ELECTRON FIELD EMISSION
PROPERTIES OF TIP BASED
EMITTERS

Richard Charles Smith

UniS

A thesis submitted to the University of Surrey, for the degree of Doctor of Philosophy.
This thesis is dedicated to my parents
Acknowledgements

I am indebted to my supervisor, Prof. Ravi Silva for his support throughout this PhD. Without his kind advice, motivation and patience, this work would not have been possible.

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Declaration

This thesis is submitted for the degree of Doctor of Philosophy at the University of Surrey. It describes the research undertaken in the Nano-electronics group at the Advanced Technology Institute of the School of Electronics and Physical Sciences between October 2001 and 2005. This work has been carried out under the supervision of Professor S. R. P. Silva and Doctor J. D. Carey. Except where referenced, this work is original and has not been the result of collaboration. No part of this thesis has been or is currently being submitted for any other degree, diploma or any other qualification.

R. C. Smith
2005

Keywords: Field emission, carbon nanotubes, carbon nanofibres, enhancement factor
Abstract

Large area displays such as laptop computers and flat screen televisions have enormous market potential. There are numerous technologies in existence today, including LCD (liquid crystal displays) and plasma, however they each suffer from unique limitations, mainly the size of the display and operating conditions. There is still a need for a method of depositing electronic materials over large areas at suitable temperatures. This is important since the construction of panels using sub-modules such as crystalline silicon wafers is very difficult and expensive. The displays based on liquid crystals that use thin film transistor (TFT) driven active matrix addressing is the most common flat screen technology at present. However, there are great problems associated with yield in fabrication, especially for screen dimensions over 14 inches. Hence the screens are very expensive. Field emission displays utilising the phenomenon of field emission in which electrons escape their work function and “jump” from the surface of the semiconductor into a vacuum has been proposed as a competing technology. Each pixel is controlled by many tip based emitters, therefore improving the yield.

This thesis explores the field emission properties and mechanisms of tip based emitters, and also explore the possibility of utilising carbon nanotubes as electron sources for field emission displays.
Publications


Presentations

1  *Electron field emission from room temperature grown carbon nanofibers, R.C. Smith.*


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<th>Description</th>
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<td>2D</td>
<td>Two dimensional</td>
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<tr>
<td>3D</td>
<td>Three dimensional</td>
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<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>a-C</td>
<td>Amorphous carbon</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>AMLCD</td>
<td>Active matrix liquid crystal display</td>
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<tr>
<td>CCD</td>
<td>Charge coupled device</td>
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<tr>
<td>CNF</td>
<td>Carbon nano fibre</td>
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<tr>
<td>CNR</td>
<td>Carbon nano rope</td>
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<tr>
<td>CNT</td>
<td>Carbon nano tube</td>
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<tr>
<td>CRT</td>
<td>Cathode ray tube</td>
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<tr>
<td>D</td>
<td>Separation</td>
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<tr>
<td>DC</td>
<td>Direct current</td>
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<tr>
<td>DOS</td>
<td>Density of states</td>
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<tr>
<td>$E_{\text{appl}}$</td>
<td>Applied electric field</td>
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<tr>
<td>e-beam</td>
<td>Electron beam</td>
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<tr>
<td>$E_c$</td>
<td>Conduction band</td>
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<tr>
<td>$E_f$</td>
<td>Fermi level</td>
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<tr>
<td>$E_{\text{loc}}$</td>
<td>Local electric field</td>
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<tr>
<td>$E_v$</td>
<td>Valence band</td>
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<tr>
<td>$E_{\text{vac}}$</td>
<td>Vacuum band</td>
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<td>FE</td>
<td>Field emission</td>
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<td>FEA</td>
<td>Field emission array</td>
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<td>FED</td>
<td>Field emission display</td>
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<td>FEED</td>
<td>Field emission energy distribution</td>
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<td>FET</td>
<td>Field effect transistor</td>
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<tr>
<td>FIB</td>
<td>Focussed ion beam</td>
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<tr>
<td>FIT</td>
<td>Fluctuation induced tunnelling</td>
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<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
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<tr>
<td>h</td>
<td>Height</td>
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<tr>
<td>IC</td>
<td>Integrated circuit</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>K-H</td>
<td>Kratschmer and Huffman</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>LED</td>
<td>Light emitting diode</td>
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<tr>
<td>MOSFET</td>
<td>Metal oxide field effect transistor</td>
</tr>
<tr>
<td>MPCVD</td>
<td>Microwave plasma chemical vapour deposition</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>PCD</td>
<td>Pulse code modulation</td>
</tr>
<tr>
<td>PDP</td>
<td>Plasma display panel</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced chemical vapour deposition</td>
</tr>
<tr>
<td>PmPV</td>
<td>Poly (p-phenylenevinylene-co-2, 5-dioctyloxy-m-phenylenevinylene)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>r</td>
<td>Radius</td>
</tr>
<tr>
<td>RGB</td>
<td>Red, green, blue</td>
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<tr>
<td>RMS</td>
<td>Root mean square</td>
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<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
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<tr>
<td>SCLC</td>
<td>Space charge limiting current</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>STN</td>
<td>Super twist nematic</td>
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<tr>
<td>TEM</td>
<td>Tunnelling electron microscope</td>
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<tr>
<td>TFT</td>
<td>Thin film transistor</td>
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<tr>
<td>TN</td>
<td>Twist nematic</td>
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<tr>
<td>TV</td>
<td>Television</td>
</tr>
<tr>
<td>u.a</td>
<td>Unit area</td>
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<tr>
<td>VFD</td>
<td>Vacuum fluorescent display</td>
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<tr>
<td>VGA</td>
<td>Video graphics accelerator</td>
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<tr>
<td>W</td>
<td>Work area</td>
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<tr>
<td>WKB</td>
<td>Wentzel – Kramers - Brillouin</td>
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CHAPTER ONE

