric field is proportional with each other, in other words, $V=KF$. If we take logarithm on both side of equation, we arrive at

\[
\ln\left(\frac{I}{V^2}\right) = \alpha \cdot \left(\frac{\Phi}{V}\right) \cdot K + \text{const}
\]

If $I$ is in amps, $V$ in volts and $\Phi$ in eV, then $\alpha$ has a numerical value of

\[
\alpha = \frac{4}{3e} \left(\frac{8\pi^2 m}{\hbar^2}\right)^{\frac{1}{3}} = 6.82 \times 10^9
\]

Now we transformed the FN-relationship equation (12) to an expression, equation (13), that can be compared with experimentally measured quantities such as $I$ and $V$. $K$ is the constant that relates to the applied voltage and the local electric field, which is determined by the geometry of the emission tip.

1.5.2 Field enhancement factor of emitters with CNT geometry

Recently many computational works\textsuperscript{22, 23} have been carried out to simulate the local electric field at the surface of single tip field emitters for a variety of geometries. The field enhancement factor $\beta$ is obtained through simulation. The axial field near the surface of various tip configurations with cylindrical symmetry has been simulated by the use of the program CIELAS2 (Granta Electronics, Cambridge, U.K.),
Figure 9  Field emission simulation setup: A single tip standing between two infinite conductive planes with potential difference $V$. 
based on the finite element method. For the geometry setup as shown in the figure 9, the simulation gives\(^2\) 

\[
\beta = 1.2 \times \left( \frac{l}{r} + 2.15 \right)^{0.9}, \frac{l}{r} < 1000
\] 

It should be noted that the field enhancement factor is only dependent on the emitter tips own geometry, the tip length \(l\) and tip radius \(r\), but is not related to the inter-electrode distance \(d\).

If only the CNT tip itself is counted, the geometry is exactly the same as shown in figure 9. In this dissertation, equation (14) is applied to calculate the field enhancement factor for individual CNT tips.

Add more words to explain the difference of the field enhancement factor.
CHAPTER TWO: LITERATURE REVIEW

2.1 Discovery and Synthesis of carbon nanotubes

In 1991, during the preparation of C_{60} using an arc-discharge evaporation method, Dr. Iijima found a new type of finite carbon structure consisting of needle-like multi-wall carbon nanotubes.\(^1\) This remarkable result attracted world-wide attention instantly and many scientists devoted their research to these new structures. Later in 1993, during the synthesis experiments of nanocapsules containing the iron-group metals, single-wall carbon nanotubes were serendipitously discovered by Iijima and Ichihash using Fe as a catalyst,\(^{24}\) by Bethune et al. using Co,\(^{25}\) and by Saito et al. using Ni.\(^{26}\)

At present, there are several techniques to produce CNTs. The carbon arc discharge, laser vaporization and chemical vapor deposition are the three most popular synthesis methods being currently being used. Each method has its own advantages and weaknesses.

2.1.1 Carbon arc discharge method

The carbon arc discharge method, by which the CNT was first discovered, is most useful because the quality of the CNTs prepared through this technique is superior to CNTs prepared by other methods and it is excellent for further studies.

The plasma in the carbon arc has a very high temperature, typically around 3500 °C. It can be used to produce many kinds of carbon materials,\(^{27,28}\) such as single-wall and multi-wall CNTs, carbon soot and fullerenes. During the typical arc discharge experiment, 5-20 mm
diameter carbon rods are used as electrodes and sources. They are separated by approximately 1mm. 20-25 Volts are applied across the electrodes and a 50-120A DC electric current is allowed to flow between the electrodes. The arc is typically operated in low vacuum of He environment. The pressure is about 500 torr. The length of the anode carbon rod decreases as a function of time and the CNTs formed on the cathode deposit.

No catalyst is needed for the MWNT synthesis and the CNTs are found in bundles in the cathode where the temperature is around 3000 °C. Carbon nanoparticles, fullerenes and amorphous carbon are found surrounding the CNTs. For the synthesis of SWNTs, catalysts are used. The most popular ones are transition metals such as Fe, Ni, or Co. Rare earths such as Gd or Y are also used as catalysts for SWNT synthesis.

The carbon arc discharge method for preparing CNTs appears very easy, but it is obvious that making high yields of CNTs is difficult and requires keeping under careful control of the experimental conditions.

2.1.2 Laser vaporization method

The second approach of CNT synthesis mentioned above is laser vaporization method. Using laser vaporization technique, high yield with > 70%-90% transformation of graphite to SWNTs were reported. The reaction is carried out in a tube furnace which is operating at 1200°C. A Co-Ni/graphite composite laser vaporization target is used. High power laser pulses are used to evaporate the target. Argon gas flow is used to carry the nanotubes from the high temperature zone to the downstream water-cooled copper collector.
CNTs synthesized using these two methods are not suitable for large-scale commercial application due to two specific reasons. The first reason is that several purification steps that must be used in order to separate the impurities from the nanotubes. These impurities include catalyst particles, amorphous carbon, and non-tubular fullerenes. The second reason is that the size of the carbon sources limits the yield of nanotubes. When the sources are consumed, the process has to be stopped and the CNTs can not be produced continuously.

### 2.1.3 Chemical vapor deposition (CVD) method

CVD techniques are used to synthesize CNTs through the carbon decomposition of carbon-containing gases. Many kinds of hydrocarbons, catalysts and substrates have been applied successfully by many groups to prepare CNTs. CNTs grow in the reaction furnace at temperature from 250 °C to 2900 °C depending on the selected gases. The growth rate is sensitive to reaction conditions, such as the temperature of the furnace, the partial pressure of the hydrocarbon gases, and their decomposition and flow rate. With careful parameters selection, both SWNT and MWNT can be prepared by CVD technique.

One major improvement of the CVD technique is that CNTs can be produced continuously. As a result, if the best conditions for growing pure CNTs could be established, this could be an excellent way to synthesize large quantities of CNTs under carefully controlled conditions. Thus the CVD method has some advantages for scale-up and commercial production. Another advantage is that the lower CVD processing temperatures allow a wider selection of substrates to be used including glass, which is very important for the flat panel display application that requires CNTs to grow perpendicular to the glass substrate. The CVD method
also has the ability to prepare CNTs with a controlled diameter and length in vertically aligned arrays.\textsuperscript{36} By adjusting the catalytic particle size and the growth time, the diameter and the length of the CNTs can be controlled respectively.

A refinement to CVD method is plasma-enhanced chemical vapor deposition (PECVD) method.\textsuperscript{37} A catalyst layer of transition metals, such as Ni, Co, Fe, is coated on the substrate. The thickness of the catalytical layer is critical in controlling the diameter of the CNTs.\textsuperscript{38} Deposition time and temperature control the length and diameter of the CNTs respectively. A DC power supply or a microwave source is used to generate the plasma. The CNTs grow in the same direction with the plasma excited by the DC power supply. The CNTs grown under alternating microwave plasma are always perpendicular to the local substrate surface.\textsuperscript{39} The array of CNTs can achieve uniformity in diameter, length, straightness, and site density over a large area.

CNTs can grow at the same time as conventional vapor-grown carbon fibers. Most of these nanotubes are multi-wall, but some SWNTs can also be produced. Vapor-grown CNTs generally show poor crystallinity due to the low operating temperature (500-1000 °C). The crystallinity is much improved after heat treatment to 2500-3000 °C in argon atmosphere.\textsuperscript{40}

Recently many researchers have been trying to refine the synthesis technique or to explore new methods to synthesize high quality CNTs to satisfy research and industry requirements. In the following sections the physical properties of CNTs and their potential applications will be described.
2.2 The electron field emission properties of CNTs

Because of their unique electrical properties, high chemical and mechanical stability, as well as their geometry, high aspect ratios, and small tip radius of curvature which means low threshold voltage, high electric field at the tip, CNTs have been shown to be very promising electron field emitters. There are many field emission measurements carried out using CNTs deposited on a substrate. However, relatively few works have been carried out using individual CNTs.

2.2.1 The FE from CNT thin films

The field emission properties from aligned CNT thin films were first reported by Walt de heer and coworkers. In their work, a CNT thin film was made. The diameter of the CNTs is about 10 nm and the length is about 1 micron. With an applied voltage of 200 volts, a FE current density of about 0.1 mA/cm$^2$ was observed from an effective emitting area around 1mm$^2$. The applied voltage and FE current satisfy the FN relationship very well. When the applied voltage reached 700 volts, FE current densities as high as 100 mA/cm$^2$ were achieved. No current degradation was observed for 200 hours with continuous voltage bias under 30µA/mm$^2$.

Later on, numerous works were done to study the FE properties of CNT thin film emitters. The geometry of carbon nanotubes, high aspect ratios, and small tip radius of curvature provide the field emitting CNTs with an extremely low threshold voltage, turn-on field, and high FE enhancement factor.

Several different approaches have been invented to synthesize either randomly aligned or uniformly aligned CNT thin films on different substrates for many kinds of potential applications.
such as flat panel display.\textsuperscript{42-45} The CNT thin film emitters show superior FE properties. Compared with conventional field emitters, the turn-on field is typically as low as 1-5 V/µm and the field enhancement factor $\beta$ is as high as 5000.\textsuperscript{46, 47} By applying larger emission fields, a field emission current density as high as 1-5A/cm$^2$.\textsuperscript{44, 48-51} can be achieved.

