Carbon nanofibers on plastic substrates : characterization and applications

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Carbon Nanofibers on Plastic Substrates: Characterization and Applications

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To Sherry, Jin Cheng and our beloved parents.

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Summary

Carbon nanofibers (CNFs) as a promising candidate for field emitters have attracted a lot of attention from the research community, due to its low field emission threshold, high aspect ratio, good chemical stability and excellent mechanical strength. Although many applications involving field emitters on planar substrates have been reported, there are only a few reports on the physics and applications of CNF based emitters grown onto flexible plastic substrates. This thesis aims to address the issues on the fabrication; characterization, reliability and applications of the CNF based field emitters on flexible polyimide film. In addition, this thesis is also devoted to study the characteristics of a single CNF in order to understand the field emission properties at sub 100 nm gap regime, its field emission noise, electrical and physical properties. The results may have significant implication on the design of vacuum nano-devices such as compact high-power frequency devices.

The CNF film on plastic substrates was prepared by an ion beam technique. Argon ions were bombarded onto carbon-coated substrates at room temperature, inducing conical protrusions of around 0.2 ~ 0.5 μm in length which possessed a long CNF of 0.3 ~ 5 μm in length and 10 ~ 30 nm in diameter. The CNFs were also abundant and uniformly distributed. The threshold field of the CNF film is around 3 V/ μm at a current density of 1 $\mu\text{A}/\text{cm}^2$; with a high field enhancement factor of ~ 3000.

The field emission mechanism of a single CNF at sub-100 nm regime has been investigated over a range of anode to CNF tip separations (S) of 20-5500 nm. The results show that the field enhancement factor (γ) is associated with the electrode separation and γ approaches to an asymptotic value of 415 or 1 when S is very large or

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very small as compared to the length of the CNF, respectively. The field emission noise characteristic of a single CNF at various interelectrode distances was found to follow $1/f$ behavior over a bandwidth of 0.01–5 Hz. The CNF nanostructure shows excellent flexibility, and is robust, as it remains intact on the substrates even after subjected to a high electrical field. The maximum field emission current density sustained by the single CNF without causing damage was estimated to be as high as $7.5 \times 10^9 \text{ A/m}^2$.

The reliability of the CNFs grown on flexible plastic substrates was evaluated by bending the CNF film at various stress conditions. The flexible CNF film remains extremely robust under various stress conditions and shows no sign of degradation even after 16 h long lifetime test. An all-plastic flexible CNF field emission device with excellent emission properties was demonstrated using phosphor-coated polyester as an anode, which allows field emitter of any shapes to be made, certainly opened up a new frontier for future novel field emission devices.

The flexible CNF film was also utilized as a multi-purpose ionization gas-sensing device by configuring the CNF film as diode structure with a Cu plate as a counter electrode. The lowest breakdown voltage for air, Ar, N₂, He, N₂O, O₂ and C₂H₂ is 400, 270, 490, 215, 540, 574 and 613 V with 5% of variations, respectively. For a fixed applied voltage of 700 V, the ionization current of the device exhibits two regions of linearity with respect to gas pressure below and above 5 Pa, suggesting that the device can be employed as a vacuum ion gauge. The gas ionization device is very robust even after more than 1 month of repeated operation and with virtually no signs of failure. Employment of the CNF film provides flexibility and could be configured in different emitter shapes for novel gas-sensing purposes.

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In addition, x-ray generation was demonstrated using the flexible CNF film as an electron source. The emitter showed resilience when exploited as a high voltage electron source for x-ray generation. The x-ray generated by the flexible emitter is capable of delivering fine images of biological samples with superior sharpness, resolution, and contrast. The flexible emitter has the potential to be applied in innovative x-ray radiotherapy and radiography applications.

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Abbreviations

Abbreviations

FE	Field Emission
TE	Thermonic Emission
ϕ	Work Function
E_f	Fermi Level
FEAs	Field Emitter Arrays
F_{on}	Threshold Field
CVD	Chemical Vapor Deposition
CNTs	Carbon Nanotubes
CNFs	Carbon Nanofibers
TEM	Transmission Electron Microscopy
ITO	Indium–Tin–Oxide
S	Interelectrode Distance
F	Barrier Field
FN	Fowler-Nordheim
F_m	Macroscopic Field
γ	Field Enhancement Factor
CT	Computed Tomography
MBFEX	Multibeam Field Emission X-Ray Source
TWT	Traveling Wave Tube
FESEM	Field Emission Scanning Electron Microscopy
PTFE	Polytetrafluorethylene
EDX	Energy-Dispersive x-ray
ED	Electron Diffraction

Abbreviations

AFM	Atomic Force Microscope
STM	Scanning Tunneling Microscope
APFED	All-Plastic Field Emission Device
CCD	Charge-Coupled Camera
MFC	Mass Flow Controller
FEL	Free Electron Laser
THz	Terahertz
SPR	Smith–Purcell Radiation

Chapter 1 Introduction

1.1 Background

1.1.1 Vacuum Microelectronics

Electronic devices are constantly shrinking in size for higher speed and more compactness; and sooner or later, the world of solid state electronics may eventually be saturated, and the size of conventional integrated circuits cannot be minimized any further.¹ Search for an alternative method is necessary, and novel nanoscale materials (e.g. carbon nanotubes) based on electron emission may prove to hold the key for tomorrow's nanoelectronics.² The area of electron emission has therefore been infused with new life due to the emergence of "*Vacuum Microelectronics*".³ This is a new branch of microelectronics based on electron emission that is different from solid-state microelectronics, whereby the electron transport in semiconducting solids is done by scattering while vacuum microelectronics relies on the ballistic motion of electrons in vacuum.²

One of the key processes in vacuum microelectronics is the generation of free electrons to vacuum, mostly by field emission (FE) or thermionic emission (TE). TE is based on a hot filament whereby it is heated to a high temperature ($> 1000\text{ }^{\circ}\text{C}$) so that the electrons have sufficient energy to overcome the work function (ϕ) of the material and escape to vacuum. On the contrary, FE requires no heating; and electrons at Fermi-level

(E_f) can escape to vacuum under the influence of a high-applied field. Besides being power efficient (requires no heating), FE is also better than TE in many ways i.e., instantaneous response to field variation,³ low electron energy spread of 0.45 eV,^{4,5} high current density⁶ and resistance to radiation and temperature fluctuation.² Due to all these attributes, FE sources have been considered the best option for vacuum microelectronics devices.²

1.1.2 Development of Field Emitter Arrays

FE usually requires a very large local field of 3000-4000 V/ μm in order to obtain useful current for FE applications.⁷ The usual way of obtaining this high local field is to use a very sharp tip.⁸ With the advent of micro-fabrication techniques, the first microtip field emitter arrays (FEAs) made of materials of high melting point (e.g. molybdenum or tungsten) known as Spindt-type FEAs, was developed in the late 1960s.⁹ Subsequently, silicon microtip arrays were introduced,⁸ and these developments of the microtip soon lead to the successful demonstration of FE displays prototype,¹⁰⁻¹² which proved to be a significant milestone in the usage of microstructure field emitters in vacuum microelectronics device.

1.1.3 The Emerging of Carbon based Materials

Even though there was success in demonstrating a FE display prototype based using the FEA microtips, the fabrication of FEAs over a large area has proven to be a difficult and expensive process, and a more manufacturing-friendly process for making the cathodes is needed.^{13,14} In addition, FEAs are too highly susceptible to surface contamination,⁸ poor environmental stability³ and high threshold field (F_{on}) which made

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them very unreliable and poor power efficient.^{3,8} The search for novel new materials for better and more reliable performance is therefore desired.⁸

In seeking appropriate material, large-area electron emission from carbon-based materials^{3,15-18} expanded lately due to its electron affinity lower than that of Mo and Si, thus providing a lower F_{on} .^{19,20} In fact *Baker et al.* in 1972 had already noted that graphite fibers showed better environmental stability than several metals suggesting that carbon based materials are uniquely suited as stable field emitter.²¹ Besides performing better than any other metal tips, carbon-based materials are chemically inert,^{3,22} and have high mechanical strength.^{13,22} In the literature, favorable FE properties have been reported from different carbon based materials namely: chemical vapor deposition (CVD) diamond,²³ amorphous diamond-like carbon,^{24,25} CVD graphite,²⁶ nanostructured carbon,²⁷ nanocomposite carbon,²⁸ polymers,²⁹ and in particular, carbon nanotubes³⁰ (CNTs) and carbon nanofibers³¹ (CNFs) showing the most promising FE characteristics.³²⁻³⁶

1.2 Motivations and Objectives

CNF is a very promising candidate for field emitters^{32,33,37,38} due to many of its excellent properties, such as high aspect ratio,^{33,39-43} low F_{on} ,⁴⁴⁻⁴⁹ tough mechanical properties⁵⁰⁻⁵² and good chemical stability,⁵³⁻⁵⁵ creating significant amount of attentions. There have been numerous reports on the fabrication and synthesis of CNFs.⁵⁶⁻⁶² However, most of the fabrication methods required high processing temperature and were constrained to grow on substrates that can withstand high temperatures, which are often rigid.⁶³ In recent advancement of fabrication techniques, CNF film can be deposited on

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flexible plastic/polymer substrates, using methods such as plasma enhanced CVD,^{64,65} solution-based method,⁶⁶ electrophoretic method,⁶⁷ and ion beam method.⁶⁸⁻⁷¹ The ion beam method for growing CNFs is employed in this research. This method is much more favorable than the rest of the synthesis techniques as it is a room temperature process, required no catalyst, and selectively grown in large area substrates.

There are numerous advantages of using flexible substrates, among many, are lower cost of producing the emitter and allowing emitter of any geometry and shape to be made for use in FE applications.⁴⁴ However, to realize the dream of flexible robust FE devices, the reliability and FE characteristics of the flexible CNF emitters must be addressed.

Also, from the perspective of incorporating single CNF electron emitter in vacuum nano-devices, the mechanism of FE from a single CNF must be investigated. Although there have been some studies on FE from single CNT or CNF at interelectrode distance down to 120 nm,^{40,72} there have not been any research until the present one to study the mechanism of FE in sub-nanometer regime gap.⁷³

In addition, for better design of cold cathode devices, the FE noise, electrical and physical characteristics of the single CNF must also be investigated. There have been studies conducted for the performance of the single CNT in terms of FE noise fluctuations,⁷⁴ maximum FE current density that it can sustain before failure⁷⁵, field induced electrostatics phenomenon,⁷⁶ and electrical transport properties,^{77,78} these information are not readily available for single CNF. The characterizations of a unique nanostructure consisting of a CNF grown on a conical base by the ion beam sputtering technique will provide interesting information for such investigations.

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This thesis is attempted to deal with the above issues. The main objectives of this thesis are:

1. To characterize the CNF films grown on plastic substrates.
2. To study the FE mechanism of a single CNF in sub-100 nm gap.
3. To characterize a single CNF in terms of FE noise stability, maximum current density, electrical and its field induced electrostatics properties.
4. To study the reliability of the flexible field emitters under stressed conditions and to demonstrate an all-plastic field emission device.
5. To investigate the ionization based gas-sensing capability of the CNF film.
6. To demonstrate x-ray generation using flexible CNF film as electron field emitters.

1.3 Major Contributions

The main contributions of this work are as follows:

1. Demonstration of excellent FE properties in CNFs on plastic substrates grown by the ion-beam technique. The excellent FE properties are related to the unique structure of the CNF and its conical base.
2. The FE mechanism of a single CNF was investigated for the first time with interelectrode separations from 20 nm to 5500 nm. The field enhancement factor was found to be associated to the interelectrode separation, which follows a modified Miller model at a large range of interelectrode separations.

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3. The noise, electrical and physical characteristics of a single CNF were studied and characterized. This information provides essential characteristics of the CNF nanostructure grown using an ion beam sputtering technique.
4. It is the first time that an all-plastic flexible field emission device with superb emission properties has also been demonstrated using phosphor-coated polyester as an anode. The all-plastic field emission device exhibited outstanding reliability under various stressed conditions.
5. The feasibility of a multi-purpose ionization gas-sensing device based on CNFs on plastic substrates was studied. The multi-purpose gas sensor shows great robustness with a wide range of gas sensing capability.
6. X-ray generation was demonstrated using CNF-based flexible field emitters showing images of superior sharpness, resolution and contrast.

1.4 Organization

The dissertation begins with Chapter 1, which describes the background, motivation and the objectives of the research. The main contributions of the thesis are also presented in this chapter.

The literature review of the CNFs is described in Chapter 2, which includes the characteristics, structure and applications of the CNF material.

The main part of the thesis begins in Chapter 3, with the characterization of the flexible CNF film.

Chapter 1 Introduction

The characterization of a single CNF is discussed in Chapter 4. This chapter probes into the FE mechanism at sub-100 nm gap regime, FE noise, electrical and physical characteristics of a single CNF.

Chapter 5 explores the reliability and stability of the flexible field emitters under various stress conditions. The demonstration of the all-plastic based field emission device is also described in this chapter.

Chapter 6 presents the demonstration of multi-purpose ionization gas sensing devices using the flexible field emitters. Chapter 7 deals with the application of flexible field emitters for x-ray generation.