1 Introduction

The introduction to this thesis gives an overview of the key subjects covered. The different types of displays, from cathode ray tubes, to the new area of flat panel displays, including liquid crystal displays (LCD), plasma display panels (PDP) and field emission displays (FED) are covered, with explanations as to their operation and advantages and disadvantages when compared to other display technologies. The theory and mechanism of electron field emission is explained, while examining the implications of the Fowler-Nordheim theory, hot electron induced emission, negative electron affinity, electron field enhancement factor and electric field screening.

The chapter concludes with a brief introduction to carbon nanotubes and three terminal field emission devices.

1.1 Displays

There are many types of displays available, each offering different advantages over the others. The cathode ray tube (CRT), a technology over 100 years old, is still the market leader for applications such as home televisions and computer screens, but demand for flat panel screens is growing daily. These thinner screens are becoming increasingly more common; very large home cinema uses plasma screens, laptop computers, mobile phones, palm desktop assistants (PDA) all use thin film transistor liquid crystal displays (TFT-LCD). New technology has led to important devices such as head up displays for the military requiring low power, lightweight and reliable displays, and mobile display and monitoring units for paramedics.
The most common flat screen, found in portable devices, is the thin film transistor (TFT) driven liquid crystal display (LCD) or active matrix liquid crystal display (AMLCD), where a TFT controls the state of a liquid crystal pixel. However, these displays can have poor viewing angles and slow refresh rates, and due to them needing large polycrystalline and amorphous silicon substrates for the fabrication of the TFT structure, they are very much limited to a screen size of 36” diagonal due to transistor yield, which in turn keeps the consumer price high.

Larger screens, over 36 inch diagonal, use a plasma to illuminate pixels. This is where a plasma is struck between two glass pillars and strikes a phosphor pixel above. Regarded as the current market leader for large area, there is no real limit on size (displays of 100 inch+ diagonal are available). However, with high power consumption, poor colour saturation, relatively low life span and high price due to complex fabrication methods, there is still a need for a new screen technology that operates at low power and is of low cost. Fig. 1.1 is a hierarchy of the most common displays available.