Because of the high chemical and mechanical stability, carbon nanotube thin film emitters also showed excellent high FE current stability and long life time. Kenneth A. Dean and co-workers have demonstrated long term FE stability from SWNT thin films.\textsuperscript{52} These FE experiments were carried out in the field emission microscope (FEM) with an ultrahigh vacuum (UHV), with a base pressure is bellow $10^{-9}$ torr. CNTs operate at 3µA without degradation with continuous operation for over 350 hours. Other results show that only when the emitting current is higher than 300 nA per CNT, can the permanent emission degradation be observed for CNT thin film emitters.\textsuperscript{53}

Field emission properties of CNT thin film emitters are only the average results of the individual emitting CNTs. It is obvious that only a small percentage of CNTs are effective and contribute to the total emission current. Due to the screen effect, the \textit{in situ} measurement for individual CNTs from dense CNT thin films is not reliable to be treated as the FE properties of individual CNT FE properties. To truly understand individual CNT’s field emission mechanism, measurement from single CNT must be carried out. However, the nano size of the CNTs makes the manipulation of CNT become extremely difficult. Thus, most of the individual CNT FE experiments are \textit{in situ} measurements from a dilute CNT thin film inside an SEM or a TEM in order to eliminate the negative influence from the neighboring shorter nanotubes and minimize the screen effect.
2.2.2 The FE from individual CNTs

The field emission properties from a single CNT were first reported by A. G. Rinzler and coworkers in Prof. Smally’s group.\textsuperscript{54} In their work, a single multi-wall CNT was successfully attached by van der Waals forces to the edge of an 8 \( \mu \)m thick carbon fiber. The diameter of the individual CNT is 8 nm. When the nanotube tip is opened by laser evaporation, greatly enhanced field emission was observed from the open ended CNT. It is hypothesized that under the high local field, an atomic chain was pulled out and played an important role in the superior field emission enhancement. With an applied voltage of 80 volts, a FE current as high as 1\( \mu \)A was successfully achieved with a vacuum as low as 10\textsuperscript{-7} torr.

The current limitation obtaining of individual CNTs is an important issue in CNT research. K. A. Dean and co-workers\textsuperscript{55} studied the current limiting effect in the FE behavior of CNTs. The experiments were performed in an FEM system with a base pressure below 10\textsuperscript{-9} Torr. They show that an individual nanotube exhibits current saturation above 100 nA of emission current, which can be explained by an adsorbate-enhanced field emission mechanism. A single, clean SWNT on the other hand shows no evidence of current saturation for emission currents as high as 2 \( \mu \)A.

The work function of CNTs is another key issue in the CNT field emission properties. The band structure will be different compared with graphite due to the high surface curvature. To understand further the FE properties of individual CNTs, the work function of CNT has to be studied. By using an \textit{in situ} transmission electron microscopy technique, R. Gao and co-workers\textsuperscript{56} have measured the work function at the tips of individual MWNTs. The tip work function is about 4.8eV and shows no significant dependence on the diameter of the nanotubes in
the range of 14-55 nm. Slightly different results were obtained by V. Semet and co-workers, when they use a scanning anode FEM to analyze FE behavior of individual MWNTs in a vertically aligned array grown on a Si wafer. Most of the MWNTs exhibited very similar emission characteristics. The work function of individual MWNT was measured to be about 4 eV. They also observed the conditioning effect, which is due to the contamination on the CNT tips when first transferred into the vacuum chamber. The emission characteristics are reproducible after the conditioning process.

*In situ* electron holography performed inside a high resolution TEM has been applied to study the magnitude and spatial distribution of the electric field surrounding individual field-emitting CNTs by John Comings and co-workers. The direct experimental observation showed that the electric field is concentrated precisely at the CNT tips, instead of concentrated on nanotube defects such as sidewall imperfections line. This observation agreed with the theoretical simulation results of the electric field distribution of the emitters with CNT geometry.

The field enhancement factor of individual CNT was also studied by J. M. Bonard and co-workers directly in SEM. The selected nanotube was 1.4µm long and 7.5 nm in diameter. A sharp conducting W anode was used to approach the chosen nanotube. The inter-electrode distance was 2.65 µm. FE properties were measured and the field enhancement factor \( \beta \), obtained from the best fit to the FN theory, was about 90, which agree with the theoretical prediction.

Because of the high electric field at the tip of the emitting nanotube, nanotube structural damage and FE degradation were observed by several groups. For SWNTs, the FE degradation is related to the field vaporization and the ion bombardment from the gas phase. These mechanisms are also believed to play a role in the degradation and failure of individual
MWNT field emitters. In the case of MWNTs, results show that the failures are mainly owing to the strong electrostatic force, the resistive heating at high emitted currents or the mechanical failure of the contact or combination of them.

2.3 Individual CNT application as AFM tips

Since the discovery of CNTs in 1991, researchers have put much effort into characterizing their properties and exploring their potential applications. Although many of these potential uses are still in the early stages, it has become clear that CNTs, because of their excellent mechanical properties and unique geometry, are perfect candidates for scanning probe microscopy (SPM) probes such as atomic-force microscopy (AFM), magnetic force microscopy (MFM) and electric force microscopy (EFM). CNTs have many excellent properties to serve as scanning probes for topographic imaging. They have an ideal tip shape, which provides improved surface resolution. The high aspect ratio and long length allow them to investigate deep and narrow surface features. They are also suitable for probing sensitive and soft surface features because of the good flexibility. Due to the mechanical properties, CNT probes have long life times and can easily survive after scanning relatively rough sample surface.

The first successful attachment of individual carbon nanotube as SPM tips is reported by H. Dai and coworkers in Prof. Smally’s group. A bundle with five to ten MWNT is attached to the side of a conventional Si tip by an acyclic adhesive. At the end of the CNT bundle, an individual MWNT sticks out and acts as the scanning tip. The attaching procedure is carried out under an optical microscope with dark-field illumination. The individual MWNT tip is typically 5-20 nm in diameter. SPM tapping mode was applied to image a 400 nm wide, 800 nm deep
trench test sample with both the conventional pyramidal silicon tip and the nanotube tip. The demonstrated results clearly exhibit those superior advantages of CNT tip. The thin, long nanotube is able to reach the bottom of the trench and give nanometer resolution without an apparent triangular artifact as shown in Si tip scanning results, which is due to the pyramid geometry of the Si tip.

Compared with conventional Si tips, CNT tips showed great advantages in observing relatively deep and narrow trenches. Due to the superior mechanical properties of CNTs, the CNT tips often survive after scanning rough surfaces which make their life time much longer than Si tips. Researchers have applied AFM with CNT tips to study nanostructures and nano-size molecules and have achieved great improved results.\textsuperscript{69-72} AFM with CNT tips are superior for imaging deep surface topography. The life time of CNT tips is at least 10 times longer than conventional silicon tips without any resolution degradation.

However, problems have plagued the fabrication of nanotube probe microscopy tips due to its nano size. The earliest approach was to pick and stick a MWNT bundle to the tips with an acrylic adhesive under an optical microscope.\textsuperscript{68} This process is difficult and time consuming. CNT bundles instead of individual CNTs were picked up. Then CVD technique was applied to grow MWNT and on a catalyst deposited tip surface directly.\textsuperscript{72} Hydrogen fluoride is used to etch nanopores on a flattened conventional Si tip. Iron catalyst is then deposited into the pores electrically and ethylene and hydrogen gas are used to grow CNTs directly on the silicon tip. The typical operating temperature is 750 °C, and the diameter of the CNTs is about 10 nm. By using precisely selected CVD parameters, SWNT tips can be also achieved by the same method.\textsuperscript{73}
The main disadvantage of the CVD method to grow CNT tips directly onto a conventional Si tip is that this method always produces multiple tips, which may generate artifacts. In addition, there is no accurate control over the orientation of the CNT tips.

In order to provide the advantage of controlling the orientation of nanotube probes, electric fields are introduced to the CNT attaching processes.\textsuperscript{74} DC arc discharge method is applied to produce MWNTs. The CNTs are normally 1-5 \textmu m long, 5-20 nm in diameter. The attachment process involves purification and alignment of CNTs using electrophoresis, transfer of a single aligned CNT onto a conventional Si tip under the observation of SEM, attachment of the nanotube on the Si tip by carbon deposition. It is believed that the high electric field induced dipole in the CNTs plays the role in the alignment of the nanotube with desired orientation.

Later on an improved process was developed to fabricate CNT directly on the conventional Si tip.\textsuperscript{75} The CNTs are prepared by well-developed CVD method. The transfer of the CNT onto the Si tip is carried out under optical microscope with the help of micro-translators. Electric fields are applied between the sample cartage and the pre-coated conducting improvement Si tip. The induced electrostatic dipole moment in the nanotubes is the reason for the attraction and the alignment due to the geometry of the field created by the cantilever tip shape. Electric current is applied to burn and separate the nanotube tips. The breaking of CNT from the sample cartage is considered to be due to the defect generated from the low temperature CVD growth. Yet without the supervision of the SEM, desired nanotube tips may not be selected during the pick up process. Curly or coiled MWNTs can be picked up. And the nanotube contact and breaking mechanism is still not quite clear.