The thesis ends in Chapter 8 with a summary of the main conclusions and recommendations for further research.

Chapter 2 Literature Review

2.1 Structure of CNF

CNF is one type of carbon nanostructures that are cylindrical or conical structures in shape. CNFs have diameters varying from a few to hundreds of nanometers with lengths ranging from less than a micron to millimeters.³¹ Like CNT, the carbon atoms in CNF are arranged in sp^2 bond.⁷⁹ This distinct structure introduces a significant change in the electronic density of states, thus producing distinctive properties for these carbon nanostructures.^{31,80} Although both CNF and CNT are based on the same sp^2 -bonded hexagonal network of atoms, there are some structural different in both types of nanostructures. A CNT is generally a sheet of graphene, i.e. a sheet of hexagonal network of covalently bonded carbon atoms or a single two-dimensional layer of a three dimensional graphite rolled up into a cylinder,³¹ while CNFs comprised of modified graphene sheets in different arrangements that are disordered and resembled carbon filaments.³¹ However, the main distinguishing characteristic of CNF from CNT can be simply a hollow structure classifying as a CNT, and a solid structure for a CNF, as seen from a transmission electron micrographs (TEM) presented in Fig. 2-1.⁸¹

Figure 2-1 TEM micrographs of CNTs and CNFs. (a) CNT, (b) CNF, (c) high resolution TEM of CNT showing a hollow structure, (d) high resolution TEM of CNF revealing the solid structure in CNF.⁸¹

2.2 Growth of CNFs on Plastic Substrates

Traditionally, field emitters were constrained to grow on substrates that can withstand high temperature due to the high processing temperature required.⁶³ Replacing the rigid substrates will certainly enable a number of unique applications; for example, in displays, photovoltaics, and macroelectronic systems.⁸²⁻⁸⁶

In recent years, several research groups have reported the fabrication of carbon nanostructures on plastic substrates for flexibility purposes. *Ma et al.* reported the growth

Chapter 2 Literature Review

of CNT film on polyimide substrates using an electrophoresis technique.⁶⁷ The polyimide (coated with titanium) was used as the cathode and a stainless steel plate was used as the anode during electrophoresis. The two electrodes were placed into a bath with solvent consisting of grinded CNT powder. By applying a 100 V dc across two electrodes for around 1-2 min, CNTs could be subsequently deposited onto the polyimide substrates, producing however unaligned and randomly distributed CNTs.⁶⁷ *Choi et al.* used a solution-based method⁶⁶ to coat CNTs onto indium tin oxide (ITO) coated polyethylene terephthalate film at temperature of ~ 150 °C. Despite giving a flexible structure, this approach also does not produce aligned CNTs needed for more practical applications (i.e., vacuum microelectronics).⁶⁴ More recently, *Hofmann et al.* managed to demonstrate aligned CNFs onto polyimide substrates using plasma-enhanced CVD at a low temperature of 120 °C.⁶⁴ Nevertheless, this method needed a catalyst layer for the growth of the CNFs.⁸⁷ It seems that all these efforts generally resulted in a number of issues namely: impurity materials, involve expensive chemicals, complex experimental procedures, unaligned nanostructures, and requirement of catalysts to control their growth, making the growth of CNF/CNT on plastic substrates expensive and complicated. Exploring much simpler, catalyst-free, room-temperature method of synthesizing aligned carbon nanostructures on plastic is therefore necessary.

It is known that energetic ions are an excellent tool for the creation of nanostructures on a surface or in the surface-near region of any kind of solid at room temperature.⁸⁸ Ion beam sputtering technique has proved to entail the formation of nanosized ripples, pyramids, conical protrusions and whiskers structures of carbon, Si and Au.^{68,89-91} Therefore, ion beam sputtering technique may offer the possibility to solve the problems

presented by other fabrication methods for growing carbon nanostructures on plastic substrates as described earlier. Thus, ion beam sputtering method of synthesizing CNFs on plastic substrates is being exploited in this study. More details about the ion beam sputtering technique as a controlled process to fabricate CNF emitters on plastic substrates will be presented later in this thesis.

2.3 *Field Emission from CNFs*

2.3.1 Field Emission Mechanism

The basic mechanism of field emitters is based on FE. FE is a quantum-mechanical phenomenon due to the wave-like properties of electrons. In this phenomenon, a potential barrier confines the electrons to the solid, where the height of the potential barrier is given by ϕ . Under a high-applied field, the width of their barrier becomes thinner (i.e. smaller than 2 nm),⁷ and the electrons close to the E_f can tunnel through the barrier and escape. This can be seen with the help of Fig. 2-2, which presents a diagram of the electron potential energy at the surface of a metal.

Figure 2-2 Diagram of the potential energy electrons at the surface of a metal.⁹²

The dashed line in Fig. 2-2 shows the shape of the barrier in the absence of an external electric field. The height of the barrier is equal to ϕ of the metal, which is defined as the energy required removing an electron from the E_F of the metal to a rest position just outside the material (the vacuum level). The solid line in Fig. 2-2 corresponds to the shape of the barrier in the presence of the external electric field. As can be seen, in addition to the barrier becoming triangular in shape, the height of the barrier in the presence of the barrier field, (F) is smaller, with the lowering given by⁹³

$$\Delta\phi = \left(\frac{eF}{4\pi\epsilon_0}\right)^{1/2} \quad (2.1)$$

where e is the elementary charge and ϵ_0 is the permittivity of vacuum. Knowing the shape of the energy barrier, one can calculate the probability of an electron with a given energy tunneling through the barrier. Integrating the probability function multiplied by an electron supply function in the available range of electron energies leads to an expression for the tunneling current density, J (A/m²) as a function of F . The tunneling current

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density can be expressed by Eqn. (2.2), which is often referred to as the Fowler-Nordheim (FN) equation.^{94,95}

$$J = \frac{e^3 F^2}{8\pi h \phi^2(y)} \exp\left(\frac{-8\pi(2m)^{1/2} \phi^{3/2}}{3heF}\right) v(y) \quad (2.2)$$

where $y = \Delta\phi/\phi$ with $\Delta\phi$ given by Eqn. (2.1), h is the Planck's constant, m is the electron mass, $t(y)$ and $v(y)$ are the Nordheim elliptic functions: to the first approximation $t^2(y) = 1.1$ and $v(y) = 0.95 - y^2$. Substituting these approximations in Eqn. (2.2), together with Eqn. (2.1) for y and values for the fundamental constants, one obtains^{94,96}

$$J = \frac{1.54 \times 10^{-6} F^2}{\phi} \exp\left(\frac{10.4}{\phi^{1/2}}\right) \exp\left(\frac{-6.44 \times 10^9 \phi^{3/2}}{F}\right) \quad (2.3)$$

J can also be expressed in term of current (I) if the emitted area (A) is known, i.e., $J = I/A$, and Eqn. (2.3) can take the form:

$$I = A \frac{1.54 \times 10^{-6} F^2}{\phi} \exp\left(\frac{10.4}{\phi^{1/2}}\right) \exp\left(\frac{-6.44 \times 10^9 \phi^{3/2}}{F}\right) \quad (2.4)$$

Eqn. (2.4) applies strictly to temperature equal to 0 K. However, it can be shown that the error involved in the use of the equation for moderate temperatures (~ 300 K) is negligible.⁹⁷

2.3.2 Field Enhancement Factor

Field enhancement factor (γ) is a very important parameter in FE mechanism. In a geometrical configuration resembling a parallel-plate capacitor, the macroscopic field (F_m) is defined by

$$F_m = V/S \quad (2.5)$$

where, V is the voltage applied across a gap or interelectrode distance (S). The F is the field close to the emitting surface (within 1-2 nm of the surface atoms), which determines

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the barrier through which field-emitted electrons tunnel. F is typically around 10^7 V/cm for metal with flat surface,⁹⁸ and is often significantly higher than F_m . To reach this value, one takes advantage of the γ : the electric field lines are concentrated around a sharp object, which is defined by the ratio of barrier field and the macroscopic field,^{7,99}

$$\gamma = F/F_m \quad (2.6)$$

and

$$F = \gamma V/S \quad (2.7)$$

From Eqn. (2.4) and Eqn. (2.7), it is obvious that γ is related to the FN equation.⁹⁵ By substituting Eqn. (2.7) into Eqn. (2.4), the emission current (I) can be expressed in terms of γ and S , so that:

$$I = A \frac{1.54 \times 10^{-6}}{\phi} \left(\frac{V}{S}\right)^2 \gamma^2 \exp\left(\frac{10.4}{\phi^{1/2}}\right) \exp\left(-\frac{6.44 \times 10^9 \phi^{3/2} S}{\gamma V}\right) \quad (2.8)$$

By taking natural logarithm of Eqn. (2.8), the FN equation can be expressed as,

$$\ln \frac{I}{V^2} = \ln \left[A \frac{1.54 \times 10^{-6} \gamma^2}{\phi S^2} \exp\left(\frac{10.4}{\phi^{1/2}}\right) \right] - \frac{6.44 \times 10^9 \phi^{3/2} S}{\gamma V} \quad (2.9)$$

and fitting the experimental I-V data to a FN plot (i.e., $\ln(I/V^2)$ versus $1/V$), will yield the estimated value of γ from the slope of the FN plot by assuming a value for ϕ and knowing the value of S .

Various physical causes of field enhancement can exist, but the simplest is a conducting microprotrusion or nanoprotrusion of a large aspect ratio (the ratio of height over the radius). CNFs like CNTs have atomically sharp tips and large aspect ratio ($>10^3$) and, as a result, much larger γ than the conventional emitters, i.e., the Spindt-type tips thus offering a lower F_{on} .¹³

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Experiments have shown that the F_{on} of CNTs and CNFs defined at a current density of 10 mA/cm^2 are at a range from $4\text{-}9 \text{ V/}\mu\text{m}$,^{34,100} significantly lower than the values reported for other electron emissive materials (Table 1). Compared to diamond emitters, CNFs and CNTs are much more stable at high current. These properties make the CNTs/CNFs attractive for technological applications such as vacuum microelectronics.⁸

Table 1 Threshold fields of different types of emitters at a current density defined as 10 mA/cm^2 .³⁵

Materials	Threshold Electrical Field (V/ μm)
1. Mo Tips	50~100
2. Si Tips	50~100
3. P-type semiconducting diamond	130
4. Undoped, defective CVD diamond	30~120
5. Amorphous diamond	20~40
6. Graphite powder	17
7. Nanostructured diamond	3-5 (unstable $>30 \text{ mA/cm}^2$)
8. CNT / CNF	4-9 (stable at $>1 \mu\text{A/tube}$)

Although the aspect ratio is an important feature of γ , experimental results do suggest that γ varies with S , especially when S get very small i.e. $S \ll$ effective height of the emitter. *Miller et al.* (known as Miller model) formulated the relationship of γ with tip length and S , which can be expressed as,¹⁰¹

$$\gamma = \gamma_{\infty} \frac{S}{S+h} \quad (2.10)$$

where γ_{∞} is the field enhancement factor at distant field (i.e. $S \gg h$), and h is the effective height of the emitter. This equation suggests that γ decreases with S and approaches zero as S becomes very small. However, γ should approach unity (no field enhancement) when the separation is much smaller (i.e., $S \ll h$) since the geometry

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approaches that of two opposing infinite planes (parallel plates), effectively eliminating geometric field enhancement. Hence, *Hii et al.*¹⁰² includes a unity term to the so-called modified Miller equation so that,¹⁰²

$$\gamma = \gamma_{\infty} \frac{S}{s+h} + 1 \quad (2.11)$$

can be used to describe the behavior of γ better. In a detailed simulation done by Edgcombe and Valdré, the value of γ_{∞} can be estimated using the expression,⁹⁹

$$\gamma_{\infty} \approx 1.2 (h/r + 2.15)^{0.9} \quad (2.12)$$

for $4 \leq h/r \leq 3000$ and r is the emitting radius. The computed γ as a function of h/r is illustrated in the fitted line of Fig. 2-4. Eqn. (2.12) is based on the assumption of a 'hemisphere on a plane' model⁷ as shown in the inset of Fig. 2-3.

Figure 2-3 Computed field enhancement factor as a function of tip height/radius. The geometry of tip and anode is shown schematically in the inset.

In the ‘hemisphere on a plane’ model, the hemisphere is used to describe the geometry corresponding to a CNT cathode, and the plane is used to simulate a flat anode.^{7,99}

2.4 Factors Affecting Field Emission Characteristics

For any practical application, a low F_{on} and prerequisite of the long-term stability of the emitting films must be fulfilled.¹⁰³ The longest test up-to-date on FE of CNT film has been performed by *Saito et al.*, who reported an increase of 11% of the applied field to maintain an emission current of 10 mA/cm² during 8000 h.⁹⁸ In this section, a review of some of the factors affecting FE characteristics will be provided which includes screening effect,¹⁰⁴ multistage effect,¹⁰⁵ Joule heating¹⁰⁶⁻¹⁰⁹, mechanical stress^{75,76} and its FE noise characteristic.^{74,110-112}

2.4.1 Screening Effect

FE display normally requires a large current density of 1 - 10 mA/cm².^{100,113} One of the obvious ways to increase the current density is to increase the density of the field emitters, however this was not the case as reported by *Nilsson et al.* during his observations from different densities (low, medium and high) of CNT films with respect to the respective FE current density.¹⁰⁴ It was reported that a dense carbon nanostructure does not actually give the highest FE current density due to the screening effect.¹⁰⁴ This effect comes into play as soon as several emitters are assembled close together, creating electrostatic interferences between the neighboring emitters. Therefore, the configuration yielding the largest current density will often not be the situation with the highest density of nanostructures. It is an ideal compromise where the length of the tubes and the

distance between neighboring emitters are both sufficient to reach a high γ , along with an emitter density that is high enough to ensure homogeneous emission at low voltage. This optimum value for spacing individual vertically aligned tubes is reported to be twice their height for minimizing field-screening effect¹⁰⁴ as shown in Fig. 2-4.