The next sections overview the current screen technologies, highlighting each ones advantages and disadvantages.
1.1.1 Cathode ray tube

The cathode ray tube (CRT) has been the benchmark display since its first appearance as an indication tube for studying alternating currents in 1897 by Karl Ferdinand Braun, the then director of the Physical Institute of Strasbourg. Shortly after, it was discovered by J. J. Thompson that the tube was based on charged particles that are now known as electrons.

The picture is made by rapidly scanning an electron beam in a vacuum tube whose inner front surface is covered by red, green, and blue (often referred to as RGB) phosphors creating a colour image. Electrons generated by a heated cathode are accelerated towards the phosphors by a static high-voltage field and deflected by magnetic fields, which, together with the electron beam current, are controlled by a video signal. As the electrons impact on the screen, phosphors are excited and emit coloured light.

The CRT is a very simple and mature device, and the production costs have been trimmed. It features advantages such as high response speed suitable for high-frame rate, high-resolution video, wide viewing angle, saturated colours, high peak luminance, and high contrast. However, due to the high-voltage field, oscillating magnetic field, and Bremsstrahlung X-rays generated by electrons hitting the screen, the CRT has been regarded as hazardous for long-term use. Fig. 1.2 is a schematic of a standard CRT.

![Fig. 1.2. Schematic of a CRT](image)

1.1.2 Liquid crystal displays

Liquid crystal displays (LCDs) are the most common type of flat panel displays and have been widely used since the early 1970's. All LCDs utilize the mechanism whereby certain
organic molecules (liquid crystals) can be reoriented by an electric field. As these materials are optically active, their natural twisted structure can be used to turn the polarization of light by, for example, 90 degrees. Two crossed polarizer’s normally do not transmit any light but if a 90°-twisted LC is inserted in between, light will be transmitted. On the other hand, applying an electric field will unwind the helical structure and the LC therefore loses its polarization-rotating characteristics. As a result, the display turns dark. An LCD consists of an array of pixels which can be individually addressed either passively or actively. Direct-view LCDs can largely be categorized into reflective and transmissive displays which utilize ambient light and light from a fluorescent backlight tube, respectively.

The main breakthrough in the development of LCDs was the invention of the so-called twisted nematic effect by Schadt and Helfrich in 1971. It is still the most prominent type of liquid crystal light modulators in modern displays. Fig. 1.3. shows the principle. A nematic liquid crystal is filled between two glass plates, which are separated by thin spacers, coated with transparent electrodes and orientation layers inside. The orientation layer usually consists of a polymer (e.g. polyimide) which has been unidirectionally rubbed, for example, with a soft tissue. As a result, the liquid crystal molecules are fixed with their alignment more or less parallel to the plates, pointing along the rubbing direction, which include an angle of 90 degrees between the upper and the lower plate. Consequently, a homogeneous twist
deformation in alignment is achieved. The polarization of a linearly polarized light wave is then guided by the resulting quarter of a birefringent helix, if the orientation is not disturbed by an electrical field. The transmitted wave may therefore pass a crossed exit polarizer, and the modulator appears bright. If, however, an AC voltage of a few Volts is applied, the resulting electrical field forces the molecules to align themselves along the field direction, and the twist deformation is unwound. Now, the polarization of a light wave is not affected and can not pass the crossed exit polarizer. The modulator appears dark. Obviously, the inverse switching behaviour can be obtained with parallel polarizers. It must be noted further, that grey scale modulation is achieved easily by varying the voltage between the threshold for reorientation (which is a result of elastic properties of LCs) and the saturation field.

To display information with a liquid crystal modulator, the transparent indium-tin-oxide (ITO) electrodes are structured by photo-lithographical techniques. For simple numerical and alpha-numerical displays, as required for watches or pocket calculators etc., segmented electrodes are sufficient. All segments are placed on one plate of the display with a common counter electrode at the opposite and can be addressed separately. If more complex data or graphics are desired, a matrix arrangement of electrodes is more convenient. Obviously, addressing of matrix displays is more sophisticated than with segmented electrodes. For large matrices it is impossible to address each pixel separately with an own supply, since space between pixels is limited and the number of connections increases as \( R \times C \), if \( R \) and \( C \) are the numbers of rows and columns, respectively.