Researchers also use magnetic field to attach and align individual CNT tip on to conventional Si tips.\textsuperscript{76} The CNTs are prepared by arc discharge. After the purification process,
they are ultrasonically broken and suspended in the solution. The conventional Si tip is pre-coated with metallic thin layer to improve conductivity. A strong magnetic field with 0.1 T is used to induce magnetic dipoles in the CNTs. The effectiveness of the attachment is due to the attraction between the induced dipole and the metal thin layer. Sixty CNT tips were successfully prepared via this method. Same as the usage of electric field, to solve the alignment problem the AFM Si tip needs to be pre-coated to improve conductivity. The length of the CNT tips prepared by this method is relatively short and there is too much amorphous contamination during the pick up process.
CHAPTER THREE: EXPERIMENTAL METHODOLOGY

3.1 Synthesis of individual nanotube tips

In our experiment, conventional chemical vapor deposition technique is used to grow micron-sized carbon fiber with a CNT core on silicon substrate. By fracturing the nanotube-containing fibers, we obtained individual CNTs supported by micron-sized carbon fibers. The nanotubes thus obtained come out as the tips of carbon fibers, and they can be handled and manipulated easily for physical measurements with the assistance of Focused Ion Beam technique.

3.1.1 Catalytic substrate preparation

The CNT samples are prepared on silicon wafers coated with nano-size iron and nickel catalytic particles. Conventional physical vapor deposition method is applied to prepare the catalytic nano-particles on the substrates. A cooke Vacuum product CV-300 vacuum chamber system is used. The pumping system consists of a mechanical vacuum pump (pumping limit: 10⁻³ torr) and a water-cooled diffusion pump (pumping limit: 10⁻⁶ torr). Iron and nickel alloy (Fe: Ni 50:50), used as the catalyst for growing CNTs, is weighed and put in a tungsten boat. Typically, we use about 1 mg of Fe/Ni metallic power for each evaporation. The silicon substrate with size 1cm by 1cm is put directly inside the vacuum chamber. It is positioned at 12-15 cm above the tungsten boat. After the chamber vacuum is pumped down to 10⁻⁶ torr, high purity (99.999%) argon gas is filled into the chamber to a pressure of 500-1000 mtorr.
Figure 10  Schematic diagram of the PVD system.
During the vaporization process, the argon molecules will greatly shorten the mean free path of the evaporated iron and nickel atoms and prevent formation of metallic films. As a result, the iron and nickel atoms will collide with each other and form nano-particles before they reach the silicon substrate. By changing the pressure of the argon gas, we can adjust the catalytic particle size. Typically at 500-1000 mtorr, we obtain particle size of 20-50 nm. The iron and nickel catalyst is evaporated by heating the W boat with an electric current of 60 ampere.

3.1.2 CCVD synthesis of carbon fiber with CNT core

Catalytically assisted chemical vapor deposition method is used to prepare the micron-size carbon fiber with CNT core. During the process, we use methane (CH₄) as the source gas to grow the CNT samples; and use argon as the carrier gas to dilute methane. The pyrolytic reaction was carried out in a Lindberg Model 58125 laboratory tube furnace. With a Model 818 temperature controller, the temperature can be adjusted.

A four-step method developed by our group is used for synthesizing the nanotube-containing micron-sized carbon fiber. The steps are described beneath in detail:

Step one: preparation for the growing process

The 5/4 inch in diameter, 6 feet in length quartz tube was first flushed with argon gas for 30 minutes in order to purge oxygen. Argon gas was also applied as the inert carrier gas to dilute the methane. After a few minutes, turn on the furnace and heat the reaction chamber to 900 °C. At the same time hydrogen gas was allowed to flow into the quartz tube to prevent the iron and nickel catalytic particles from oxidization.
Figure 11  Experimental setup of the CNT synthesis
Step two: the growth of the nanotube core

When the temperature at the center of the quartz tube reached about 900°C, hydrogen gas was turned off. The methane gas was allowed to flow into the chamber. The flowing rates of the methane and argon gases were kept at 10 sccm and 65 sccm respectively under one atmosphere. By keeping the quartz tube at this constant temperature after roughly 30 minutes the nanotube core is formed by the following pyrolytic reaction:

$$\text{CH}_4 (g) \xrightarrow{\text{catalyst, } 900°C} \text{C} (s) + 2\text{H}_2 (g)$$

where s and g designate solid and gas phases respectively.

Step three: The growth of the amorphous carbon layer

Keep the flowing rate of argon gas the same and shut down the supply of methane gas to stop the growth of the carbon nanotube core. After the furnace was heated to about 950°C in about 5 minutes, then methane and hydrogen gases were allowed to flow into the quartz tube again. The flow rates of argon, methane and hydrogen gases were kept at 65 sccm, 10 sccm and 65 sccm respectively. The furnace was kept at this constant temperature for 30 minutes so that an amorphous carbon layer could form outside the nanotube core.

Mechanically, fiber layers grown in a hydrogen rich environment appear to be more brittle than those grown under conditions of low hydrogen concentration. This amorphous carbon layer between the CNT core and the outside micron-sized carbon fiber can greatly help to increase the probability for the nanotube to stick out from the carbon fiber as its tip when fracturing the carbon fiber.
Figure 12  CNTs grown by CVD after step 2
(a) Long parallel CNTs grown in the same direction with the gas flow are suitable to be the CNT core for the outer layer fiber prepared by later steps. (b) CNTs form a web connection.
Keep the flowing rate of argon gas and shut down the supply of methane and hydrogen gases to stop the growth of the amorphous carbon layer. After the furnace was heated to about 1000°C in about 7 minutes the methane gas again was allowed to flow into the quartz tube. The flowing rates of argon and methane gases were kept at 65 sccm, 10 sccm respectively. The furnace was kept at this constant temperature for 30 minutes giving the carbon fiber time to grow up to 0.5 - 1.5 µm.

The nanotube-containing carbon fiber is suitable for further fabrication under controllable conditions. By increasing the process time or even the process temperature of the fourth step, thicker nanotube-containing carbon fibers can be obtained. It is also obvious that a thicker fiber is easier to manipulate. However, the nanotube core tends to break at the same location as the fiber and no CNT tip sticks out if the fiber is too thick. The reason is that in order to break thicker carbon fibers, larger mechanical forces have to be applied. When we apply larger forces, more likely the nanotube core would be broken during the same time. Also by breaking the larger size fiber, longer sharp picks are obtained at the broken edge. It is just like breaking wood rods in micro view, sharp picks are always obtained. Even though sometimes the nanotube did stick out from the larger size fiber, it may even shorter than the sharp picks from the fiber broken edge. Experimental results show that the chance for nanotube core sticks out as the tip for nanotube-containing carbon fiber with outer layer 0.5 um-1.5-um in diameter is the largest.

After the four-step synthesis, the nanotube-containing micron-sized carbon fibers are fractured by mechanical forces. A sharp blade is applied to crush the fibers grown on the silicon substrate to pieces.
Figure 13  Carbon fiber with CNT tip

Figure (a) and (b) show CNT tips with different length. In (b) the CNT tip is bent during the breaking process.
3.1.3 SEM and TEM characterization

3.1.3.1 SEM

After the four step sample preparation, SEM and TEM are applied for CNT tip sample characterization.

The SEM provides a high-resolution image of the sample with a high depth of field. Electrons are emitted from a thermionic or field emission electron gun. They are accelerated by a voltage of 1-50 kV between the cathode and the anode. A two- or three-stage condenser lens system is used to focus the electron beam to the sample surface. The beam diameter is around 1-10 nm with beam current $10^{-12}$-$10^{-10}$ A. A deflection coil system in front of the last lens scans the electron probe in a raster across the specimen in conjunction with the beam of a cathode ray tube. The intensity of the cathode ray tube is modulated by secondary electrons or backscattered electrons signals recorded to form an image. The magnification can be increased simply by decreasing the scan coil current and keeping the image size on the tube constant.

The large depth of focus, the excellent contrast and the straightforward preparation of solid specimens are the reasons for the considerable success and widespread use of SEM in the imaging of surfaces. However, the surface topography imaging by transmission electron microscope is superior by one order of magnitude in resolution.

In this dissertation, the SEM used is a JEOL 6400F at MCF. It can provide a resolution of 2nm. A tungsten cold cathode field emission gun is used to generate an electron probe size of 2 nm. The accelerating voltage varies from 1 to 30 kV. The SEM was used to observe the nano-
size carbon tubes and help to identify the position of carbon fibers with CNT tips for FIB fabrication process.

### 3.1.3.2 TEM

Different from SEM, much higher voltages 100-300 kV are applied to accelerate the electrons in TEM from thermionic or field emission cathode. Electrons interact strongly with the sample atoms by elastic and inelastic scattering. For better transmission and resolution, the specimen must therefore be very thin, typically of the order of 5-100 nm. The electron-intensity distribution after the transmission of the specimen is imaged with a three- or four-stage lens system onto a fluorescent screen. A CCD camera coupled with the fluorescent screen is used to record the image digitally. Both primary beam (bright field) and Bragg-reflected beam on axis (dark field) imaging modes are used to give microscopic information with a resolution of the order of 0.1-0.3 nm.