Figure 2-4 Illustration of the optimum CNT spacing for minimizing screening effect.

In order to eliminate or reducing screening effect, some groups reported lowering the concentration of catalyst mixture in order to control the CNT/CNF density.^{104,114} This method however produced only “curly” non-aligned CNT/CNF. *Teo et al.* demonstrated the controlling of the density of CNF/CNT using plasma enhanced CVD by either varying the process parameters i.e., gas ratio, catalyst material or by patterning the catalyst.^{34,115} The CNFs produced by patterning the catalyst is the most promising in controlling the carbon nanostructures’ density, as uniform arrays of free-standing aligned CNT/CNF could be deposited at precise locations as demonstrated in Fig. 2-5 (c). It is advantageous that the CNFs are uniform and well spread so that the screening effect from adjacent CNFs are minimum.³⁴ From the FE results for different CNF densities (i.e., densely packed CNFs, sparse forest of CNFs and array of individual CNF), it is evident

that the patterned array of individual vertically aligned CNFs has the most desirable FE characteristics, i.e. highest γ , as seen in Fig. 2-6.

Figure 2-5 SEM images of CNF film. (a) Densely packed forest of CNFs containing 10^9 nanofibers/cm². (b) Sparse forest of CNFs containing 10^7 nanofibers/cm², and (c) array of individual, vertically standing CNF, well spaced apart, at twice its height.³⁴

Figure 2-6 FE results from the dense forest, sparse forest, and array of CNFs of Fig. 2-5.

Inset showing the corresponding FE plots.³⁴

2.4.2 Multistage Effect

It is well known that the aspect ratio and/or the geometry of the field emitter greatly affect the FE characteristics.^{7,99} Huang *et al.* reported a giant γ of 18,800,¹⁰⁵ from single carbon nanostructure grown on a commercially available carbon cloth by a thermal CVD technique.¹¹⁶ The F_{on} of 0.4 V/ μm for a current density of 1 mA/cm² was believed to be the lowest reported F_{on} for carbon-based nanostructures at this point of writing.¹⁰⁵ The reason for this high γ is attributed to a multistage structure of the carbon nanostructures, which can lead to a very large γ at the tip of the smallest nanotube in the chain, and

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consequently to a very strong FE. In the case of a multistage structure (i.e., 3 different stages) as exemplify in Fig. 2-7, the total field enhancement, (γ_{total}) for the multistage structure can be computed to be the *product* of the field enhancement factors of individual stages,¹⁰⁵ i.e., $\gamma_{total} = \gamma_A \times \gamma_B \times \gamma_C$.

CNF grown using an ion beam sputtering technique will be able to benefit from a large γ due to its multistage structure consisting of a conical base with an ultra long CNF.⁶⁹

Figure 2-7 Illustration of a nanostructure having multistage geometry that is made up of 3 stages i.e., A, B and C with its corresponding field enhancement factors: γ_A , γ_B and γ_C .

2.4.3 FE Noise Characteristics

Monitoring stability and performance of field emitters is becoming increasingly important for vacuum microelectronic devices. Measuring low-frequency noises in such devices (the $1/f$ noise being the dominating component) can be a good indicator to monitor these parameters.¹¹⁷ In the investigation of current fluctuation or noise performance at room temperature, the noise power spectral density are often used to study the $1/f$ noise of an electron emitter.¹¹⁸ The noise power spectral density function $S_n(f)$ of the $1/f$ noise is proportional to $1/f^b$, where b normally lies within the range 0.7–1.5.¹¹⁹ In recent years, there have been reports on $1/f$ noise characteristic in several different field emitters, i.e., tungsten tip, diamond film, ZnO nanostructure and CNT.^{74,118,120,121} For example, in the study of noise in the tungsten field emitter, *Timm et al.* found that the $S_n(f)$ revealed a $1/f^{3/2}$ characteristic. This was believed to be due to the presence of impurity atoms of low ϕ from residual gases diffusing over the emitter's surface.¹²⁰ In the case of ZnO nanowires, *Dong et al.* also observed similar $1/f^{3/2}$ behavior implying that the noise characteristic could be similar to tungsten field emitter.¹¹⁸ However, in recent studies on noise performance of CNT, *De Jonge et al.*⁷⁴ reported $S_n(f)$ following a $1/f$ behavior, suggesting that noise mechanism in CNT could be different from tungsten tip or ZnO nanostructure emitters⁷⁴

2.4.4 Mechanical stress and Joule Heating

Bonard et al. reported that a small externally applied voltage of a 1–4 V could charge and deflect the CNT as shown in Fig. 2-8 (b) and 2-8 (c). This caused the induced charge to be distributed at the tip of the CNT, resulting in the deflection of the CNT.⁷⁵ The deflection could be strong enough to rip the CNTs from the surface of the substrates, and

affecting their FE characteristics.⁷⁵ The emitter-substrates contact is therefore a mechanical weak point in emitters grown on planar substrates.^{75,122} In addition, if there is a high enough applied field,⁷⁵ the CNT could be brought to complete destruction caused by resistive heating or Joule heating as shown in Fig. 2-8 (d). This will eventually degrade the FE characteristics. Joule heating was first reported by *Purcell et al.* due to local intense heating of up to 2000 K induced by high FE current.^{106,123} This phenomenon defines the upper limit for the FE current that can be obtained from an individual nanostructure before the nanostructure either became rupture or completely destroy.

Figure 2-8 (a)-(d) SEM micrographs of a nanotube of 4.56 μm in length and 5 nm in radius at (a) 0, (b) 2, and (c) 4 V applied voltage before and (d) after destruction of the tube at a high applied field.⁷⁵

2.5 Field Emission based Applications

Since the discovery of CNTs, there is also a considerable amount of interests in other carbon nanostructure such as CNFs. The high aspect ratio, small tip radius, and other remarkable physical properties of the CNF make them a very unique material with a whole range of promising FE applications.¹²⁴⁻¹³¹ In the following sections, the potential FE applications of CNT/CNF are reviewed.

2.5.1 Field Emission Display

In recent years, a lot of progresses have been made in using carbon-based field emitters for FE display. Several groups have investigated their application as electron emitters in FE displays.^{12,132} Most recently *Choi et al.* from Samsung demonstrated a fully sealed 4.5 in. three-color CNT FE display that has 128 addressable lines and works in diode configuration as exhibited in Fig 2-9 and 2-10. Subsequently, *Lee et al.* presented the working prototype for a 9 inch FE display.¹³² These FE display structures usually consist of two sets of glass plates: CNT stripes on the patterned cathode glass and phosphor-coated ITO stripes on the anode glass, separated by a 200- μm spacer. By applying a potential difference of a few kV across the cathode (CNT) and the anode (phosphor coated ITO), field-emitted electrons will accelerate toward the anode and cause the generation of light through excitation of the cathodoluminescent phosphor. An image can be obtained by addressing selectively the different positions of the matrix, which can either be monochrome or in color if each pixel is divided in red, blue and green sub-pixels.

Figure 2-9 Schematic diagram of a field emission display setup.¹²

Figure 2-10 The Samsung 4.5 in. full-color CNT field emission display.¹²

2.5.2 X-Ray Tube

X-ray sources are widely used in industrial, medical, and scientific instruments. The traditional method of generating x-rays is based on TE. It comprises of a metallic filament (cathode) that acts as a source of electron when it is heated resistively to a very high temperature. The accelerated electrons (that are emitted) are bombarded on a metal target (anode) to generate x-rays. However, x-ray system using a thermionic electron emission cathode normally requires a water-cooling system due to heat converted from input power, thus making it difficult to construct a compact one.^{129,133} X-ray sources using FE cathodes on the other hand have several intrinsic advantages over the thermionic x-ray tubes,¹³⁴ including low operating temperature,¹³¹ fast response times,^{127,135} and no heating needed.¹³¹ Utilizing the advantageous characteristics of the carbon-based FE emitters, miniature x-ray sources¹³⁶⁻¹³⁹, pulsed x-ray sources^{129,140} and micro computed tomography (CT) based x-ray sources¹⁴¹⁻¹⁴³ have been developed, showing much improved performance, for both industrial and medical applications.^{131,136-}

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For example, *Sugie et al.* used CNTs grown on a tungsten wire as a primary electron source. They showed that even at a moderately low pressure of 2.66×10^{-5} Pa, the CNT could have a stable operation for more than 1 h and enabled the acquisition of clear x-ray images.¹⁴⁴ *Zhang et al.* then reported a compact and efficient x-ray source built in a diode configuration using the CNTs grown on a tungsten wire.¹³¹ Compared to the exposure time of 1 h for the preliminary x-ray tube,¹⁴⁴ the working efficiency of the x-ray tube improves remarkably which resulted from the diode design.¹³¹ *Yue et al.* also reported a x-ray source using CNT on a planar metal disc that can readily produce both continuous

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and pulsed x rays with a programmable waveform and repetition rate.¹³⁴ A total emission current of 28 mA was obtained from a 0.2 cm² CNT cathode. The x-ray intensity is shown to be sufficient to image a human extremity at 14 kV and 180 mA. Pulsed x-ray generation with a repetition rate greater than 100 kHz was readily achieved by programming the gate voltage.

In more recent advancement, several groups have revealed the concept of micro-CT x-ray imaging using multibeam FE x-ray source (MBFEX).^{127,141-143}

Figure 2-11: Schematic diagram of the multi-beam x-ray imaging system. It includes a MBFEX source, a sample stage, an x-ray area detector, and a computer workstation.¹⁴²

The MBFEX source is comprised of a field emitter array with five CNT emitting pixels that can generate a scanning x-ray beam as shown in Fig. 2-11. It is capable of

generating a scanning x-ray beam to image an object from multiple projection angles without mechanical motion. As demonstrated, the device could provide a cathode current of 100 μA at 40 kV with less than 300 μm focal spot size from each of the emitting pixel.¹⁴² Since no mechanical motion is needed and the electronic switching time is generally negligible the MBFEX system has the potential to simplify the system design and lead to a fast data acquisition for tomographic imaging.

2.5.3 Gas Sensor

Gas sensors operate by a variety of fundamentally different mechanisms.¹⁴⁵⁻¹⁵⁶ Ionization sensors¹²⁶ work by fingerprinting the ionization characteristics of distinct gases, but they are limited by their huge, bulky architecture, high power consumption and risky high-voltage operation. *Modi et al.* first reported the use of CNTs for ionization gas sensor.¹²⁶

The CNT ionization sensor made use of their nanometer scale tip radius ($r < 15 \text{ nm}$); that generate very high electric field at relatively low voltage, creating very high nonlinear electric field near the tips.^{7,33,99,157} Therefore lowering breakdown voltage several-fold in comparison to traditional electrode. This hastens the breakdown process due to formation of a 'corona' or conducting filament of highly ionized gas that surrounds the CNT tips.¹²⁶

Figure 2-12 Schematic setup of sensor showing CNT film as the anode, 180 μm thick glass insulator plates, and Al plate as cathode

This CNTs based ionization device (Fig. 2-12) was used to detect the identity of several gas species, i.e., helium, argon, nitrogen, oxygen, carbon dioxide, ammonia and air. It had been shown that different gases exhibited different unique breakdown voltages. The unique breakdown voltage provides the ‘fingerprint’ for the gas to be identified.

126,145,149

The use of CNTs based ionization device can thereby enabling compact, battery powered and safe operation of such sensors, which could be deployed for a variety of applications, such as environmental monitoring, sensing in chemical processing plants, and gas detection for counter-terrorism.¹²⁶

Besides employing carbon nanostructure as a gas detector based on gas ionizations, *Bower et al.* recently demonstrated the fabrication and characterization of an on-chip electron-impact ion source based on CNTs electron source as an integrated cold cathode vacuum gauge.¹⁵⁸ The device was made of a cathode with aligned CNTs, a control grid,

and an ion collector electrode. Its operation as a miniature vacuum ion gauge was also shown to be at a higher operating pressures range than traditional ion gauges.