Fig. 1.4. A passive matrix display layout.
The number of electrical connections with a matrix display can be reduced by using crossed row and column stripe electrodes at the front and exit glass plates, as schematically drawn in Fig. 1.4. The pixels are determined by the crossing points between the row and column electrodes, and, in principle, can be addressed by applying a voltage between the corresponding stripes. However, arbitrary pixel patterns cannot be generated by this, but need a more complex driving scheme to allow independent addressing of pixels and to avoid cross talk problems. These driving schemes are known as time multiplexing. Since time multiplexing with crossed electrodes takes advantage of the inherent dynamic properties of liquid crystals, they are often called passive matrix displays.

![Diagram of a matrix display with TFTs](image)

**Fig. 1.5. Thin-Film-Transistor or active matrix displays.**

A technique to obtain good optical contrast with time multiplexing of a matrix display is to provide each pixel with its own electronic switch. These are Thin-Film-Transistor (TFT) or active matrix displays, shown in Fig. 1.5. Rows and columns, cross-over insulators, thin film transistors (amorphous silicon) and transparent pixel electrodes are placed on a glass plate by photo-lithographical techniques. The opposite plate contains the common counter electrode. Since the electro-optically active part of the display is reduced by the TFTs to typically between 30 and 60 %, additional masks are required to block light leaking through the non-active parts and hence to improve the contrast of the display. In total, 6 to 9 lithographical steps are necessary, which makes the fabrication process of these displays more expensive.
1.1.3 Plasma display panel

A plasma display panel (PDP) is essentially a matrix of tiny fluorescent tubes which are controlled in a sophisticated fashion. There are two main types, DC and AC, of which the latter has become mainstream because of its simpler structure and longer lifetime. This section treats the AC type.

A plasma discharge is first induced by the positive period of an AC field and a layer of carriers is formed shortly thereafter on top of the dielectric medium. This causes the discharge to stop but is induced again when the voltage changes polarity. In this manner, a sustained discharge is achieved. The AC voltage is tuned just below the discharge threshold so the process can be switched on and off by adding a relatively low voltage at the address electrode.

The discharge creates a plasma of ions and electrons which gain kinetic energy by the electric field. These particles collide at high speed with neon and xenon atoms, which thereby are brought to higher energy states. After a while, the excited atoms return to their original state and energy is dissipated in the form of ultraviolet radiation. This radiation, in turn, excites the phosphors which glow in red, green, and blue (RGB) depending on the nature of the phosphor used. Since each discharge cell can be individually addressed, it is possible to switch the pixels on and off.

Fig. 1.6. Principle of an AC plasma display panel. Image modified from [2].
CHAPTER ONE Introduction

To generate colour shades, the perceived intensity of each RGB colour must be controlled independently. While this is done in CRTs by modulating the electron beam current, and therefore also the emitted light intensities, PDPs accomplish shading by pulse code modulation (PCM). Dividing one field into eight sub-fields, each with pulse weighted according to the bits in an 8-bit word, makes it possible to adjust the widths of the addressing pulses in 256 steps. Since the eye is much slower than the PCM, it will integrate the intensity over time. Modulating the pulse widths will therefore translate into 256 different intensities of each colour. The number of colour combinations is therefore \(256 \times 256 \times 256 = 16,777,216\).

At first, PDPs had problems with disturbances caused by interference between the PCM and fast moving pictures. By fine-tuning the PCM scheme, this problem has been eliminated. While PDPs are relatively light weight and can be manufactured at a thickness of 3-4 inches, they still consume prohibitively high power. The luminous efficiency, i.e. the amount of light for a given amount of supplied electric power, is still at approximately \(1 \text{ lm/W}^2\), about 10% of some other display technologies. Also, the discharge process causes sputtering of the cells which inevitably reduces lifetime. With a new protective dielectric layer of MgO, however, this problem has largely been solved.