The TEM used in MCF is the Philips Tecnai. It is a state of the art TEM that can be operated 300 keV with a field emission source. Its capabilities are extremely powerful including an energy dispersion x-ray detector and a parallel electron energy loss spectrometer. It has a resolution of 0.24 nm. It has up to 1,000,000X magnification for TEM and 10,000,000X magnification for scanning TEM. The spot size can be reduced to < 0.3 nm for chemical analysis and micro-diffraction studies. The TEM was used to identify the hollow core of the nanofilaments, to make sure that they are MWNTs.
Figure 14  TEM characterization of CNT probes
(a) zoom out image (b) zoom in image: clearly show that the carbon filament has hollow structure is CNT, the diameter is about 22 nanometer, the outside coating is the conductivity improvement nanometer metal layer  for SEM observation.
3.2 FIB pick-up process

3.2.1 FIB technique

Focus ion beam technology is based on the application of the field emission ion sources called liquid metal ion sources, which can produce an extremely narrow beam of ions that can be focused to <10 nm with a current density in the focused spot as high as 10 A/cm². The two main features of the FIB tool that are most important are the capability to remove material from the sample by sputtering (micro-machining) and to add materials to the sample by ion induced reactions (deposition) at sub-micron dimensions. FIB technology is extremely useful for the semiconductor industry, and is also increasingly used in materials research in industry and academia.

It is possible that handling the nanotube-containing micron-sized carbon fibers by FIB technique could affect the individual carbon nanotube tip physical properties measurement results. The reason is that the ion beams used for imaging, cutting and depositing can change the mechanical and electronic characters of CNTs. At the ion beam energy 30 keV and beam current 100 pA, the carbon nanotube can be damaged in a few seconds. To minimize the damage to the nanotube, we used a minimal dose to image the nanotube. For the cutting and depositing procedures, high ion beam energy and current have to be applied. We have to keep the nanotube tip far away from the ion beam to minimize the damage to the nanotube. As a result, no FIB image of the nanotubes tip is obtained during the picking up process. In order to identify the carbon fiber objects for FIB fabrication, SEM images are applied.
3.2.2 Sample cartage preparation

The carbon nanotube tip samples on the silicon substrate are not ready for FIB fabrication yet. We have to lift them up and make more free space for the picking up process. Thus, High purity silver paint for SEM sample preparation purchased from PSI Company and 75 µm tungsten wire are used to help picking up the fractured carbon fiber with nanotube core. We first apply a small amount of the silver paint at the end of a small piece of the tungsten wire; we then use the tungsten wire to attach some fractured nanotube-containing carbon fibers randomly from the "carbon fiber forest".

Even though the probability for carbon nanotube core to stick out from the outside carbon fiber is greatly enhanced by the middle layer of the amorphous carbon prepared by step three, the density and purity of the usable samples (carbon fibers with nanotube tip) are still quite low. This implies that we always get some carbon fibers without nanotube cores or nanotube-containing carbon fibers without nanotubes sticking out at the end of the tungsten wire. There are many reasons. (1) During the fourth step, the operating temperature is already higher than the self-decomposing temperature of the methane. As a result, carbon fibers without nanotubes core can be grown simultaneously as we grow the outer carbon layer. (2) Once we get a carbon fiber with nanotube tip, there may be another fiber piece without any tips which is broken from the same original fiber. (3) The nanotube tips may be accidentally damaged during the pick-up process. The high mechanical forces we use to fracture the nanotube-containing fiber can easily destroy the nanotube tips. Thus, FIB technique is used to clean the un-wanted carbon fibers and pick up
Figure 15  CNT sample cartage
A 75 micron size tungsten wire with silver paint on the top attaches many micron size carbon fibers. The arrow shows a carbon fiber with CNT tip.
the carbon fibers with nanotube tips so as to accommodating for the field emission property experiment. Two methods are employed in the picking up procedure.

### 3.2.3 Pick up method

#### 3.2.3.1 Method one: eliminating the un-wanted carbon fibers

If the angle between the orientation of carbon fibers with nanotube tips and that of the tungsten wire is less than 60 degree, by adjusting the orientation of the tungsten wire, we can prescribe the orientation of the carbon fiber, and put the nanotube tip directly forward. We can then use it for further electrical properties test since the tungsten wire, silver paint we use and the fiber itself are all conductive. All else that to be done is just to eliminate other un-wanted carbon fibers.

The Ga focus ion beam is employed to cut the extra un-wanted carbon fibers. Focus the beam on a thin line just across the carbon fibers which we want to get rid off. Since the fiber is only about one micron in diameter, with the beam energy and current setting at 30keV and 500 pA respectively, the cutting should finish in one min for each individual fiber.

If there are too many carbon fibers, getting rid of them all is very inconvenient. During the cutting off process, another serious problem was also found. Due to the high energy of the Ga beam, a huge amount of heat will be generated by the ion beam and sample atoms bombardment. The temperature right under the focusing area is extremely high, the high temperature keeps the carbon material in the liquid phase. In the mean time, the other end of the carbon fiber is floating
Figure 16  Schematic diagram for FIB pick-up method one
in the vacuum. Because of the micron size of the “carbon liquid”, the surface tension is relatively high. It will pull the free fiber piece back to the other fiber piece stuck on the sample cartage. After the FIB milling, the local temperature is dropped down quickly and the two carbon fiber pieces will join together. The process will not end until the Ga ion beam mills all the fiber pieces down to the end. It is very time consuming and some times the work can not even be done at all.

To solve the problems mentioned in the first way, a new method is developed to pick up the individual CNT tips directly. This time another function of FIB—depositing is employed as well as milling.

**3.2.3.2 Method two: direct pick up with micro manipulator**

For the purpose of picking up the carbon fibers with nanotube tips directly, a micro manipulator is installed into the FIB chamber. A metal needle is launched on the manipulator. In order to align perfectly the carbon nanotube tip with a tungsten filament, an intermediate fiber is first picked up. The intermediate fiber helps to arrange the angle between the carbon nanotube tip and the tungsten filament much easier. The detailed pick up procedure is described below:

[1] We etched a tungsten filament in a concentrated KOH solution and made the filament tip radius as small as around one micron meter.

[2] We mounted the etched W tip and the tungsten sample cartage inside a FEI Vectra 200 focused ion beam system.
Figure 17(a) & (b) FIB images of detail pick-up processes
Figure 17(c) & (d)  FIB images of detail pick-up processes
Figure 17(e) & (f)  FIB images of detail pick-up processes
Figure 17(g) & (h)  FIB images of detail pick-up processes
[3] FIB milling function is first employed to etch a two micron size slot on the top of the tungsten tip. The Ga ion beam energy and beam current is 30keV and 1000pA respectively. It is shown by Figure 17 (a).

[4] FIB milling function is also applied to etch another two micron size slot on top of the metal needle with the same beam parameter described in step [3]. It is shown by Figure 17 (b).

[5] With the help of the micromanipulator, move the metal needle to a carbon fiber such that the end of the fiber rested in the small slot. Then platinum metal is deposited at the contact of the fiber and tungsten tip to form a rigid bond. The Ga ion beam energy is 30keV and the beam current is 50pA. The fiber is used as the intermediate fiber mentioned before. This step is shown by figure 17 (c).

[6] Choose the proper length of the intermediate carbon fiber, typically about 50 micron meter long, so that the intermediate fiber can be reused for the next CNT tip fabrication process. Apply the FIB milling function and cut the intermediate fiber off from the sample cartage. The Ga ion beam energy and beam current are 30keV and 500pA respectively. This is shown by figure 17 (d).

[7] Apply the FIB milling function to make another small slot at the free end of the intermediate fiber. The ion beam parameter is same with step [6]. It is shown by figure 17 (e).

[8] Move the fiber with the nanotube tip into the small slot and apply FIB welding function to weld the junction.

[9] With the same beam parameter setup described in step [6], apply the FIB milling function to cut the fiber with nanotube tip off from the sample cartage. The results of step [9] and [10] are shown by figure 17 (f).
With the help of the micromanipulator, move the end of the nanotube containing fiber without nanotube tip into the small slot prepared on the top of tungsten filament and apply the FIB welding function to deposit Pt at the junction, forming a rigid bond. The Ga ion beam energy is 30keV and the beam current is 50pA.

Finally a 30keV and 500pA ion beam is applied to cut the carbon fiber with nanotube tip off from the intermediate fiber. The intermediate fiber is now ready for next CNT tip fabrication. It is shown by figure 17 (h).

The geometry of a carbon fiber is a cylindrical. When touching with a plane surface or another cylinder (another carbon fiber), the contact area is only a single line or even a single point. Before each welding process, a small slot is always made at the desired contact position to avoid point to point or line to line contact, and to make sure the welding junction is strong enough to survive in the further fabrication process.

From the detailed FIB procedure we can see that during each fiber cutting process, both ends of the fiber are stabilized. Therefore, the “shrinking” problem we have in the first method is automatically solved. It looks like the second method takes more steps yet it really is much faster in achieving the better objective compared with method one. Each welding or milling process can be done within two minutes. The whole process for a single CNT tip fabrication can be finished within half an hour.