2.5.4 High Power frequency Devices

Although solid-state technology dominates the market of power components for frequencies up to a few GHz,¹³⁰ vacuum tube technology demonstrates a recognized superiority for devices combining high frequency operation, high power output and high efficiency.¹⁵⁹ Traveling wave tubes (TWT), based on thermionic cathodes are however bulky and heavy, and take up valuable space and weight budget in a satellite, and any miniaturization of the current TWT would give rise to cost savings in a satellite launch, and aid the implementation of micro-satellites.⁸

The most effective way to reduce the size of a TWT is via direct modulation of the e-beam, for example, in a triode configuration. Cold cathodes with the ability of being modulated at high frequencies do not presently exist. 'Spindt Tip' technology does not perform well because of the high capacitance caused by the spacing between the cathode and grid which is filled with an insulator (typically SiO₂ or Al₂O₃), and hence could only be used to provide the primary beam of a TWT.¹²⁵

In the case of carbon nanostructure, the grid can be located at an extended distance 10–100 microns from the emitters where the space between emitter and grid is vacuum with a consequent reduction in grid/cathode capacitance of the order of 20–50 times, allowing for high frequency operation of the grid.¹²⁵ However, to be competitive with thermionic cathodes, the CNT cathode should deliver current densities in the range 1–2 A/cm²; in real terms, a few milliamperes of directly modulated current is required which can be accelerated over a few kilovolts to the anode to give the tens of watts

required in a telecommunications amplifier. CNT film with aligned CNTs are preferred over 'spaghetti' (unaligned) type CNTs, as unaligned CNTs cannot produce the emission current densities required.¹²⁵

Figure 2-13 Schematic of a CNT based vacuum microwave amplifier based on a RF triode.¹²⁵

*Milne et al.*¹²⁵ described a CNT-based vacuum microwave amplifier using aligned arrays of CNTs. A schematic of a triode type amplifier is shown in Fig. 2-13. The vacuum microwave amplifier is based on the modulation of the high FE current from the CNT array to the anode to give the tens of watts required in a telecommunications amplifier. The high current densities that can be extracted from the aligned CNT array made this CNT based amplifier feasible.⁸

Chapter 3 Characterization of CNF films on Plastic Substrates

3.1 Introduction

The integration of low-dimensional nanomaterials with polymeric substrates provides a diverse set of properties for the development of flexible novel vacuum nano-devices. The lightweight, excellent electrical, optoelectronic and piezoelectric properties of conductive nanotubes and nanobelts act to dramatically increase the functionality of low-cost polymer substrates and have the potential to enable low-cost flexible electronics.^{160,161} As a result, these general features are driving efforts to develop revolutionary low-cost flexible vacuum nano-devices from nanomaterial building blocks. Of the nanomaterials, which can be integrated with polymer substrates, CNT and CNF are especially attractive due to their, tough mechanical strength, high thermal conductivity and superb FE properties.¹⁶⁰

However, the fabrication of CNT/CNF often requires a high processing temperature, which significantly limits the choice of substrate materials and fabrication processes.⁶³ Although recent efforts by many groups⁶⁴⁻⁶⁷ resulted in the synthesis of CNT/CNF films on flexible substrates as elaborated in Chapter 2, these development generally resulted in complex experimental procedures, needed expensive chemical and unaligned carbon nanostructures, making the growth of carbon nanostructures on plastic substrates expensive and complicated. In this dissertation, a much simpler ion beam sputtering method is being employed. This method is much more favorable than the rest of the

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synthesis techniques as it can produce aligned carbon nanostructures at room temperature, required no catalyst, selectively growth of nanostructures and scalable for large area. In addition, this method also resulted in a unique carbon nanostructure that consists of a conical protrusion and an ultra long CNF, which can offer exceptional FE characteristics due to a multistage effect, minimum screening effect and a high aspect ratio. Unless otherwise indicated, all the results presented in this thesis are based on CNF films grown on plastic substrates.

In this chapter, CNFs grown by an ion beam technique on plastic substrates are described. The morphology and structure of the CNFs are characterized. The FE properties of the CNF based flexible emitters are also investigated. These studies will be imperative toward the realization of flexible CNFs based vacuum nano-devices.

3.2 Experimental Details

The CNFs were grown on 140 μm thick commercially available Kapton polyimide foils. For synthesis of CNFs, a layer of carbon-coated film on the polyimide film was bombarded with obliquely incident Ar^+ using Kaufman-type ion gun at room temperature (Iontech. Inc. Ltd., model MPS 3000 FC). The ion beam was focused at an incidence angle of 45° from the normal to the surface. This is because oblique Ar^+ bombardment is more suitable for ion-induced CNF growth than sputtering at normal incidence. The diameter of the Kaufman-type ion gun was 6 cm while the energy of the beam employed was 1 kV. The sample was then irradiated at room temperature for 60 min.

The dimensions and morphology of the CNFs were characterized by the field emission scanning electron microscopy (FESEM, JSM 6340F) at a working vacuum of

3.6×10^{-4} Pa and at electron beam energy of 10 kV. For TEM measurements, the CNFs were scratched from the plastic substrates and directly deposited on a Cu grid covered with carbon film. The detailed study was then carried out by TEM (JEOL JEM-2010) operating at 200 kV, using bright field image and selected area diffraction.

For the FE measurements, an ITO coated glass was used as an anode, which was separated from the CNF-covered cathode by a 100- μ m Polytetrafluorethylene (PTFE) spacer. The tested emission area was 0.28 cm^2 (6 mm in diameter). FE measurements were then carried out in a parallel plate configuration at a base pressure of 1.33×10^{-4} Pa with applied voltages sweeping from 0 to 1200 V. The emission current was measured by an electrometer (Keithley, 6127) and the results were displayed to a computer via LabView user interface.

The Raman spectra were taken with Renishaw micro-Raman spectrometers, equipped with 514.5 nm laser line as the excitation source. The incident laser was focused on the sample through an optical microscope, and the resolution is 1 cm^{-1} .

3.3. Microstructure Characterization

Fig 3-1 (a) shows the SEM micrographs of the CNFs after the ion beam irradiation; the CNF appears to grow on a conical base and inclined at a certain angle. This is due to oblique ion bombardments; many micro-protrusions were created and massive re-deposition of C atoms onto these conical protrusions thus created the CNF. The method of sputtering at an angle is also much higher in efficiency for CNFs grown than sputtering at normal incidence. The oblique sputtering can enhance the formation of surface roughness, thus creating more nucleation sites inducing CNFs growth.⁷⁰ The

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CNFs grown are abundant and uniformly distributed as seen from the Fig. 3-1 (a) with an estimated CNF density of around $\sim 4.5 \times 10^7 \text{ cm}^{-2}$. The CNF structure grown on conical bases is advantageous as each individual CNF has now much more spacing between adjacent fibers, therefore minimizing or diminishing screening effect.¹⁰⁴ The length of the CNF ranged between 0.3 and 5 μm while diameter is estimated at around 10 to 30 nm, growing on conical protrusion of around 0.2 $\sim$ 0.5 μm , as observed in Fig. 3-1 (b). The energy-dispersive x-ray (EDX) spectroscopy shows that carbon is the only element detected. The TEM micrograph shows an individual CNF, which measured approximately 15 nm in diameter as noticed in Fig. 3-1 (c). There was no hollow structure observed in CNF, identifying them as different from CNTs.¹⁶² There is also no clear boundary between a CNF and a conical carbon tip as seen from the TEM micrograph. The electron diffraction (ED) pattern of the top region of the CNF consists of diffused rings indicating the amorphous nature of the CNFs as observed in Fig 3-1 (d). It had been reported that CNTs synthesized by plasma-enhanced CVD at 120 $^{\circ}\text{C}$ were low in graphitization quality.⁸⁷ This information may provide indication that the amorphous nature of our CNF structure may be a feature of carbon nanomaterials grown at low temperatures. It should be also pointed out that no diffraction spot originating from non-carbon materials was detected in the ED, further confirmed the impurity free nature of our CNFs.

Chapter 3 Characterization of CNF films on Plastic Substrates

Figure 3-1 (a) SEM image of the CNF arrays with estimated density of $4.5 \times 10^7 \text{ cm}^{-2}$. (b) High magnification SEM micrograph showing an individual ultra fine CNF. (c) TEM image of a CNF. (d) The corresponding electron diffraction pattern of the CNF.

According to the TEM and SEM images, the overview of the likely growth mechanism of sputter-induced CNF is illustrated in Fig. 3-2. The first step is to induce the nano- to micro-sized surface protrusions on the carbon coated surfaces by ion bombardments at 45° . Enhancing the surface texturing using oblique sputtering by focusing the ion beam at an angle can control the conditions of the protrusions. The protrusions were formed by the re-deposition of sputter ejected carbon atoms from the

surface onto the sidewall of the conical protrusions. These carbon atoms can then diffuse toward the tips during sputtering. The surface diffusion is thought to be the reason for the ion-induced CNF growth.^{68,69,71} Another extra evidence could be inferred from, is the boundary-less structure of the CNF-tipped cone in Fig. 3-1 (c) that CNFs grew via surface diffusion of carbon atoms from the tips of the conical base.

Figure 3-2 Schematic representation of the growth mechanism of ion-induced CNF.

3.4 Raman Spectroscopy

To further examine the possible type of carbon-carbon bond in the CNF, Raman spectroscopy was employed. As seen in Fig. 3-3, peaks are observed at 1595 cm^{-1} indicated the graphitic layers sp^2 bonding (G peak), and at 1355 cm^{-1} corresponded to the sp^3 bonding defective structure (D peak). At closer examination at the region from 1590 cm^{-1} to 1650 cm^{-1} , there is another peak which overlaps with the G peak at 1620 cm^{-1} , which is the D' peak. This D' peak was interpreted by others to be due to discontinuity of

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hexagonal carbon layer planes such as finite crystallite size and also to edge planes of crystallites,^{163,164} which could be well due to the low in graphitization quality of our room temperature grown CNFs. These three peaks corresponded to similar wave number of CNFs observed by *Toyoda et al.*¹⁶⁵

It is well known that the intensity ratio of peak D (I_D) and peak G (I_G) signifies the degree of graphitization of carbon nanomaterials,^{81,165,166} and a smaller than 1 ratio correspond to relative good degree of order and graphitization, such as CNTs.⁸¹ By using the lowest intensity count between these two peaks as the reference point, the relevant structure intensities I_D and I_G can be obtained by integrating the curve along the wave number.¹⁶⁷ The resulting ratio of I_D/I_G for our CNFs was found to be 1.10 confirming the lower in graphitization quality of CNFs when compared to CNTs.⁸¹

Figure 3-3 Typical Raman spectrum of the CNFs film.

3.5 FE Characterization

One of the criteria for good FE properties is to provide a low electron scattering path (low resistance).¹⁶⁸ The resistivity of the CNF films on the polyimide substrates was found to be $2 \times 10^{-2} \Omega\text{cm}$ using a four point probe method, which is comparable to the resistivity of multi-walled CNT film.¹⁶⁹

The I-V measurement of the CNF emitters is presented in Fig. 3-4 (a). It is apparent that the current increases with the applied field in an exponential fraction, as a small change in the applied voltage can cause a large change in the emitted current. The F_{on} to obtain current density of $1 \mu\text{A}/\text{cm}^2$ and $1 \text{ mA}/\text{cm}^2$ were measured to be around $2.8 \text{ V}/\mu\text{m}$ and $8 \text{ V}/\mu\text{m}$ respectively, performing better than what was reported for CNFs grown by plasma-enhanced CVD.³⁴

The γ can be estimated from the emission data by using a FN plot, assuming a value for ϕ and substituting the value of S ($100 \mu\text{m}$ for PTFE spacer). The choice of the value of ϕ is often subjected to controversy, as surface conditions varies greatly among the carbon nanostructures and will affect their ϕ .¹⁷⁰⁻¹⁷² The ϕ for CNF was then taken to be same as graphitic carbon at $\sim 4.5 \text{ eV}$. The value of 4.5 eV agreed well with numerical calculation as reported by *De Jonge et al.*,¹⁷² as well as average experimental results found in measuring a collective of CNTs by a Kelvin probe technique.¹⁷⁰ The typical FN plot is displayed in Fig. 3-4 (b); the F-N plot can be approximately fitted to a straight line, implying that emission current is indeed due to FE mechanism. From the slope of the FN plot, the γ was estimated to be around 3000, confirming the low F_{on} obtained from the I-V characteristics earlier. The γ of the CNFs is similar with γ reported on CNFs grown on graphite plate and CNT grown on Si.^{70,131} This high γ obtained could be due to few

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reasons; (1) the high aspect ratio of the ultra-fine long CNF, (2) minimum screening effects from the well spaced CNFs grown by ion beam sputtering and (3) multistage effect caused by the unique nanostructure consisting of a conical base and a ultra long CNF. These FE qualities of the CNF emitters prove to be valuable for flexible vacuum microelectronics devices.

Figure 3-4 (a) The typical I-V characteristics of the CNF emitters, (b) showing the corresponding FN plot.

3.6 Summary

In summary, CNFs were prepared on plastic substrates by an ion beam technique at room temperature. The length of the CNF is ranged between 0.3 and 5 μm and diameter of around 15 to 30 nm. The CNFs grown on top of a conical base of approximately 0.2 ~ 0.5 μm in length were abundant and uniformly distributed. Raman spectrum of the CNFs confirms that the CNFs were low in graphitization quality. The F_{on} of the CNF films is around 3 V/ μm and 8 V μm at a current density of 1 $\mu\text{A}/\text{cm}^2$ and 1 mA/cm^2 , respectively; with a high γ of ~ 3000 .