Despite these problems, PDPs are promising because of their modest requirements on manufacturing technology. Compared to TFT-LCDs, which use photolithographic and high-temperature processes in clean rooms, PDPs can be manufactured in less clean conditions using low-temperature and inexpensive direct printing processes. Also, PDPs feature wide viewing angles, no susceptibility to magnetic fields, and are easy to scale up for wall-hanging TV applications.

1.1.4 Vacuum fluorescent display

VFDs (Vacuum Fluorescent Displays) are an alternate type of flat panel display, invented in Japan in 1967. They work by suspending a small cathode in a rectangular vacuum tube, and heating it to just below incandescence (visible glowing), electrons are emitted in all directions. One side of the tube is coated in phosphor, and a metal grid with pixel-sized holes cut in, separating the cathode from the coating. The controller chip supplies a voltage to the metal grid, individually switching pixels. An example of a VFD is shown in Fig 1.7.
The end result is that VFDs are much, much brighter, and much easier to read at a distance than LCD and plasma, and can operate at relatively low voltages. The output light is also more distinctive than that of LCDs. Their downsides include their price, and their higher current requirements.

![Image of a VFD display](image)

**Fig. 1.7. A display application of a VFD [3].**

### 1.1.5 Organic light emitting diode

Organic light emitting diodes (OLEDs) are brighter, thinner, lighter, and faster than the normal liquid crystal display in use today. They also need less power to run, offer higher contrast, look just as bright from all viewing angles and are - potentially - a lot cheaper to produce than LCD screens.

Because they generate their own light, light-emitting diodes (LED) have long been considered the route to a better display. Conventional LED displays have been used successfully in giant screens usually seen in outdoor advertising or as billboard sized screens and displays in open air music concerts, but these cannot be easily adapted to the small, high-resolution screens found in notebook computers. However, the OLED is an LED of a totally different kind - based on carbon-based molecules instead of inorganic semiconductors.

Various companies have already shown off the most recent OLED developments - mostly for portable devices, where the new displays really shine. Motorola has incorporated an OLED display (from Pioneer) in its Timeport line; eMagin and IBM have teamed up to create a prototype OLED display for a "wearable" computer; and Pioneer also introduced an OLED display for a car radio. At the larger end of the technology, Sony is set to exhibit a display with a 13" diagonal suitable for notebook computers or TVs, which points to the future of OLED. In the future Sony intends to start selling much larger TV screens that are 20 to 30 inch across.

In addition, Sanyo (Japan) and Kodak Inc have joined together to form one of the largest partnerships to develop small molecule OLEDs for displays that range from mobile phones to
portable displays and desktop computers. Fig. 1.8 shows Kodak’s 2.2-inch diagonal, full-colour active matrix OLED display.

![2.2" diagonal full colour OLED display](image)

Fig. 1.8. 2.2" diagonal full colour OLED display [4].

On the other end of the spectrum, CDT, (Cambridge Display Technologies) have licensed their long molecular chain PPV polymers to a number of large multinationals to develop products. Companies include Philips and Epson. Epson is helping to develop a printable OLED solution with CDT for consumer products. Samsung recently unveiled a prototype 40” diagonal OLED display at the Society for Information Displays (SID) 2005 conference.

1.1.6 Field emission display

The process of extracting electrons from the surface of a material is known as electron field emission, and is discussed in section 1.2 of this chapter. Extracted electrons are accelerated towards a phosphor screen to illuminate it, much in the same manner as the electron beam in a conventional CRT, however, one advantage of the field emission display, (FED), are that they can be thin.

![A simple field emission display](image)

Fig. 1.9. A simple field emission display. Electrons flowing from the micro tips, by electron field emission, illuminate the phosphors [5].
The fundamental technologies of the field emission display devices are based on the LCD and CRT technology. The FED has many advantages, compared with conventional LCD and CRT, such as high performance, low cost, and low power consumption and higher image quality.

Field emission units are arranged in a matrix format to display an image on a phosphor screen, as shown in Fig. 1.9. When the micro-tips are activated, electrons will flow onto the phosphor, at a high bias voltage, exciting it. The base plate of a field emission display is fabricated by integrated circuit, (IC) & TFTLCD technology. The main advantage here is that the yield of the fabrication is not as important as in TFTLCD screens. If, say, 20% of the micro-tips in an individual pixel are inactive, the corresponding pixel will probably still work. Whereas, in TFTLCD screens, if one TFT is inactive then the corresponding pixel will not work.