Figure 18 shows the individual CNT amount on tungsten filament. After we get the individual CNT tip sample on the clean tungsten filament, it is easy to mount the sample on the field emission set up, ready for field emission experimental test.
Figure 18  SEM images of individual CNT field emitter
(a) Zoom in SEM image shows the detail structure of the CNT tip. (b) Zoom out SEM image shows the geometry of the CNT field emitter.
3.3 Field emission application setup

3.3.1 Vacuum system

Balzer’s turbo-molecular pump TPU 330 is used to obtain the high vacuum environment for the field emission experiment, and Balzer’s rotary vane vacuum pump DUO 016B is used to supply the environmental vacuum for the turbo-molecular pump. After continuous running of the vacuum system overnight and baking under 150°C, a vacuum of $10^{-8}$ torr can be achieved.

3.3.2 Sample holder

After the FIB fabrication, the CNT emitter is mounted on a home-made platform for field emission measurement. The platform is made of vacuum compatible insulator with the ends of two fine-thread stainless steel screws facing each other as counter electrodes. The end of one screw is polished to a mirror finish, while the other screw has a step at the end so the CNT emitter can be attached with silver paint. The CNT emitter is pointed at the center of the mirror finish end of the other screw perpendicularly. The distance between the two can be adjusted under optical microscope to within 5 µm. The typical distance between the CNT and the counter electrode is 50 – 200 µm for the field emission measurement.
Figure 19  Schematic diagram FE sample holder
Figure 20  Optical image of a field emitter in front of the mirror smooth anode. d is the tip-anode distance.
Since the top surface of the anode screw is extremely smooth it can be viewed as a mirror. When the tip of the sample is very close to the plane, by shining the field emission tip with strong light, the image of the tip and the tip itself can be easily observed under microscope by tilting the sample a small angle away from the horizontal plane. With the help of an objective lens with a scale bar, the uncertainty in the distance measurement between the sample’s tip and its image is about 5 micron. The scale bar inside the objective lens is pre-calibrated with an objective micrometer.

3.3.3 Data acquisition

The high voltage for the field emission is applied by EG&G model 556 high voltage power supply. KEITHLEY model 485 autoranging picoammeter is used to monitor the electron field emission current from the carbon nanotube tip. KEITHLEY 195A digital multimeter is used to measure the electric potential difference between the anode and nanotubes tip cathode. In order to prevent the carbon nanotube tip from accidental discharge, a 10MΩ resistor is serially connected into the circuit. Programs based on Labview 5.0 are used to control the IEEE 4882 card for data acquisition. The program detail is described in appendix A. The electric circuit connection is shown by Figure 21.
Figure 21  Electric circuit for CNT FE testing
3.4 Scanning probe tips setup

3.4.1 AFM

AFM images show significant information about surface features with unprecedented clarity. The AFM can examine any sufficiently rigid surface either in air or with the specimen immersed in a liquid. The field of view can be varied from nanometers, up to sizes larger than 100 µm, so that data can be compared with other information obtained with lower resolution techniques. The AFM provides superior topographic contrast without expensive sample preparation.

The tip, which is mounted at the end of a small cantilever, is the heart of the AFM instrument because it is brought to close contact with the sample and gives rise to the image through its interactions with the surface. The tip-cantilever assembly typically is fabricated from silicon or silicon nitride. The essential parameters are the sharpness of the apex, measured by the radius of curvature, and the aspect ratio of the whole tip.

There are basically four mechanisms for AFM to image a sample topography and gain information of the sample surface. (a) Contact-mode AFM— Measures topography by sliding the probe’s tip across the sample surface. Contact mode AFM can operate in both air and fluids. (b) Tapping-mode AFM— Measures topography by tapping the surface with an oscillating tip. This eliminates shear forces which can damage soft samples and reduce image resolution. Tapping-mode is available in air and in fluids. This is now the technique of choice for most AFM work. (c) Phase Imaging— Provides image contrast caused by differences in surface adhesion.
and viscoelasticity. (d) Non-contact AFM— Measures topography by sensing Van der Waals attractive forces between the surface and the probe tip held above the surface. It provides lower resolution than either contact AFM or tapping-mode. In order to protect our CNT tip and increase the life time, and at the same time not to sacrifice the resolution, the tapping-mode is applied for CNT tip test.

The superior mechanical properties and unique geometry make individual carbon nanotubes ideal for scanning probe microscopy tips. Atomic force microscopy with carbon nanotube tips allows us to image relatively deep features of the sample surface at nanometer resolution. The angle between the CNT tip and conventional AFM cantilever is a critical issue for carbon nanotube AFM tip application.

In this dissertation, Digital Instruments Veeco Metrology Group Multimode SPM is used to test the individual CNT probe. This instrument is designed to image specimens with sizes no larger than 1.5 cm by 1.5 cm. A series of interchangeable scanners enables the unit to provide images from atomic level to 175 µm in size. The samples are fixed on the top of the scanner. As the scanner moves back and forth, the sample moves with it, allowing the probe to extract information from the sample surface.

3.4.2 FIB process for AFM tip fabrication

The FIB pick-up process discussed in section 3.2.3.2 is a very reliable and controllable process. The CNT tip position can be controlled to within 50 nm. By arranging the angle between the intermediate fiber and the CNT containing fiber, plus the five degree of freedom movement of the FIB sample holder (3 parallel and two rotational), we can make the nanotube
tip perfectly align with the tungsten filament axis or align to any arbitrary direction within 2° of accuracy. Due to the flexibility of the FIB fabrication, and the precise angle arrangement of the nanotube tip orientation, we can also mount our individual CNT tip perfectly perpendicular onto a conventional AFM cantilever.

The detailed pick up process for AFM application is almost identical to the process for field emission tips pick up. It involves first etching a slot on the tip of the micro-manipulator and then moving it to a carbon fiber such that the fiber is resting in the slot. Then platinum metal is deposited at the contact of the fiber and the tungsten tip to form a rigid bond. The beam energy and current are set at 30 keV and 50 pA, respectively, during the deposition process. Then a 40 µm segment of the fiber is cut off from the substrate. Next, we use this intermediate fiber to pick up the CNT-containing fiber. Finally, we put the CNT-containing fiber inside the slot fabricated at the conventional AFM silicon tip pyramid and deposited platinum metal to weld the fiber to the silicon tip. Then, the “intermediate” fiber is cut off from the CNT-containing fiber. The detail steps are shown in figure 22.

Several CNT tips have been picked up as AFM probes. Figure 23 (b) shows an SEM image of the AFM cantilever with CNT tip after FIB fabrication. An enlarged SEM image near the tip of carbon fiber is shown in figure 23 (a). After that, the conventional AFM cantilever with CNT tip is just simply mounted onto the AFM for further testing.
Figure 22 (a) & (b) FIB images of detail CNT pick-up processes as AFM probes
Figure 22 (c) & (d)  FIB images of detail CNT pick-up processes as AFM probes
Figure 22 (e) & (f) FIB images of detail CNT pick-up processes as AFM probes
Figure 22 (g) & (h)  FIB images of detail CNT pick-up processes as AFM probes
Figure 23 SEM images of AFM cantilever with CNT tip
CHAPTER FOUR: EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Field emission experimental results

4.1.1 Field emission from sharpened tungsten tip for reference

Tungsten is widely used as a field emission material. It is easily etched to sub-micron size by electrochemical methods. It is ideal as a reference for the individual CNT field emitter.

The reference tungsten tip is prepared by electrochemical etching method. The DC power supply is set as 10 Volts and the concentration of KOH solution is 1 mol/L.

The SEM image (figure 25 (a)) shows that the radius of the tungsten tip is about 80 nanometer. After the chemical etching, the tungsten tips are cleaned by de-ionized water and mounted on the cathode with conducting silver paint. The tip and anode plane distance is carefully adjusted under the optical microscope. Field emission results are shown by figure 26.

In figure 26, the solid square data were taken at the tip-anode distance \( d = 65 \, \mu \text{m} \). The open circle data were taken under the condition \( d = 205 \, \mu \text{m} \). From the FE I-V characteristics, we can see that with different inter-electrode distance \( d \), the field emission properties are approximately the same. If we use the voltage applied to generate 0.1 nA emission current as the turn on voltage, the turn on voltage is about 230 volts. The SEM image taken after the FE test (figure 25 (b)) showed that the radius of the tungsten tip does not change much, no serious field vaporization occurred. The experimental results show that for the same tungsten tip, the inter-
Figure 24  Schematic diagram of electrochemical etching to prepare tungsten tips
Figure 25  SEM images of the reference tungsten tip
(a) The SEM image taken before the FE testing. (b) The SEM image taken after the FE testing with maximum 20 nA emission current.
Figure 26 FE results from a clean tungsten tip
electrode distance does not affect the field emission properties. This can be explained by simple theoretical considerations below.

In our particular FE experimental setup, the geometry is as follow: the radius of curvature of the emitters \( r = 0.01\text{~}1 \mu\text{m} \), the tip-anode distance \( d = 50\text{~}300 \mu\text{m} \), the size of the anode plane is a couple of millimeters. Compared with \( r \) and \( d \), the anode is large enough to be treated as an infinite conducting plane.