Chapter 4 Characterization of a single CNF

4.1 Introduction

The future of molecular electronics lays in our ability to understand and engineer the properties of nanometer scale material such as a single CNT and CNF.¹⁷³ One area of special attention is to exploiting them as miniature electron source in vacuum nano-devices, such as compact high-power frequency devices,¹⁷⁴ which is expected to be more efficient and delivered much higher power than the solid-state counterparts.¹⁷⁵

It is well known that the properties of nanostructures would strongly dependent on their shape, size and its structure.¹⁷⁶ The electrical property of CNT for instance, depends on the helical angle of how the graphitic sheet is being rolled in forming a tube shape structure. However, many reports on carbon nanostructures focus on the properties measured from a large quantity of carbon nanostructures, which represent an average value over all individual nanostructures' properties.¹⁷⁶ For instance, γ value is often an average value among the nanostructures, due to field screening of adjacent nanostructures, and geometrical non-uniformity of the individual nanostructures.¹⁰² Thus, the unique characteristics of individual nanostructure could be shadowed. It is therefore not practical to design vacuum nano-device based on characteristics of large arrays of CNT/CNF. Hence, in order to provide better designs over vacuum nano-device, it is imperative to fully characterize an individual nanostructure. Although there have been some reports on the characteristics of single CNT,^{74,76,176} the studies on the individual CNF are scarce.

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In this chapter, we will present the characterization results of a single CNF measured by a nanomanipulator incorporated inside a FESEM. The following characteristics of the CNF were studied:

- i. FE characteristics at sub 100 nm gap.
- ii. FE noise characteristics.
- iii. Field induced electrostatic force in the CNF.
- iv. The maximum FE current sustained by the CNF without causing damage.
- v. Intrinsic resistance of the CNF nanostructure.

These results will provide important understanding on the physics of the single CNF toward its potential application in vacuum nano-devices.

4.2 Experimental Details

The experiments were carried out in a high vacuum FESEM with a base pressure of 1.33×10^{-5} Pa. Probe tips (Zyvex) of diameter around 200 nm were employed in the experiments (i.e., FE measurements, noise measurements, etc). The probe tip was controlled by a Zyvex nanomanipulator, which had a coarse mode and providing controlled Cartesian motion over large distances (12 mm of travel with 100 nm resolution) and a fine mode for extremely smooth and precise motion (100 μ m of travel with 5 nm resolution). This precise movement of the probe tip made the FE experiment extremely accurate. The employment of the high magnification LEO 1550 series FESEM also facilitate to resolve the interelectrode spacing in nanometer accuracy. The probe tip contains five I/O channels, for specific electrical measurements with the incorporation of

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a Keithley electrometer. The applied voltage for the electrical measurement was provided by a high-stability power supply that is being incorporated in the nanomanipulator.

In FE measurement, the geometry of the anode is important.⁹⁹ Basic assumption of FE mechanism is based on a flat anode,^{95,99} and simulation results have indicated that γ is sensitive to the electrodes geometry.¹⁷⁷ As such the anode with diameter of 200 nm was chosen, which is much greater than the diameter of the CNF so that the anode appears to be flat and will not affect γ .⁹⁶

The FE measurements were carried out in a high vacuum SEM with a base pressure of 1.33×10^{-5} Pa. Two probe tips have been employed in the FE setup. One probe was used as an anode while another one was used as the cathode. The ‘cathode’ probe was contacted to individual CNF (next to the conical base of the CNF) to establish electrical connection while the ‘anode’ probe was on top of the CNF tip, so that there was an interelectrode spacing, S between the CNF tip and the anode. S was varied from 5500 nm to 20 nm and the F_{on} is defined to be 10 nA of the emitted current. To avoid resistive heating caused by a high emission current, a current limit of 1 μ A was imposed.¹⁷⁸ The electron beam of the SEM was being blanked out during the FE measurement in order to shun the effect of electron beam on the FE results.

For the FE noise measurements, a constant applied voltage of 80 V was applied at a sampling rate of 10 Hz for a period of 60 min for two different S (200 nm and 500 nm). The applied voltage of 80 V was chosen so that the emission current was kept below 1 μ A. For measurements of the intrinsic resistance of the CNF and its conical base, the probe tip was manipulated to touch various positions of the CNF. An applied voltage was

subsequently raised from 0 to 20 V. The limit of 20 V is imposed to protect the CNF against resistive heating.¹⁷⁸ From the I-V data, the resistance can then be subsequently calculated.

4.3 Finding a Single CNF

It is important to locate a suitable site for performing the characterizations of an individual CNF. The suitable site should ideally contain just a single CNF or few CNFs that are well spread apart around their vicinity. This criterion is needed to avoid interferences from surrounding CNFs (i.e., field screening effect),¹⁰⁴ and to provide the probe tip with more free space to maneuver. For instance, if there are too many CNFs packed too closely near a chosen site, the probe tip can easily short other CNFs while performing characterizations on an individual CNF; since the substrate is at 0 V (grounded).

As our CNF film has a densely population of around $\sim 4.5 \times 10^7 \text{ cm}^{-2}$ as observed from Fig 3-1 (a) in Chapter 3, it is intricate to locate a single CNF or well separated individual CNF. A good method to find such a location is to first find a site with a particle resided on it as indicated by the 'Box' as shown in Fig 4-1 (a) and 4-1 (b). Then, by sweeping the probe tip across the particle, the particle could be removed and an open site could be uncovered as shown in Fig 4-1 (c). Majority of the CNFs situating below the particle, together with the particle will be removed through the sweeping action. A clean area is now exposed with a handful of CNFs as displayed in Fig. 4-1 (c). As seen in Fig. 4-1 (d), one of these sites as highlighted in white arrow contains a single CNF and can be selected for further measurements.

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Figure 4-1 SEM micrographs on method to locate a single CNF. **(a)** A resided particle on the CNF film as indicated by the 'Box', **(b)** magnification of the particle resided on the CNF film, **(c)** removal of the particle revealing a 'clean area', **(d)** magnification of the clean area consisting handful of CNFs as indicated by the white arrow, **(e)** location of a single CNF, and **(f)** magnification of the single CNF.

4.4 FE of a Single CNF at Sub-100 nm

Prior to the FE experiment, a single CNF was located without any CNFs in the vicinity using the method outlined in the previous section. The isolated single CNF has an effective height of 1 μm inclusive of the CNF tip and its conical base as exhibited in Fig. 4-2 (a). The diameter of the CNF is around 16 nm as estimated by Fig 4-2 (d).

Figure 4-2 (a) SEM micrograph of an isolated single CNF and an anode probe. (b) Schematic diagram of the specimen orientation and field emission setup inside the SEM, (c) and (d) are the SEM micrographs of anode and CNF tip with separations of 100 and 20 nm, respectively.

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Fig. 4-3 (a) illustrates the current versus applied field for various S . As S decreasing, F_{on} is getting larger as shown in Fig. 4-4 (b) inferring a diminishing γ . The F_{on} is increased from 15 to 1250 V/ μm as S reduced from 5.5 μm to 20 nm. The FN plots for various S are illustrated in Fig. 4-3 (b). Most of the FN plots can be fitted very well by a straight line indicating the FE of the single CNF follows the FN law.

Figure 4-3 (a) Emission current against applied field as a function of S . **(b)** FN plot for various S . Fit is to a FN theory.

Fig. 4-4 (a) shows the experimental γ values obtained from the FN plots as a function of S . The γ value is falling asymptotically from 360 to 5 when S decreases from 5.5 μm to

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20 nm. As γ is approaching unity, the CNF and the anode are approximately a parallel plate. From the data in Fig. 4-4 (a), it is clear that Eqn. (2.11) fits the data well, and it yields a value of γ_{∞} equal to 415 for a known emitter height.

The total effective height of the CNF and its conical base is taken to be 1 μm . The radius of the CNF is 8 nm. Using these values and Eqn. (2.12), the γ_{∞} is determined to be 94 which is much less than the value obtained using Eqn. (2.11). The discrepancy could be due to the fact that our emitter is having a multistage geometry (i.e. the CNF is on the tip of the conical protrusion). *Huang et al.*¹⁰⁵ has shown that the γ of emitters with a multistage structure is a product of the individual field enhancement factors of individual stages as explained in Chapter 2. In this regard, the γ of the conical base and CNF is computed using Eqn. (2.12) to be 6 and 69, respectively. The overall $\gamma_{\infty} = 414$ which is in excellent agreement with the value obtained using Eqn. (2.11). The following parameters are used for the computation, conical base: $h = 300$ nm and $r = 80$ nm and CNF: $h = 700$ nm and $r = 8$ nm. The modified Miller equation is a reasonable empirical model to describe the behavior of γ varies with S over a large range of values. At large S , (i.e. $S \gg h$) γ stabilizes to a constant value, which is a function of h and r . At small S (i.e. $S \ll h$) γ approaches unity where two electrodes resemble a flat parallel plate with no field enhancement.

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Figure 4-4 (a) Calculated γ using FN equation as a function of S . The data are fit with the modified Miller equation, (b) F_{on} as a function of S .

4.5 FE Noise Characteristics

The stabilities of the emitted current of a single CNF at 2 different interelectrode distances, $S = 200$ and 500 nm were determined by running the source at a constant voltage of 80 V at a sampling rate of 10 Hz for a period of 60 min. To obtain the best

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performance, field emitters usually have to be flashed (i.e., quickly heated) regularly or operated under extremely high vacuum $\sim 10^{-8}$ Pa with special electronic feedback loops to stabilize the current.¹⁷⁹ It should be noted that, no prior heating on the CNF tip was done for cleaning the CNF tip. However, an alternative cleaning method was used. This was done by touching the CNF tip with the probe tip, and then supplying a current of 300 nA between them. In this way, Joule heating will be initiated on the CNF tip, inducing a high temperature at the tip.^{106,123} The current of 300 nA is carefully chosen so that it is enough for Joule heating to occur and at the same time minimizing the effect of field evaporation on the CNF.¹²³

As evident from Fig. 4-5 (a), there is no sign of current degradation, as current fluctuations for both conditions (500 nm and 200 nm) were low at within 4 ~ 7% and well maintained at 130 nA and 300 nA correspondingly. The good stability of the current fluctuations could be attributed to a clean CNF tip that is free from adsorbates.⁷⁴

The use of different S will enable different fields, i.e., 160 V/nm and 400 V/nm, to be applied to the CNF. From the results, it is strongly imply that different applied fields will not have any significant effects on the stability of the cathode. However, the magnitudes of the emission currents for both conditions are different, which can be ascribed from the different in applied fields (e.g., 160 V/ μm and 400 V/ μm for $S = 500$ and 200 nm, respectively).

The frequency characteristics of the emission process for different S were subsequently investigated. This is done by converting the current fluctuating results from time domain to frequency domain using a Matlab program. As shown in Fig. 4-5 (b), the noise power spectral density function, $S_n(f)$ for both conditions exhibit a $1/f^\beta$ relationship

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over a bandwidth of 0.01 ~ 5 Hz. Linear fitting the results for interelectrode spacing = 500 nm and 200 nm, give $b = 0.97 \pm 0.02$ and 1.005 ± 0.05 , respectively. Thus, $S_n(f)$ of the single CNF emitter gives a $1/f$ trend, such that $S_n(f)$ is proportional to $1/f$. The $1/f$ noise characteristic in CNF is similar to CNT reported by *De Jonge et al.*⁷⁴ The noise performance in CNF could be as good as the noise performance in CNT.⁷⁴

Figure 4-5 (a) FE current fluctuations at $S = 200$ nm and 500 nm for a period of 60 minutes, (b) noise spectral density of the corresponding current fluctuations at $S = 200$ nm and 500 nm.

4.6 Field induced Electrostatic Force

The deflection and straightening of a single CNF was demonstrated by applying an electrical field with different polarity. Fig. 4.6 (a) illustrates a slightly bend CNF at distance S of approximately 200 nm. When a voltage of ~ 5 V is applied, it is observed that the CNF align itself to the direction of the applied electric field as exemplify in Fig. 4-6 (b). In the case of a negative applied voltage (-5 V), the straightened CNF can be deflected away from the tip probe as displayed in Fig. 4-6 (c). This dynamic deflection or straightening of the CNF toward an applied field is caused by the highly elastic nature of the carbon nanostructure.¹⁸⁰ This behavior has also been observed by other groups while studying the characteristics of individual CNT in a SEM.^{75,76,176}

The highly flexible nature of the CNF facilitates the bending or straightening of the structure upon an electric field, however the actual cause for the phenomenon is due to the field-induced electrostatic forces. The applied voltage can charge up the CNF and induce charges mostly at the tip of the CNF. For example, the CNF is initially assumed to be neutral charge because of grounding (0 V) of the CNF substrates. The CNF became negatively charged when the positive voltage was applied at the probe tip (5 V), causing the CNF to align itself parallel to the positively charged probe tip. When the probe tip reverses its polarity, the CNF deflected away as seen in Fig. 4-6 (c) owing to the electrostatic force. The CNF is indeed very flexible and sensitive to the electrostatic force, as it can be straightened, bent and recovered to its original shape (reversible) when subjected to an electric field of different polarities.