To produce a colour image, arrays of red, blue and green phosphors are illuminated by emitted electrons exciting them. With small, densely packed red, green and blue phosphors, over a large enough area, full colour video can be achieved. A possible application for field emission displays is in imaging equipment for medical instrumentation. Whilst the reliability of the display would be key in such an application, a published work in 1999 [6] highlighted some of the specifications for field emission displays in the medical industry. Table 1.1 shows a comparison of requirements for film, high and good picture quality.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Film-Quality</th>
<th>High-Fidelity</th>
<th>Good-Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (cm)</td>
<td>35 x 43</td>
<td>30 x 36</td>
<td>24 x 30</td>
</tr>
<tr>
<td>Pixels</td>
<td>4,000 x 5,000</td>
<td>2,500 x 3,000</td>
<td>1,200 x 1,500</td>
</tr>
<tr>
<td>Pixel size (mm)</td>
<td>0.08</td>
<td>0.12</td>
<td>0.2</td>
</tr>
<tr>
<td>Refresh rate</td>
<td>Static</td>
<td>Static-80 Hz</td>
<td>Static-80 Hz</td>
</tr>
<tr>
<td>Maximum luminance (cd/m²)</td>
<td>2,000</td>
<td>1,000</td>
<td>240</td>
</tr>
<tr>
<td>Minimum luminance (cd/m²)</td>
<td>1</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Gray-scale levels</td>
<td>850</td>
<td>680</td>
<td>530</td>
</tr>
<tr>
<td>Emission</td>
<td>Lambertian</td>
<td>Lambertian</td>
<td>Lambertian</td>
</tr>
<tr>
<td>Colour</td>
<td>Monochrome</td>
<td>Monochrome</td>
<td>Monochrome</td>
</tr>
<tr>
<td>Veiling glare ratio</td>
<td>&gt;1,000</td>
<td>400</td>
<td>150</td>
</tr>
<tr>
<td>Large-area distortion</td>
<td>&lt;0.1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Diffuse reflectance (nit/lux)</td>
<td>0.025</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Specular reflectance (nit/nit)</td>
<td>0.024</td>
<td>0.002</td>
<td>0.005</td>
</tr>
<tr>
<td>Vertical viewing angle</td>
<td>Full</td>
<td>±45°</td>
<td>±30°</td>
</tr>
<tr>
<td>Horizontal viewing angle</td>
<td>Full</td>
<td>±60°</td>
<td>±45°</td>
</tr>
</tbody>
</table>

Table 1.1. Specification for a field emission display for medical imaging. [6]
1.2 Field Emission

Electron field emission is the process of extracting electrons from the surface of a material under the influence of an externally applied electric field. This field, together with the image charge effects of the material, sufficiently distort and lower the vacuum energy band so that electrons can quantum mechanically tunnel through, and escape into the vacuum.

The emission process is mainly dependant on the work function ($\phi$) of the material, any field enhancement factor (geometric or otherwise) and the applied electric field. The understanding of the process of field emission has been described by several different mechanisms. Fig. 1.10 illustrates the different accepted field emission mechanisms.

![Field Emission Diagram]

**Fig. 1.10. The different physical mechanisms that may occur on a metal surface upon the application of an electric field.**

Generally, as the applied electric field is increased, thermionic emission over the top of the surface barrier (or work function, $\phi$) will occur, followed by emission over the field-reduced barrier (Schottky emission). Field emission will then occur partially over the barrier, if the temperature is high enough, and partially through the barrier. As the temperature is decreased, electrons will be emitted from the Fermi level having tunnelled through the barrier (Fowler-Nordheim tunnelling) and finally, at high fields, emission from below the Fermi level is possible (ballistic electron emission).
1.2.1 Field emission theory

Below is the theory of how an externally applied electric field, together with the image charge effects of a material, can change the vacuum energy band. Fig. 1.11 is an energy band diagram of this process.