Simulation results show that the electric field distribution at the apex of the field emitter with round whisker shape is approximately the same as that of ideal round metal ball with same curvature.\(^{85,86}\) Now the condition can be simplified as a conducting sphere with potential \(-V\) located in the front of an infinite conducting plane with zero potential, which is shown in figure 27 (a). The electron field near the tip of this round whisk shape emitter can be solved using the image method of the classical electrodynamics theory. Instead of the grounded conducting infinite plane, the image conductive sphere at position \( 2d \) with potential \( V \) can build exact electric field distribution in our interested area, \((0<x<d)\) and also satisfy the boundary condition. It is shown by figure 27 (b).

Since \( d\gg r \), the positive metal ball can be viewed as point charge. This is another solvable condition by electrostatic image method. According to the theory, the electric field then is equivalent to that due to three point charges:

\[
Q_1 = -Vr, \quad x_1 = 0, \quad Q_2 = \frac{-Or}{2d}, \quad x_2 = \frac{r^2}{2d}, \quad Q_3 = Q, \quad x_3 = 2d
\]

The electric field on the \( x \) axis for \( r<x<d \) can be described by equation (15):

\[
E = \frac{Q_1}{(x-x_1)^2} + \frac{Q_2}{(x-x_2)^2} + \frac{Q_3}{(x-x_3)^2}
\]
For the local electric field at the apex of the sharp tip, \( x \) is approximately equal to \( R \). Consider \( d \gg R \), the results can be further simplified as

\[
E = -\frac{V}{R} - \frac{Q}{R} \frac{d}{R^2} + \frac{Q}{R^2} \left( \frac{x}{2d} \right) \]

It means that the local electric field that is responsible for the field emission at the apex of a sharp tip is only related with the applied voltage and the tip radius. It is independent to the tip-anode distance \( d \).

Now we can plug equation (17) into equation (13)

\[
\ln \left( \frac{I}{V^2} \right) = \frac{\alpha \cdot \phi^2 \cdot R}{V} + \text{const}
\]

Here \( R \) is the radius of the tip. By plotting the \( \ln(I/V^2) - 1000/V \), the linear curve fitting slope should be equal to:

\[
\text{Slope} = \frac{\alpha \cdot \phi^2 \cdot R}{1000}
\]

Again \( \alpha = -\frac{4}{3e} \left( \frac{8\pi^2 m}{h^2} \right)^{\frac{1}{2}} \approx 6.82 \times 10^9 \)
Figure 27  The image methods for estimation of the local electric field at the apex of a sharp tip in front of the plane anode
For tungsten the typical number of $\phi$ is 4.5 eV. From the linear curving fitting slope, the R can be calculated as:

for $d = 65 \, \mu m$, the fitted slope is equal to 4.1 which corresponds to a radius of $R \sim 50 \, nm$. For $d = 205 \, \mu m$, the fitted slope is equal to 3.2, which corresponds to a radius of $R \sim 60 \, nm$. The results obtained from the FE experiment are very close to the value $R = 80 \, nm$, obtained by the SEM images.

### 4.1.2 Field emission from individual CNT tip

After FIB pick up process, the individual CNT field emitter is mounted on the FE setup for the measurement. A CNT-containing carbon fiber is fabricated on a 50 $\mu m$ tungsten wire chemical etched to a conical shape with a radius of curvature of 1 $\mu m$. The carbon nanotube sticks out as the tip of the fiber. Typically, the diameter of the carbon nanotube is about 20 to 50 nm; the length is from 0.1 to 10 $\mu m$. The diameter of the carbon fiber is about 1$\mu m$ and the length can be various from 5 $\mu m$ to 50 $\mu m$.

Figure 28 shows the zoomed in and zoomed out SEM images of the individual CNT field emitter. In this particular CNT field emitter, the diameter of the nanotube is about 48 $nm$, the length is about 3$\mu$m, and the diameter of the carbon fiber is about 1.4 $\mu m$.

Figure 29 (a) and (b) show the FE I-V characteristics of the individual CNT emitters. In this case, the tip-anode distance is 150$\mu$m and the chamber vacuum is $10^{-7}$ torr. The field emission data show the conditioning effect. When we initially increase the applied voltage, the turn on voltage is around 140 volts. Then the applied voltage is increased to around 200 volts and the emitting current reached up to 100 nA. The highest emitting current is kept at 100 nA to
Figure 28  SEM images of individual CNT emitter

(a) The zoomed in image shows the detailed geometry of the CNT tip. (b) The zoomed out image shows the field emitter.
Figure 29  FE results from individual CNT emitter

The square data is due to the conditioning effect. After that, the round data and triangle data are repeatable.
prevent possible damage of the CNT emitting tip. After keeping the emitting current at this level for 5 minutes we turned off the applied voltage gradually and then turned it on again. The turn on voltage for the CNT emitter then decreased to 120 volts, the I-V data are more stable compared with the first test circle and can be repeated very well as shown by the solid circle data and solid triangle data. This can be explained by the conditioning effect. Just before the CNT tip is transferred into the vacuum chamber, contamination can occur at the apex of the CNT emitting tip. Submicron particles can be absorbed on the tip. When the CNT tip first started to emit electrons the adhesive contaminants will evaporate at the same time. The evaporation procedure made the I-V characteristics unstable and unrepeatable. After keeping the CNT emitter operating at 100nA for a few minutes, the submicron particles are totally vaporized and the emitting properties become much more stable.

In order to calculate the field enhancement factor of the CNT tip “only” from the experimental data, the local electric field $E_0$ at the apex of the carbon fiber without the presence of carbon nanotube tip has to be estimated first. Due to the complicate geometry of the combination of the carbon fiber and the tungsten wire, $E_0$ is difficult to calculate accurately. Fortunately its magnitude can be estimated by using equation (17) $E_0 = V / R$, here $R = 0.7 \, \mu$m is the radius of the carbon fiber. The electric field $E$ around the CNT tip, which dominates the field emission, can be expressed as $E = \beta E_0$, or $E = \beta V / R$. Here $\beta$ is the field enhancement factor due to the CNT tip itself. Now equation (13) can be written as

\begin{equation}
\ln \left( \frac{I}{V^2} \right) = \frac{\alpha \cdot \phi^3 \cdot R}{V \beta} + \text{const}
\end{equation}

\begin{equation}
\text{Slope} = \frac{\alpha \cdot \phi^3 \cdot R}{1000 \beta}
\end{equation}

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The slope from the linear curve fitting is 2.7±0.2

For carbon material, the work function is about 5 eV. It gives

$$\beta_{\text{experimental}} = \frac{a \cdot \phi^2 \cdot R}{1000 \cdot \text{slope}} = 20$$

Based on the equation (14), the field enhancement factor $\beta$ of the CNT emitter with $l = 3 \, \mu\text{m}$ and $r = 24 \, \text{nm}$ can be calculated as

$$\beta_{\text{theoretical}} = 1.2 \times (\frac{l}{r} + 2.15)^{0.9} = 90$$

Or alternatively, we can use the estimation we obtained above—equation (17). The local electric field around the apex of the CNT tip and the carbon fiber can be estimated as $E = V/r$ and $E_0 = V/R$ respectfully. Therefore

$$\beta = \frac{E}{E_0} = \frac{R}{r} \approx 30$$

Again, here $R = 0.7 \, \mu\text{m}$ is the radius of the carbon fiber and $r = 24 \, \text{nm}$ is the radius of the CNT tip. Still, the experimental result is smaller than the theoretical estimation.

There are several reasons why the experimental value is smaller than the theoretical estimation. CNT prepared by low temperature CVD method has poor crystallinity and defects. The local electric field is responsible for the field emission. The defects tend to affect the local field distribution and weaken the field at the emitting apex. As a result, the experimental value always reflects the non-ideal reality, while theoretical estimation gives ideal upper bond. Under the high emission current, the defects also work as heating resistances and burn the nanotube shorter and shorter. Because of the nanosize of the CNT, the current density in the CNT is
extremely high even though the emission current is only about 100nA. In this case, the diameter of the emitting CNT tip is about 50 nm. For the emitting current of 100 nA, the current density of the MWNT is as high as $10^4$A/cm$^2$. From the theoretical simulation result of the CNT enhancement factor equation (14), smaller tip length $l$ will result smaller field enhancement factor.

One thing is worth to be pointed out. Here the field enhancement factor is due to the CNT tip itself, excluded the enhancement fact of the sharp tungsten tip. Considering our millimeter electrode sizes, the field enhancement factor due to the whole SNT field emitter is in the range of 100,000.

Experimental results also showed that at large emission currents, the CNT tip can be irreversibly damaged. After keeping the CNT tip at 10 $\mu$A emitting current for 10 minutes, (the emitting current density is as high as $10^6$A/cm$^2$) the nanotube tip burned away totally. The SEM images clearly showed that the nanotube tip is evaporated after the high emission current treatment.

The SEM image taken after the field emission experiment shows that the micron sized carbon fiber and the welding junction of the fiber and the tungsten wire always survived the high emission current treatment even when the CNT tip burned away. The carbon fiber and the welding junction are mechanically stronger than the nanometer sized CNT even though their Young’s modulus are much smaller than that of CNT. It also indicates that the conductivities of the carbon fiber and the welding junction from the FIB process are good and Joule heating is tolerable even under the high emitting current condition.
Figure 30 SEM images of the CNT emitter (a) before and (b) after high emission current

(a) After low emission current but before the high emission current. (b) After the high emission current
After the CNT tip burned away, we measure the resistance of the whole setup without the nanotube tip by adjusting the inter-electrode distance \( d \) to zero and making the carbon fiber directly contact the mirror polish screw surface. The total resistance including the contact resistance measured was about 2000\( \Omega \).