From the SEM micrographs as shown in Fig 4-6, it is observed that the CNF nanostructure is also extremely robust, as the CNF and its conical base remain intact even

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upon a high electrical field (i.e., $5 \text{ V} / 200 \text{ nm} = 25 \text{ V}/\mu\text{m}$). This is ascribed to the excellent adhesion between the substrate and conical base, and between the conical base and the CNF wire. This feature will provide significant contribution to the reliability of the CNF electron source.

Figure 4-6 SEM micrographs of the CNF (a) before applying 5 V, (b) after applying 5 V and (c) after applying -5 V.

4.7 Maximum Current Density

The maximum current that a single CNF can withstand was measured by bringing the anode in contact with the CNF tip as shown in Fig. 4-7 (a). The CNF failed at 92 V and ~

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15 μA , as can be seen in Fig. 4-8. The two remaining CNF segments are attached to cathode and anode as shown in Fig. 4-7 (b). It shows that the CNF is ruptured at or near its middle. It suggests that the failure is likely due to resistive heating similar to the failure mechanism of CNT.⁷⁵ The maximum current density of the CNF before failure was determined to be $7.5 \times 10^9 \text{ A/m}^2$, which is comparable to CNT.⁷⁵ It appears that the FE current of the CNF can be as high as 15 μA without causing damage.

From the I-V data as shown in Fig. 4-8, the resistance of the CNF and its conical base is estimated to be $\sim 6.1 \text{ M}\Omega$. This resistance is too high for the entire CNF nanostructure as typical resistance for a CNT/CNF is roughly between 40 and 110 $\text{k}\Omega/\mu\text{m}$.^{75,181} The high measured resistance of the CNF is mainly attributed to the contact resistances. The measurement of the intrinsic resistance of CNF is important as it is directly related to its electrical properties (i.e. electronic transport). In the next section, we will proceed to investigate this issue in greater details.

Figure 4-7 SEM micrographs of the CNF in contact with the anode (a) before, and (b) after failure

Figure 4-8 I-V characteristic of the CNF.

4.8 Intrinsic Resistance

Fig. 4-9 (a) illustrates the SEM image of the CNF nanostructure contacted by the probe at the tip of the CNF (point x). The length of the CNF is $\sim 2.4 \mu\text{m}$ and its conical base is $\sim 0.3 \mu\text{m}$. The total resistance for the whole structure is $\sim 8 \text{ M}\Omega$ which is similar to what we have measured in the previous section ($\sim 6.1 \text{ M}\Omega$ for a $1 \mu\text{m}$ structure). This resistance value is too high for CNF and its conical base. Other sources of resistance (i.e., contacts resistance) should account for the high resistance of the structure. As shown in Fig. 4.9 (b), there are four resistance components in series namely: C1, C2, CNF and conical base. C1 is the contact resistance between the probe and the CNF tip. C2 is the contact resistance between the probe (this probe is grounded) and the substrate. In order to estimate the intrinsic resistance of the CNF, it is necessary to eliminate the resistance contribution due to the contacts. This is accomplished by taking another measurement at

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a particular point *y* as seen in Fig. 4.9 (c) and 4.9 (d). The CNF nanostructure was contacted by the probe at 0.2 μm above the tip of the conical base, which had a resistance of 7.67 $\text{M}\Omega$. The intrinsic resistance of the CNF and conical base can be calculated by finding the resistance at various contact points *x*, *y* and *z*. Hence, the intrinsic resistance of the CNF and conical base are $\sim 360 \text{ k}\Omega$ and $100 \text{ k}\Omega$, respectively. The resistivity of the CNF is determined to be $\sim 3 \times 10^{-3} \Omega\text{cm}$, assuming uniform length of 2.4 μm and 9 nm in radius. The resistivity of the CNF is higher compare to the resistivity of an individual CNT of $\sim 1 \times 10^{-4} \Omega\text{cm}$.¹⁸² The relatively high resistivity of the CNF could be due to the amorphous nature of the structure, which was grown at low temperatures, i.e., disordered graphite is non-isotropic for its electrical properties in nature, therefore yielding a high resistivity.

The total contact resistance for C1 and C2 were then obtained by contacting the probe tip closer to the bottom of the conical base (point *z*) as represented in Fig. 4.9 (e) and (f), which gives a resistance of 7.54 $\text{M}\Omega$. This elucidates the high resistance of the structure is mainly due to the contacts. Nevertheless, the contact resistance measured here was well within the range of resistances (i.e., between 300 $\text{k}\Omega$ to 400 $\text{M}\Omega$) for single CNT measured by *Bonard et al.*⁷⁵ The resistance and the resistivity of the various components are tabulated in Table 2.

Table 2 The resistance and resistivity of various components in the structure.

Resistance Components	Intrinsic Resistance ($\text{k}\Omega$)	Resistivity (Ωcm)
CNF (2.4 μm)	360	3×10^{-3}
Conical Base (0.3 μm)	100	N.A
Contacts (C1 + C2)	7540	N.A

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Figure 4-9 (a) and (b) are SEM micrograph and schematic diagram showing the probe tip touching the CNF nanostructure at x, top of CNF tip, respectively. (c) and (d) are the SEM micrograph and schematic diagram showing the probe tip touching the CNF nanostructure at y, 0.2 μm above the tip of the conical base, respectively. (e) and (f) are SEM micrograph and schematic diagram showing the probe tip touching the CNF nanostructure at z, bottom of the conical base respectively.

4.9 Summary

In summary, the FE mechanism at sub-100 nm gap regime, FE noise, electrical and physical characteristics of a single CNF were studied. It was demonstrated that the modified Miller equation is a reasonable empirical model to describe the behavior of γ varies with S over a large range of values. The γ will approach to an asymptotic value of 415 and 1 as $S \gg h$ and $S \ll h$, respectively. The FE current fluctuation is relatively stable at merely 4 to 7% regardless of the difference in applied fields. It also displays a noise power spectral density function that follows a $1/f$ noise behavior at various S over a frequency bandwidth from 0.01 ~ 5 Hz. Furthermore, the CNF is found to be extremely robust as it shows excellent elasticity and remains well intact on the substrates even upon a high electrical field. The maximum allowable current density of a single CNF is also found to be as high as 7.5×10^9 A/m² before failure.

Chapter 5 All-Plastic Field Emission Devices

5.1 Introduction

In previous chapters, we have characterized the CNF film and a single CNF grown on flexible substrates. These results are very significant and served as the foundations to access the applicability of CNFs for flexible electronics. However, one of the biggest challenges in flexible electronics lies with the reliability and lifetime of the devices under mechanical stresses induced from mechanical flexing of the substrates.⁸² The reliability and stability of the flexible CNF field emitters under various stressing conditions remain unexplored. Therefore, in this chapter, we will study the reliability and stability of the flexible CNF emitters under substantial stresses. The all-plastic flexible field emission device (APFED) is also demonstrated. The ability to grow reliable CNFs on low-cost flexible substrates may open up numerous fields of applications such as x-ray radiotherapy,^{134,139,131} and “rollable” FE displays.⁴⁴

5.2 Experimental Details

In order to measure the FE properties of the flexible CNF emitters under various bending conditions, an adhesive copper conducting tape (3M) was used as the anode, with thickness of 100 μm and separated by a 100- μm PTFE spacer. The copper tape, the spacer, and the polyimide CNF film are cut to the same dimensions to form a $1 \times 2 \text{ cm}^2$ flexible field emitter device. A hole of 6 mm was punched through the spacer and, hence, the exposed emission area was 0.28 cm^2 . The exposed area was kept the same throughout

the FE experiment for all bending conditions. The same device was bent to different curvatures and directions (inward or outward bending for tensile or compressive stress, respectively). Three different cylindrical structures of diameters 5, 10, and 25 mm were employed in the FE experiments.

A Nikon optical measuring microscope mm-40 is employed to check the consistency in the gap distance between the copper anode and the CNF polyimide film separated by a 100- μm spacer. A small gap of $5 \times 3 \text{ mm}^2$ was made on top of the PTFE spacer rather than the usual 0.28 cm^2 hole made at the center, so that a gap was observed between the cathode (CNF film) and anode (copper tape) when viewed in cross section. The flexible emitter was then fixed onto a 25 mm cylindrical structure and observed by the optical microscope.

In order to demonstrate the feasibility of constructing an APFED, a ZnS:Ag phosphor coated polyester sheet (Eljen Technology) of 250 μm thick was used as a flexible anode, with a central emission wavelength of 450 nm. The flexible emitter was then mounted on a 25 mm diameter cylindrical structure with applied voltages ranging from 500 to 1300 V. The emission spots were then captured using a charge-coupled camera (CCD).

5.3 FE Reliability

The F_{on} of the emitter at flat condition (or no bending) was approximately $3.2 \text{ V}/\mu\text{m}$ whereas the F_{on} for emitter under various stressing conditions changed slightly from $3.1 \text{ V}/\mu\text{m}$ to $4.2 \text{ V}/\mu\text{m}$ for a current density of $1 \mu\text{A}/\text{cm}^2$ as shown in Fig 5-1. The average F_{on} for all the conditions is $\sim 3.65 \text{ V}/\mu\text{m}$. This is comparable to CNTs grown on polyimide substrates and CNFs grown on the graphite plate.^{70,131} No hysteretic-like behavior is

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observed on the curves and no remarkable changes in the F_{on} can be observed under different bending curvatures for both tensile and compressive stressed emitters. These facts strongly imply that stresses do not have significant effect on the F_{on} of the CNF emitters.

Figure 5-1 FE measurement (I-V) of the flexible CNF emitters at different bending curvatures.

The emission data were fitted onto a FN plot using Eqn. (2.9), and the values of the γ could be estimated from the slope of the FN plot by assuming a ϕ of 4.5 eV for graphitic carbon.¹⁷⁰⁻¹⁷² The γ of the CNF emitters at various stress conditions ranged from 2300 to

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3100. The average γ obtained for all conditions to be 2700, which was quite comparable to γ of CNFs obtained in Chapter 3 (i.e., ~ 3000).

For the stable FE, good adhesion is required between the base substrates and emitters as any field strong enough that exerted on the CNFs during FE can peel off the CNFs from the substrates causing current decay and arcing.¹²² Fig. 5-2 shows the SEM micrograph of a bended flexible CNF emitter (radius of curvature = 2 mm), the terrific adhesion of the CNFs on the polyimide is manifested even under severe bending. It suggests that the CNF is robust and tough, suitable for uses in practical FE devices. Indeed, the same device has been bent in various conditions for many times and no noticeable changes in the FE properties can be observed.

Figure 5-2 SEM micrograph showing a bended flexible CNF field emission device,

As explained earlier, the emitted current, I is dependent on F , ϕ , S and aspect ratio of the CNF emitters as elucidated from Eqn. (2.9). As shown in Fig. 3-1 (a) in Chapter 3, the

CNFs are uniformly distributed. The ϕ and aspect ratio of the CNFs are assumed to be uniform throughout the emitted area. It is hence important to check the gap between the anode and cathode of the flexible CNFs emitter under various bending conditions in order to appreciate the results obtained earlier. Fig. 5-3 (a) and 5-3 (c) are the schematic diagrams of the devices under tensile and compressive stress conditions, respectively. The corresponding cross-sectional views of the flexible emitter at both conditions are shown in Fig. 5.3 (b) and 5.3 (d). The average gap distance obtained for several measurements was around $100.5 \mu\text{m} \pm 10\%$ and $99 \mu\text{m} \pm 9\%$ variation for tensile and compressive stressed samples, respectively. These deviations at the gap differences at various points, therefore accounted for the changes in F_{on} and γ achieved earlier.

If we considered the average F_{on} of around $3.65 \text{ V}/\mu\text{m}$ for different stressing conditions at a 10% discrepancy in emitter to anode distance, the calculated F_{on} variation will be ranging from $3.3 \sim 4.1 \text{ V}/\mu\text{m}$, which is consistent with what we obtained from the experimental results. The same argument can also be used to explain the inconsistency in experimental γ under different stressing conditions. At a $\pm 10\%$ discrepancy of 2700 (average γ), the calculated variation of γ will range from $2400 \sim 3000$, which agrees well with the experimental results. This implies that keeping consistent gap distance between anode and cathode of the flexible emitter is the key for stable FE. The fluctuations of F_{on} and γ for roughly 10% are concluded to be due to the difference of gap distances between anode and cathode of the flexible emitter. As the anode, cathode and insulation spacer were made from different materials, therefore creating an emitter structure having different Young's moduli, and as a result, the bending between respective materials were different when a force was applied to the emitter structure. Choosing materials with

comparable Young's moduli and properly securing of the anode, insulation spacer and the cathode can minimize this inconsistency.

Figure 5-3 (a) and (b) are the schematic diagrams of the device under tensile stress and optical microscope image of the gap distance as indicated by the “box,” respectively. (c) and (d) are the schematic diagrams of the device under compressive stress and the corresponding optical images of the gap distance, respectively.

5.4 FE Stability

The emitter was put to a lifetime stability test, and a field of 10 V/ μm was applied to the emitter in flat and stressed conditions for duration up to 16 h (Fig. 5-4). The average

current densities of the emitter under unstressed and tensile stressed conditions were measured to be around $7.25 \times 10^{-5} \text{ A/cm}^2$ and $7.11 \times 10^{-5} \text{ A/cm}^2$, respectively. The degradation of current densities at both conditions were low and well maintained at around $7.18 \times 10^{-5} \text{ A/cm}^2$ after 16 h of emission testing. The emitter is indeed very robust regardless of planar or curved conditions.