Compared with the W tip, the CNT field emitter showed better FE properties. Due to the sharper tip radius, the initial turn on voltage is almost half as low as that of tungsten tip. After the conditioning cycle, the FE current is more stable and larger emitting currents can be droved from the individual CNT tips. No FE degradation observed at 100 nA emitting current for CNT emitters. Yet for tungsten tip, The SEM image shows that it already partially burned away under the same emitting current.

Recent research results show that damages and degradations to the CNT field emitters were mainly due either to mechanical failure of the contact between the CNT and the metal support or heating of the contact resistance between the CNT and the metal support\(^6\). Our FIB assisted fabrication of individual CNT emitters showed good contact between the CNT tip and metal support. In our test, The CNT emitters never failed due to mechanical failure or heating of the contact between CNT and metal support. In our case, the failure was mainly due to the evaporation of the nanotube itself. We suspect that this could be due to the relatively poor vacuum we have in the vacuum chamber.
Figure 31  Partially burned away W tip
The SEM image is taken after 100nA 5 minutes treatment.
4.1.3 Field emission from the curved CNT tips

During the pick up process, the CNT tip can be bent either by the CNT-containing fiber breaking process or the FIB pick up process. When breaking the CNT containing fiber, the large mechanical forces applied for carbon fiber breaking may be the cause of the CNT tip bending. In the FIB pick-up process, the CNT bending may be due to the accidental exposure to ion beam bombardment. Individual carbon nanotubes can be bent even after exposing under the ion beam with a beam current of 500pA for a few seconds. We also observed the electron field emission from the curved CNTs.

In figure 32, the SEM image of a curved CNT tip is shown. The loop radius is about 300 nm. The curved CNT field emitter is mounted in the same FE setup for the field emission test. The field emission results obtained from this curved CNT tip are shown in figure 33. The tip anode distance \(d\) is kept as \(d = 150 \mu\text{m}\) and the emission current is in the range of 1nA~100nA. Again when the curved CNT emitter was first transferred into the vacuum chamber the conditioning effect was observed which is shown by data a. After the conditioning effect, the I-V characteristic can be repeated very well. From the \(\ln(I/V^2)\) vs. \(1000/V\) graph, we can see that the I-V characteristic satisfy the FN relationship very well. During the FE experiment, extremely low turn on voltage around 50 volts was observed. To obtain emission current 100 nA, the applied voltage is only about 70 volts.

After several testing circles, the applied voltage was increased so that larger emitting current as high as 5μA was achieved. The curved CNT field emitter was kept at this operating condition for about two minutes and then the applied voltage was reduced so that the emission
Figure 32  CNT loop one
The loop radius $R \approx 300$ nm
Figure 33  FE characteristics of CNT loop one
Figure 34 FE characteristics of CNT loop two
Figure 35  SEM images of CNT loop two
current was decreased to 1nA ~ 100nA range. The purpose of keeping the CNT loop under high emitting current for a short time is to try to burn the CNT partly away so that a single CNT tip emitter can be obtained. It was found that the I-V characteristic changed and it can be repeatable very well. The new I-V characteristic is shown by Figure 34.

The SEM image taken after the emission experiment shows the detailed geometry of the CNT loop emitter after high emitting current treatment. Under the high local electric field, the bent CNT is straightened and partially burned away. The high local electric field will induce electric dipoles inside the CNT body. They tend to align with the same direction of the high local field. It forms another CNT loop with a much smaller radius R~40nm. The I-V FE properties shown by figure 34 are the direct results from the field emission of the smaller CNT loop emitter.

The I-V characteristics obtained from the smaller CNT loop are similar compared to those of the larger CNT loop. The linear curve fitting slopes obtained from the FN plots have almost the same value for the two CNT loops. The field enhancement factor of the CNT loops can be calculated by equation (19) from the linear curve fitting slopes obtained from the FN plot. For the larger CNT loop,

$$\beta_{\text{experimental}} = \frac{\alpha \cdot \phi^2 \cdot R}{1000 \cdot \text{slope}} = 34$$

For the smaller CNT loop,

$$\beta_{\text{experimental}} = \frac{\alpha \cdot \phi^2 \cdot R}{1000 \cdot \text{slope}} = 31$$

Here R~ 0.4 µm is the radius of the carbon fiber.

It means that the field enhancement effect for CNT loops with the same diameters but different loop radii are almost same. It can be explained that the field enhancement effects are
due to the geometry of the emitters, in the case of CNT loops, the diameter of the CNT and the loop radius. Since the CNT diameter is smaller than the loop radius by at least a factor of two, it is the dominant factor. For the CNTs with same diameter but different loop radius, the geometry field enhancement effects are almost the same.

The turn on voltage for the smaller CNT loop emitter is only about 40 volts, smaller compared with the larger loop’s 50 volts and much smaller compared with the CNT tip’s 120 volts. That is probably due to the fact that the turn on voltage is related the work function of emitting material, which is associated with the band structure. The band structure of the heavily bent CNT is quite different from that of the ideal CNT side wall so that the work function is dramatically decreased. It is easier for electrons to escape. The voltage required for generating the same emission current will also be smaller.

4.2 AFM application results

After the individual CNT tip is mounted on the conventional AFM cantilever, it is ready for AFM testing. Figure 36 shows the SEM zoomed in and zoomed out images of the CNT scanning tips under test. It includes a conventional AFM cantilever with a pyramid tip. The micron sized carbon fiber with a nanotube tip is fabricated on the top of the pyramid tip. The CNT tip is perfectly aligned vertically with the AFM cantilever. The CNT radius is about 20 nm and the length is about 150 nm. We choose a shorter CNT tip for AFM applications because it is stiffer than a longer CNT tip. Our experiences indicate that the life time of the CNT tip is usually longer. In order to protect the CNT tip without sacrificing the image resolution, AFM tapping mode is used for the experimental test.
Figure 36  SEM images of CNT tip as AFM probe
For comparison, we also use a brand new conventional silicon tip from digital instrument for the same test. The sample is a standard AFM calibration sample. In the tapping mode, the AFM cantilever is first tuned to its resonance frequency. The fiber piece fabricated on the AFM silicon tip will change slightly the total mass of the cantilever. As a result, the resonance frequency of the cantilever with CNT tip is slightly smaller compared with the conventional silicon tip because of the additional mass added on.

### 4.2.1 Force curve comparison

The force curves are obtained by first approaching the scanning tips to the testing sample surface, after the tip touches the surface, it is pulled back. The interaction force of the tip-surface along with the tip-surface distance is automatically recorded. When using tapping mode, the image resolution is as good as using contact mode. It is also good for the life time of the CNT tip. Yet the tip-sample interaction force which is shown by the force curve is not very clear. In tapping mode, the cantilever with the CNT tip is vibrating with its resonant frequency. Instead of showing the tip-sample interaction force, the force calibration plot shows the vibration amplitude of the cantilever. It does not show the force between the tip and sample directly. Yet in contact mode, there is no additional AC signal to drive the cantilever to vibrate in its resonance frequency. The force curve gives the direct information of the interaction force. It can be used to test the tip-surface interaction force with careful tip engagement even for tapping mode.

Figure 37 shows force curve comparison results. The Y component shows the deflection of the cantilever. It is directly proportional to the interaction force between the scanning tip and the sample surface based on Hook’s law. The X component shows the Z height of the tip, which
Figure 37  Force curve comparison
reflects the distance between the tip and the sample surface. Figure 37 (a) shows the force curve when trying to engage the cantilever with the CNT tip to the sample surface and then pulling it back after touching. Figure 37 (b) is obtained from the new standard silicon tip. There is a huge peak when we try to retract the silicon tip after it touching the calibration sample surface. The peak is due to the attraction force between the silicon pyramid body and the sample surface. Yet the same peak shown in the CNT force curve graph is much smaller. This means that it is really the nanotube tip touching the sample surface instead of the micron sized carbon fiber because the body of the nanotube tip itself is very small; the attracting force between the sample surface and the CNT should be relatively small.

**4.2.2 Resolution comparison**

An AFM with CNT tip allows us to image relatively deep features of a sample surface with nanometer resolution because of its sharp tip radius and high aspect ratio.

Figure 38 shows the AFM image comparison results obtained by CNT tip and conventional silicon tip. It is clear that the images obtained from the flat sample surface have no observable difference between silicon and CNT tips. But at the sharp trench edge, the difference is more obvious. In our AFM testing experiment, the radius of the nanotube tip used is about 10 nanometer, which is about the same size as that of a conventional silicon tip. Therefore we can hardly tell the difference these two images. Yet due to the unique geometry of the CNT tip, i.e. the high aspect ratio, there is a definite advantage in using CNT tips to image a sharp step in a sample. Figure 38 shows the step-height comparison when the scanning area is further zoomed in
Figure 38  Resolution comparison
Figure 39  The cross-section comparison of the sharp edge
to the sharp edge of the trench. From the step-height comparison, we can see that a small step at the sharp edge can be detected by the CNT tip, yet the same step did not show up in the image scanned by conventional silicon tip. Because of the high aspect ratio of the CNT tip, it is able to detect the details of this sharp edge. For the conventional silicon tip, the image of the same edge is convoluted by its pyramid shape. The small step is mashed in that artificial image and can not be observed.