Figure 5-4 FE stability as a function of time at an applied field of $10 \text{ V/}\mu\text{m}$ for flat and tensile stressed ($r = 25 \text{ mm}$) emitter for a period of 16 h.

Additionally, the CNF emitters grown by ion beam sputtering had recently been reported by *Tanemura et al.* to be self regenerative with stable and long-sustained emission even after 40 h of operation.¹⁸⁵ It was reported that typical rod-like projections with a round tip were produced as seen in Fig 5.5 after the long hours of FE lifetime test. Their growth was due to the surface diffusion of carbon atoms generated by sputtering of the carbon cathode with ionized residual gas molecules during the FE process at low

vacuum pressure (i.e., $\sim 5 \times 10^{-4}$ Pa).¹⁸⁵ These newly grown CNFs could be responsible for the observed stable and long-sustained emission under a non-ultrahigh vacuum condition. Thus, this self-regenerative effect of the CNF emitters is believed to further enhance the lifetime and stability of the APFED even under low vacuum.

Figure 5-5 Typical SEM image of the emission area taken after the lifetime test for 40 h, with typical rod-like projections with a round tip and entangled CNFs newly grown during the FE process.¹⁸⁵

5.5 Realization of a APFED

In order to demonstrate the feasibility of constructing an APFED, a ZnS:Ag phosphor coated polyester sheet (Eljen Technology) was used as a flexible anode. The phosphor on plastic substrates is meant for ionization ion detection such as alpha particles, thus the

light efficiency for electron is low. The anode has to be conductive in order to attract electrons from the emitter, thus a thin layer of 10 nm Pt was deposited onto the phosphor. This conductive layer must not be too thick as the field electrons might not be able to penetrate through the Pt layer and bombard the phosphor layer. Figure 5-6 shows the APFED mounted onto a cylindrical object (radius = 25 mm) with an emission area of 0.28 cm^2 . The emission area of the APFED was captured by a CCD camera with an applied field of $5 - 13 \text{ V}/\mu\text{m}$, showing fairly uniform emission as illustrated in the inset of Fig 5-6. The concept of APFED may open up opportunity in future “rollable” display which is lightweight, flexible (i.e. can be made to whatever shapes for better viewing angles) and high resolution (i.e. nanosized pixels are possible with CNF tips).

Figure 5-6 Photograph of the APFED mounted on a 25 mm diameter structure. The inset shows the emission spots captured from the phosphor-coated plastic substrates at an applied field of $13 \text{ V}/\mu\text{m}$.

5.6 Summary

In summary, an APFED with excellent FE properties has been demonstrated using CNFs as field emitters. The flexible CNF field emitters are robust and reliable under various stress conditions and severe lifetime test.

Chapter 6 Multi-Purpose CNF Gas Sensing Devices

6.1 Introduction

In recent years, CNTs based gas ionization sensors for mass spectrometry¹²⁶ and vacuum gauge¹⁵⁸ have been demonstrated. These applications made use of the sharp tips or aspect ratio of the CNTs that create very high fields concentrated on its tips and significantly lower the breakdown voltages when compared to conventional electrodes with no nanostructures on it.¹²⁶ It can facilitate the development of battery-powered gas sensor, which is more compact and safer to use. Typically CNTs are grown on substrates coated with a metal catalyst; the adhesion of CNTs to the substrates is therefore weak and can be easily prone to damage.¹⁸⁶ In gas ionization device, a strong electric field applied between the cathode and anode will create a corona discharge that will generate an electron avalanche across the electrodes. This might cause the emitter to be damaged by the bombardment of residual gas molecules. Despite of diode or triode configurations, the emitters will be subjected to ions or electron bombardments respectively, which will limit the lifespan of the devices¹⁸⁷ and exploring the use of robust electron emitters in ionization gas sensor remained a challenge.

It has been demonstrated from previous chapters that the flexible CNF field emitters are extremely tough and reliable even undergoing various stress conditions and severe lifetime test. The CNF based gas sensor is expected to be robust due to the unique ion beam based growth technique.⁶⁸ The CNFs grown on the tips of the conical protrusions, provide not only strong adhesion to the substrate, but also greatly amplify the γ of the

CNFs emitter due to the multistage effects.¹⁰⁵ Therefore the CNFs emitter should be better suit for demanding gas ionization sensor application.

In this chapter, CNF-based ionization gas sensing devices prepared on plastic substrates have been studied. This type of flexible gas sensor can be applied at extreme locations that required gases monitoring or sensing which might be irregular that made flexible gas sensor exceptionally practical.

6.2 Experiments Details

Fig. 6-1 shows the schematic diagram of the gas ionization measuring configuration which is similar to the set up by *Kim et al.*¹⁸⁸ A 200 μm thick PTFE spacer separates the distance between the cathode and anode, and the device area is made of a $10 \times 10 \text{ mm}^2$ CNF film. Prior to the experiment, the base pressure of the chamber was evaluated to $1 \times 10^{-4} \text{ Pa}$ in order to ensure the chamber with minimized residual gas molecules. One specific gas was then introduced to the chamber via a mass flow controller (MFC) and a throttle valve controlled the gas pressure. To measure the breakdown voltage or ionization current of a specific gas at a particular pressure, the flow rate of the MFC was first varied till the corresponding gas pressure was achieved, then the throttle valve was tuned till the pressure became stable, after which the measurement was proceeded. In order to study the breakdown voltage of different gases (i.e. air, Ar, He, N_2 , N_2O , O_2 and C_2H_2), a voltage ranging from 200 to 1300 V was applied to one of the gases with a pressure between 0.1 and 300 Pa. The device was connected to an electrometer in series, once the predefined ionized current of 0.1 mA was attained; the corresponding voltage was then recorded, which would be the breakdown voltage of the gas under test. Test was

also repeated at 3 Pa with both electrodes made of copper and the breakdown voltage of air was determined to be 1500 V as compared to 960 V when the CNF cathode was used. It suggests that breakdown field of air can be reduced by 40% if the CNF cathode (CNF as cathode and Cu as anode) is used which is comparable to the CNT based ionization gas sensor on Si.¹²⁶ Next, the ionization current of the device as a function of pressure was investigated for all the different type of gases (air, Ar, He, N₂, N₂O, O₂ and C₂H₂), where this characteristic can be used to evaluate the suitability of the device as a cold FE vacuum gauge. By applying a fixed bias of 700 V across the cathode and anode of the device, the ionization current of a specific gas with various pressures can be measured. The value of 700 V is chosen, as the voltage is sufficient to cause breakdown for the seven gases with pressure greater than 5 Pa as shown in Fig. 6-2. For comparison between different electrode configurations with breakdown voltages, breakdown voltages at specific gas pressures of 3, 10 and 100 Pa was recorded once the predefined ionization current of 0.1 mA was reached. The structure of the CNFs was also analyzed by FESEM after more than 15 h of operation as a multi-purpose gas sensor.

Figure 6-1 Schematic of the CNF gas-sensing device in diode configuration with copper and CNF film as anode and cathode, respectively. The gap between anode and cathode is $\sim 200 \mu\text{m}$.

6.3 Unique Breakdown Voltages of Different Gases

Fig. 6-2 illustrates the typical breakdown voltage of seven common gases, namely: air, Ar, He, N_2 , N_2O , O_2 and C_2H_2 as a function of pressure. The entire seven gases show a trend partially similar to the characteristics of the Paschen's Law.¹⁸⁹ Paschen's Law states that the breakdown voltage of a gas is a non-linear function of the product of the gas pressure and the gap distance. The Paschen curve is a theoretical relationship of the

gas breakdown voltage with respect to ionization current of two parallel electrodes (i.e. flat Cu/Cu electrodes) when immersed in a gas, as a function of the gas pressure and electrode separation.¹⁸⁹ As seen in Fig. 6-2, the distinct minimum of each gas or also known as the Paschen's minimum (Paschen's minimum of air, Ar, N₂, He, N₂O, O₂ and C₂H₂ is 400, 270, 490, 215, 540, 574 and 613 V, occurring at the pressure range from 90 to 100 Pa) occurs at the circumstances whereby the electron's probability to ionize any gas molecules is the lowest, as the mean free path is just barely sufficient for the electrons to gain kinetic energy and causing gas ionizations. This clearly indicates that if the pressure and hence the collisions is further decreased as seen on the left of the minimum, the only way to increase the chance of ionizations is to raise the voltages. Whereas on the right of the minimum, the gas density increases and electrons now make more collisions than at the Paschen's minimum, which means a reduction in the mean free path of the electrons, so with the same applied field when compared to that at the minimum, the electron gains less kinetic energy between collisions. This in turn increased the dielectric strength, thus a higher field is needed.¹⁸⁹ However due to the non-linear field effect near the CNF tips, which reduces the breakdown field at higher gas pressure, the breakdown field seems to show a steady result with an average of around 8% above the Paschen's minimum at the pressure range from 20 ~ 300 Pa for all the different gases except He, rather than following the trend of a Paschen curve (i.e. breakdown field increases with increasing gas pressure). It should be noted that Paschen's Law is based on uniform electrical field.

Figure 6-2 Breakdown voltages of air, Ar, N₂, He, N₂O, O₂ and C₂H₂ as a function of gas pressure.

All the gases distinct breakdown voltages (Paschen's minimum) at a particular pressure are summarized in Fig. 6-3. The fluctuation of the breakdown voltages at various gas pressures is only $\sim 5\%$ for 5 separate measurement readings for all the gases, suggesting that repeatability is good. The device is capable of identifying a specific gas with a known pressure. At pressure higher than 20 Pa, all of the gases except helium exhibit constant breakdown voltage. The rationale for this distinctive characteristic of helium from the rest of the gases may be attributed to its lower atomic mass. The atomic mass for air (assuming a mixture of 78%, N₂ and 21%, O₂), Ar, N₂, He, N₂O, O₂ and C₂H₂

Chapter 6 Multi-Purpose CNF Gas Sensing Devices

is 14, 40, 14, 4, 44, 16 and 26, respectively. It is therefore intricate to detect helium at low pressure because of the mass of the gas, helium being the lightest of the seven gases, requires a much higher concentration (higher pressure) in order to cause a gas breakdown. While the rest of the gases under test, having a higher atomic mass can have more constant breakdown field at a wider pressure range at about 8% above its specific Paschen's minimum (i.e. 20 to 300 Pa). This characteristic is, therefore, practical for distinguishing gases except low mass gases like helium at an unidentified pressure range from 20 to 300 Pa.

Figure 6-3 Paschen's minimum of different gases, air, Ar, N₂, He, N₂O, O₂ and C₂H₂.

6.4 Ionization Current of Different Gases

The ionization current varies logarithmically with respect to pressure of air, Ar, N₂, He, N₂O, O₂ and C₂H₂ as shown in Fig. 6-4. As pressure is proportional to concentration,

Chapter 6 Multi-Purpose CNF Gas Sensing Devices

which increases the probability for ionizations since there are more gas molecules available for collisions. It is noticed that there are two regions of linearity for pressure below and above 5 Pa. In the region between 0.1 and 5 Pa, the applied voltage is less than the breakdown voltage where the ionization current is less than 1 mA. When the pressure > 5 Pa, the ionization current of all the gases surge in a faster rate, it is due to the fact that more electron avalanche events will occur at that pressure range. If the applied voltage is set at a higher value, the linear region can be extended to a wider pressure range. Hence, the device can be employed as a miniature cold FE vacuum gauge. Currently vacuum gauges are based on thermionic source, which required a lot of power and difficult to miniaturize.¹⁵⁸ The device is also capable of detecting a mixture of gases such as in the case of air.

Figure 6-4 Ionization current versus gas pressure of different gases. A voltage of 700 V is applied to the device.

Under normal conditions (without any external electric field), there are no free electrons to carry a charge and the gas is a good insulator. However, when a sufficient high electric field is applied between the cathode and anode, a corona discharge either positive (CNFs as anode) or negative (CNFs as cathode) can occur. After the discharge, the gas will become a conductor due to the formation of an electron avalanche. Table 3 exemplify the comparison of breakdown voltage between a positive corona, a negative corona and also both electrodes made of CNFs at several gas pressures. It should be noted that the CNF film was from the same batch and having similar density. The breakdown voltage only slightly reduced from 400 to 390 V if both the electrodes were made of CNF film. However, the breakdown voltage is not stable with a wider range of fluctuation (~10%). This may be caused by the non-linear field effect at both electrodes that not only reduce the ionization voltage but also influence the inconsistency of the breakdown voltage. Gas ionization breakdown voltage of either negative or positive corona is having comparable value with stable breakdown voltage at each tested pressure; however, negative corona appears to be a better candidate with a slightly lower breakdown voltage. This could be associated with the free electrons getting repelled away from the CNF tips once ionizations were established creating secondary ionizations. In addition, new electrons emitting from the CNF tips due to the high applied field will accelerate toward the anode creating secondary ionizations which leads to a higher ionization current and a lower breakdown voltage, when compare to positive corona.