4.2.3 Life time comparison

The excellent mechanical properties of an individual CNT make its life time longer than that of the conventional silicon tip. CNT tips are more flexible, therefore the risk of CNT tips being damaged when scanning rough sample surfaces is dramatically reduced. For our unique fiber-CNT tip geometry, the outer carbon layer is a perfect natural protection for the nanotube tip core, which can further increase the lifetime of the CNT tip. Also during the pick up process, with the assistance of SEM identification, we choose shorter nanotube tip lengths for AFM testing, since for a shorter CNT tip, it is stronger, and usually the life time is longer.

Figure 40 shows the scanning tip life time comparison results. Figure 40 (a) shows the CNT tip before the sample scanning. Figure 40 (b) shows the sample CNT tip after 2 hours of continuous scanning. Figure (c) is the SEM image of a new silicon tip before scanning and figure 40 (d) is the same tip after one hour of continuous scanning. After two hours continuous scan, the shape of the CNT tip did not show any obvious change. Yet the conventional silicon tip is completely blunted after only one hour of continuous scan. The results show that without the
Figure 40  Life time comparisons of CNT tip and Si tip
resolution degradation, the life time of the CNT tip for AFM could be much longer compared with that of the conventional silicon tip.

4.2.4 AFM images scanned by curved CNT tips

During the FIB fabrication, curved CNT tips are also picked up to use as the AFM tips. Figure 41 shows the SEM images of an AFM cantilever with a curved CNT tip. The curve radius is about 0.4 µm. During the AFM test, the standard calibration sample with trench space 1µm is used for the test. The width of the trench is only 0.5 µm. Figure 42 shows the AFM images scanned with curved CNT tip. First, the calibration sample is oriented that the trench is parallel with the nanotube curve; the image is shown by Figure 42 (a). The calibration sample is then rotated 90 degree. The result is shown in Figure 42(b). The AFM image is rotated 90 degree to compare with Figure 42 (a). When the nanotube curve is parallel with the trench, it can still reach the bottom of the trench. It should be noted, the trench does not show exactly the square shape. The reason is that the CNT curve and the trench are not exactly parallel to each other. When the sample is rotated with 90 degree, the CNT curve is perpendicular with the trench. The radius of the CNT curve is about the same dimension as the size of the trench. Therefore, the curved CNT tip can hardly reach the bottom of the trench and the calibration sample shows almost no steps at all.
Figure 41 SEM images of an AFM cantilever with a curved CNT tip
Figure 42 AFM images scanned by the curved CNT tip

(a) The CNT curve is parallel to the trench. (b) The CNT curve is perpendicular to the trench.
CHAPTER FIVE: CONCLUSION

5.1 Achievement

In this dissertation, a novel technique based on the focused ion beam technology was developed to fabricate individual CNT probes. The individual CNT tips can be orientated in any direction. They can be easily aligned to a desired direction within 1~2 degrees. In the fabrication, only mechanical forces are involved in the process. It is quite reliable and controllable. Due to the flexibility of the FIB technique, the CNT tip can be fabricated on any geometry of solid materials. In this dissertation, individual CNT tips are successfully fabricated on both clean tungsten wires for FE applications and on conventional AFM cantilevers as AFM probes.

5.1.1 Achievement from individual CNT field emitter

As field emitters, the CNT tips show excellent properties. Because of the small tip radius curvature, the field enhancement factor is very large. The direct benefit is that the turn on electric field and operating voltage are dramatically reduced. The mechanical and chemical stabilities make CNTs more likely to survive under high emitting current and electrostatic forces due to the high surface field even under relatively low vacuum. In our particular CNT field emission experiments, a field enhancement factor $\beta \sim 20$ is observed for the CNT tip itself. It is slightly smaller than the computational prediction. If counting the whole CNT field emitter, a $\beta$ as high as 100,000 has been achieved. In the mean time, a turn on voltage as low as 120 volts was achieved in the FE experiment from straight individual CNT tips. In this dissertation,
electron field emission from the sidewall of individual CNTs was first observed. Extremely low turn on voltages of 35 volts was achieved in a CNT FE experiment with a curved CNT tip.

FIB assisted fabrication also provides better CNT electrode contact, since the CNT is the core of the outer carbon fiber layer. The electric and mechanical contacts between the CNT and the carbon fiber outer layer are near optimal. The rigid contact made by FIB welding between the micron size carbon fiber and the tungsten wire is strong and also has good conductivity. The results show that the contact resistance is less than 2000Ω. The mechanical strength and low resistivity of the rigid contacts helps them remain intact under high emission current, resistive heating, and intense electric static force. No contact failure was observed in our entire study. The failure of the CNT emitter in our case is only due to the quality of the CNT tip itself.

5.1.2 Achievement of individual CNT tip as AFM scanning tip

With the 5 nm position precision of the scanning ion beam and full orientation of the FIB sample stage, the full CNT orientation alignment can be easily achieved by the FIB technique. It has great advantages in AFM scanning tip applications. It is well known that the orientation of the scanning tip is a very critical issue. Good orientation alignment helps to eliminate artificial sample surface structures during image acquisition. During the FIB assisted individual CNT scanning tip fabrication, only mechanical forces are involved for the attachment and alignment; no electric force or magnetic force is required. The AFM cantilever is not required to be pre-coated to improve the conductivity. Therefore, the fabrication procedure is simplified. The detailed FIB fabrication processes also self-prove that it is reliable and controllable. No multiple
tips will be produced and the tip length can be controlled by the CNT tip selection under the observation of SEM.

AFM with CNT tips show significant improvement compared with conventional silicon tips in many distinctions such as reliable images and long life times. The high aspect ratio of the CNT tip provides it with the ability to eliminate the artificial features especially at some sharp edges. It helps to achieve more trustworthy images from specimen with rough surfaces. The excellent mechanical properties of CNTs make them easier to survive during the sample scan. As a result, compared with the conventional silicon tips, the life times of the CNT scanning tips are much longer. For our unique fiber-CNT tip geometry, the outer carbon layer is a perfect natural protection for the nanotube tip core, which further increases the lifetime of the CNT tip.

5.2 Research improvement

5.2.1 FIB instrument improvement

The FIB instrument applied in this dissertation is FEI 200 single ion beam from FEI Company. The ion beam is applied both for the fabrication work and the imaging process. Yet due to the high momentum of the ion beam, even during the imaging process, it can damage the CNTs. The damage will result in structural changes of the CNT, affecting the electric and mechanical properties of the CNT. It will have an effect on the individual CNT field emission properties measurements and lower the threshold of the maximum emission current. The structural change may also shorten the lifetime of the CNT tip in the AFM scanning tip application or even be the reason of the CNT bending and not being suitable for AFM
application. To minimize this negative effect, SEM is used to identify the targeting CNT tip and during the FIB pick up process, the CNT tips are always kept outside the screen, which is the ion beam scanning area, with great care. It makes the process nontrivial. Fortunately, it is easy to be improved by using the FIB dual beam system. An electron beam with same energy of the ion beam has much smaller momentum due to the smaller mass. It can hardly cause the structural change of the CNT tip. The electron beam can be used for CNT tip identification and image acquisition. The focused ion beam is applied for fabrication. The CNT tip identification and the fabrication can then be carried out in the same working chamber. It will simplify the sample preparation for the FIB fabrication and simplify the FIB fabrication steps. Much time and effort can be saved and the potential damage of the CNT tip due to the ion beam bombardment can be greatly reduced.

5.2.2 CNT tip improvement

The CNT core is prepared by low temperature CVD technique. There are always defects and decrystallization. During the FE experiments, they tend to affect the local electric field distribution and lower the field enhancement factor $\beta$. They also work as heating resistance, burning the CNT tip away. It is the failure mechanism of the individual CNT field emitter. The low temperature CVD defects will also harm the mechanical properties of the CNT tip as the scanning tip of AFM. The lifetime of the CNT tip will become shorter.

To minimize the defects and improve the quality of the CNT tip, other optional method such as arc discharge can be applied for the synthesis of carbon nanotube cores. Because of the high temperature (as high as 3500 °C), the CNTs prepared by arc discharge method have few
defects and can be used as the CNT core. Subsequently, conventional chemical deposition method can be used to prepare the carbon fiber outer layer. It is believed that individual CNT field emitters with few defects will have larger field enhancement factors and higher thresholds for the field emission current can thus be achieved.

Another major improvement that can be done is that instead of using MWNT, individual SWNTs can be applied as the tips. Compared with MWNTs, SWNTs have even smaller diameter. The diameter of a typical SWNT is only about 1~4 nm. In the FE applications, individual SWNT emitters will result in higher field enhancement factors and the turn on voltages will no doubt be smaller. In addition, the single graphite layer of the SWNT extremely simplifies the theoretical simulation work. In AFM applications, the scanning tips made by MWNTs can only provide similar resolutions compared to conventional silicon tips. The resolution will be improved to the atomic level with the application of the SWNTs as AFM tips.
APPENDIX: LABVIEW DATA ACQUISITION
LIST OF REFERENCES


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