Table 3 Comparison of breakdown voltage with different electrode configurations for gas pressures of 3, 10 and 100 Pa.

Electrode		Breakdown voltage at gas pressure (V)		
Cathode	Anode	3 Pa	10 Pa	100 Pa
Cu	CNF	985	490	430
CNF	Cu	960	460	400
CNF	CNF	935 ~ 990	435 ~ 480	390 ~ 440

Fig. 6-5 (a) and (b) display the SEM micrographs of the CNF-tipped cone-like nanostructures before and after more than 15 h of operation as a multi-purpose gas sensor. The actual operation of the device was span for about 4 weeks. The density of the CNF is estimated to be around $3 \times 10^7 \text{ cm}^{-2}$. As shown in inset of Fig. 6-5 (b), some of the CNF tips are bent slightly as compared to the as-grown sample however most of the CNF tips remain intact. This could be due to the ion bombardments generated by the gas molecules during the measurement. It is noted that the bending of CNFs can only be observed after long operational hours ($> 10 \text{ h}$). The bending of the CNFs could probably be due to a cloud of electrostatic charges that are formed upon gas breakdown near the CNFs' tips. (In an event of gas ionizations, equal amount of positive ions and negative charged particles can be created. This could generate a strong negative field or positive field that can deflect the CNF wire (if CNF is negatively charged or positively charged). This phenomenon is illustrated in Chapter 4 (section 4.6), whereby a strong electric field can bend the CNF as shown in Fig. 4-6. Nevertheless, even after prolong bombardments from gas ions; the conical bases and the CNF tips remain intact, the good adhesion of the CNF and its conical base will greatly improve the lifetime of the device. The CNF arrays with conical base are indeed very robust.

Figure 6-5 SEM micrographs of the CNF arrays, (a) before gas sensing operations, (b) after more than 15 h of operations, inset showing the close-up of a single “bend” CNF.

6.5 Summary

In summary, we have demonstrated a multi-purpose CNF based gas-sensing device. The device is not only able to “fingerprint” a wide spectrum of different gases at a distinct breakdown voltage but also can be employed as a vacuum gauge. The robustness of the device is attributed to the low operation voltage and strong adhesion between the CNF and conical base.

Chapter 7 Field Emission X-Ray Source

7.1 *Introduction*

There have been a lot of literatures documented for CNF and CNT based x-ray sources for industrial and medical applications.^{127,128,131,140,190} These x-ray sources operate based on FE from carbon nanostructures, which is favored over TE due to several reasons i.e., low operating temperature, instantaneous response time, and potential for miniaturization.¹²⁷ However, these emitters are grown on metal tips or planar substrates, which is often rigid and expensive.^{127,128,131,140} On the other hand, our CNFs grown on flexible polyimide substrates is robust, and can provide more innovative designs for the cold cathode since emitter of any geometry and shape can be made.⁴⁴

In this chapter, we will demonstrate the usage of flexible CNF emitters as a high voltage electron source for x-ray generation. The flexible emitter has the potential to be applied in innovative x-ray radiotherapy and radiography applications.

7.2 *Experiments Details*

The field emitters are made of CNF film of dimension $1 \times 2 \text{ cm}^2$. The experimental system is an open type x-ray tube with a beryllium window directing the x-ray in a vertically upward direction as illustrated in Fig. 7-1. The location of the window is at 7 cm away from the target. The x-ray tube housing consists of a stainless steel structure connected directly to a turbo molecular pump. A high voltage feedthrough was used to allow electrical connection to the flexible emitter cathode, which was connected to a

Chapter 7 Field Emission X-Ray Source

pulse voltage generator. The pulse power supply was operated at 600 Hz with output voltage ranging from 10 to 25 kV. The anode used in this experiment was a copper block connected to electrical ground. For measuring of the x-ray dosage, a Ludlum 2241 dosimeter with high sensitivity and response time is used. The dosimeter was directly placed on top of the beryllium window for maximum x-ray detection at an applied voltage of 16 kV for 30 min.

Figure 7-1 Schematic diagram of the x-ray tube using flexible emitters as electron source.

7.3 X-Ray source

Fig. 7-2 is a photograph showing the mock-up arrangement of the flexible emitter and the copper anode when inside the x-ray tube. The x-ray source in this experiment was

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configured in a diode structure. The advantage of a diode structure resulted in a compact and a low-cost system, which is significantly much simpler and more efficient, as no extra gate electrode, was needed as in a triode structure. The surface of the copper anode was angled approximately 45° to assist x-ray emission. The radius of the emitter curl was approximately 3 mm.

Figure 7-2 Photograph of the x-ray cathode-anode.

Fig. 7-3 (a) and 7-3 (b) show the x-ray images of a *Bougainvillea* flower obtained from the flexible emitter exposed for about 45 s using 13 kV. From the images, it can be clearly seen that the flexible x-ray source produces high quality picture with high resolution on the biological sample. The flexible emitter x-ray was able to resolve the fine details in the flower as enlarged in Fig. 7-3 (b), in addition to the veins on the petals as indicated by the two white arrows in Fig. 7-3 (a). The thickness of the vein was approximately to be 250 μm . This shows that the flexible emitter is capable of emitting

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sufficient current to generate the x-ray flux necessary for a high signal to noise ratio even at such a low voltage.

(a)

(b)

Figure 7-3 Radiograph of a Bougainvillea flower. **(a)** The flower was imaged at 13 kV using the flexible x-ray source, showing clearly good contrast and resolution. The two arrows indicated the trace of the flower veins on the petals. **(b)** An enlargement of the stigma area as indicated by the white square, showing clearly the details captured.

7.4 Stability of the FE X-Ray Tube

The stability measurement of the flexible x-ray source operating at 16 kV was measured by a dosimeter (Ludlum 2241). The fluctuation of the x-ray output was low and at a merely 4% fluctuation as shown in Fig. 7-4. This implies that the flexible CNF emitters have excellent durability for use as high power electron emitter sources. Although the stability is highly dependent on the emission stability of the pulsed power generator, the graph is a good demonstration that the emitter did not degrade even under such a high voltage and current. The same emitter has been tested for x-ray generation for several months and showed no sign of failure. There are no obvious differences in terms of x-ray stability and image quality of a biological sample when the flexible emitter is used as compared to a CNT emitter on a tungsten tip¹³¹ under identical x-ray generation conditions.

Figure 7-4 X-ray stability as a function of time.

Chapter 7 Field Emission X-Ray Source

This work has demonstrated the viability of using flexible emitter as an electron source for x-ray application. There could be many possible applications of the flexible emitter, one such potential would be in radiotherapy. Most miniature x-ray tube for radiotherapy applications used a thin layer of target material coated on the x-ray window.^{189,190} In this transmission mode arrangement, x-ray efficiency is severely lowered as radiation is required to transverse through a thick layer of target material before hitting the targeted organ. The use of beryllium as the window material is not favorable as beryllium is harmful to human beings. Using flexible emitter would allow us to circumvent these limitations and improve the efficiency of the x-ray emitted from the system. As polymers generally have lower absorption coefficient of x-ray as compared to metals, they made excellent candidate for this applications.

As shown in Fig. 7-2, the emitter demonstrates sufficient flexibility for it to be curl into a radius of ~ 3 mm while retaining its FE ability. The use of such flexible emitter would allow for greater choices of x-ray tube design previously not possible in medical radiotherapy. It would be possible to make an x-ray transparent emitter as the window with a concave target surface to achieve focused x-ray thereby reducing the spot size of the x-ray spot. This would allow for more precise radiotherapy treatment rather than the usual diverging x-ray source.

7.5 Summary

In summary, we have demonstrated x-ray source using a flexible emitter based on CNFs. The x-ray generated at the voltage of 13 kV was sufficient to produce radiograph image of a *Bougainvillea* with superior sharpness, resolution and contrast.

Chapter 8 Conclusions and Future Work

8.1 Conclusion

The CNF film on plastic substrates grown using an ion beam technique at room temperature was characterized. The CNFs exhibit a high γ of 3000, and a low threshold field of 2.8 V/ μm at a current density of 1 $\mu\text{A}/\text{cm}^2$. These excellent FE characteristics of CNF nanostructure are attributed from its structure of an ultra-fine long CNF with a conical protrusion. This unique structure offers superb FE properties for vacuum microelectronics devices.

Electron FE from a single isolated CNF in a gap down to 20 nm by manipulating the anode electrode within the SEM was investigated. It was found that the modified Miller equation is a reasonable empirical model to describe the relationship of γ varies with S over a large range of values. These studies will enhance our understanding of FE mechanism of single CNF at sub-100 nm gap, which is imperative for future vacuum nano-devices.

Next, the FE noise, electrical and physical characteristics of a single CNF were studied and characterized. From the results, it was indicated that the CNF shows a superb FE current stability and displays a noise spectral density following a $1/f$ relationship at various S over a bandwidth of 0.01 – 5 Hz. Also, it was found that the CNF could sustain a current density as high as $7.5 \times 10^9 \text{ A}/\text{m}^2$ before failure. In addition, it was demonstrated that the CNF is extremely robust, as it remains well intact on the substrates even upon a high electrical field. The single CNF nanostructure is indeed very tough and

Chapter 8 Conclusions and Future Work

stable, which are vital attributes for vacuum nano-devices. An APFED with outstanding FE properties using CNFs as cathode and phosphor-coated polyester as an anode has been successfully demonstrated. The APFED offers brilliant stability and reliability under various stress conditions and severe lifetime test. The concept of APFED may open up opportunity in future “rollable” display which is lightweight, flexible and high resolution.

The viability of a multi-purpose CNF based gas-sensing device on plastic substrates has been investigated. It was shown that the multi-purpose gas sensor is exceptionally robust and reliable with a wide range of gas sensing capability. Furthermore, x-ray generation using CNF film on a flexible substrate was also studied. From the results, it was proven that the flexible x-ray source is capable of producing radiograph image with superior sharpness, resolution and contrast. The use of such flexible emitter would allow for greater choices of x-ray tube design previously not possible in medical radiotherapy and in industrial.

8.2 Recommendations for Further Research

This dissertation has been mainly devoted in the study of flexible CNF emitters and utilizing them as an electron source for various FE based devices. The reliability and stability studies of the APFED set the foundation work needed toward the realization of functional flexible emitters in vacuum nano-devices. The work on the APFED can be also extended to high voltage applications such as an “*All Plastic X-Ray Source*” to produce a low-cost compact flexible x-ray system. In such an x-ray system, the cathode (CNF emitters on polyimide substrates), target (i.e., Cu tape) and the x-ray window (i.e., polyimide) are all made of plastic. The use of plastic makes flexibility feasible and allows

Chapter 8 Conclusions and Future Work

the all-plastic x-ray source to be made to any geometry and shapes. The all-plastic x-ray source will have the potential to be employed in novel x-ray applications for industrial and medical applications.

Next, the research done on the FE of a single CNF in this thesis may provide important implication for the understanding of FE mechanism needed in compact free electron laser (FEL) for high frequency device i.e., terahertz (THz) source.¹⁷⁴ In recent progress, *Floreani et al.* has revealed the concept of vacuum nano-devices using single field emitter as FEL for THz generation,¹⁹¹ and a potential candidate could be single CNF.^{174,192} The fact that the electron beam from a single CNF is relatively easily modulated¹²⁵ and can lead to the formation of electron pulse beam, which will effectively enhances the THz radiation due to the coherent effect.¹⁹³ Fig. 8-1 shows the schematic diagram of a single CNF emitter for the THz generation. In this device, when a sheet of electron beam (emitted by the single CNF) passes over the surface of a metallic diffraction grating and radiates into a mode of an open resonator formed by two metallic mirrors (the grating partially covers the lower mirror). The radiation is then fed back onto the beam and bunches the electrons. If the proper conditions of synchronism between the electron beam velocity and the phase velocity of an evanescent wave traveling along the grating are met, coherent radiation results,¹⁹⁴ this phenomenon is called the Smith–Purcell effect. The radiation is called Smith–Purcell radiation (SPR),¹⁹⁵ which covers a broad band ranging from visible light to millimeter waves in accordance with the grating constant, the electron beam velocity, and the angle of observation of the light.¹⁹⁶

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Figure 8-1 Schematic diagram showing the concept of the compact CNF FEL.

However, it is not easy to fabricate only one single CNF emitter at the moment, therefore in order to realize such a compact FEL or other novel miniature electron source, the capability of growing only single CNF emitter and pinpoint it to whatever locations or substrates must be explored and acquired. It is strongly believed that the success of implementing the above recommendation, practical point source CNF emitter for compact innovative applications can be realized in the near future.

Appendix I: List of Publications

Appendix I: List of Publications

1. T. T. Tan, **H. S. Sim**, S. P. Lau et al., "X-ray generation using carbon-nanofiber-based flexible field emitters," *Applied Physics Letters* 88, 103105 (2006).
2. **H. S. Sim**, S. P. Lau, H. Y. Yang et al., "Reliable and flexible carbon-nanofiber-based all-plastic field emission devices," *Applied Physics Letters* 90, 143103 (2007).
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4. **H. S. Sim**, S. P. Lau, L. K. Ang et al., "Field emission from a single carbon nanofiber at sub 100 nm gap," *Applied Physics Letters* 93, 023131 (2008).

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