When an electron is considered to be at a distance $x$ from the material, a positive charge is induced on the surface of the material. There is now a force between the electron and the surface ($-x$ from the electron). This is a positive charge, and called the image charge, and the force, called the image force, is described by,

$$ F = \frac{-q^2}{4\pi(2x)^2\varepsilon_0} = \frac{-q^2}{16\pi\varepsilon_0 x^3} $$  \hspace{1cm} (1.1) $$

Where $\varepsilon_0$ is the permittivity of free space, and $q$ is the charge of an electron.
The work done during the path of the electron (between infinity and \( x \)) is given by:

\[
E(x) = \int_{\infty}^{x} F \, dx = \frac{q^2}{16\pi\varepsilon_0 x}
\]  

(1.2).

This energy is the potential energy of the electron at the distance \( x \).

Now when an external electric field, \( E \), is applied, the potential energy (measured down from the \( x \) axis) is given by:

\[
PE(x) = \int_{\infty}^{x} F \, dx = \frac{q^2}{16\pi\varepsilon_0 x} + qEx \quad eV
\]  

(1.3).

The Schottky barrier lowering, or image force lowering, \( \Delta\phi \), and the location of the lowering, \( x_m \), as seen in Fig. 1.11 are given by the condition:

\[
\frac{d[PE(x)]}{dx} = 0
\]  

(1.4).

where

\[
x_m = \sqrt{\frac{q}{16\pi\varepsilon_0 E}} \quad cm
\]  

(1.5).

and

\[
\Delta\Phi = \sqrt{\frac{qE}{4\pi\varepsilon_0}} \quad V
\]  

(1.6).

From equations 1.5 and 1.6, at a high electric field, the Schottky barrier is lowered and the effective work function, \( \phi \) eV) is reduced. For example, for an electron in a field of 10 V\( \mu \)m\(^{-1}\), using equations 1.5 and 1.6 we get \( \Delta\phi=0.12 \) V and \( x_m=60 \) Å. Thus, at high fields the Schottky barrier is considerably lowered, and the effective metal work function is reduced.
Modifying the metal – vacuum diagram seen previously in Fig. 1.11, it can be shown that increasing the electric field, the Schottky barrier is lowered and the affective work function, ($\phi$ eV) is reduced. Fig. 1.12. shows how increasing electric fields increasingly lower the vacuum band.

1.3 Field emission mechanisms

1.3.1 Fowler-Nordheim theory

This theory was created as a means to explain electron field emission from metals into a vacuum. The model states that electrons can quantum mechanically tunnel from the Fermi level, $E_F$, through a potential barrier from a metal into a vacuum [7]. The following assumptions were made:

1. Free electron model approximation
2. Temperature = 0 K
3. Surface was smooth and planar
4. Potential barrier between metal and vacuum is a superposition of an applied electric field and an image force

When Fermi-Dirac statistics [8] and Wentzel, Kramers, and Brilluoin (WKB) approximations [8] are applied to the theory, it gives rise to the following simplified expression.

\[
I = \frac{aA \beta^2 V^2}{\phi} \exp \left[ -\frac{b\phi^2}{\beta V} \right]
\]  
(1.7)

Where:

- \( I \): Emission current in Amperes
- \( A \): Emission area in mm\(^2\)
- \( \phi \): Work function of the metal in eV
- \( a \) and \( b \): Constants with values \( 1.54 \times 10^6 \text{ AeVV}^{-2} \) and \( 6.83 \times 10^7 \text{ eV}^{-3/2} \text{V}^{-1} \) respectively
- \( \beta \): A geometric factor defined as the local electric field at the metal surface divided by the applied field, often referred to as enhancement factor

![Diagram illustrating Fowler-Nordheim theory](image)

**Fig. 1.13.** Fowler-Nordheim theory showing distorted vacuum energy band allowing electrons to quantum mechanically tunnel from the Fermi level through the vacuum band into the vacuum

It is possible to show that the voltage-current data for field emission behaves in a manner which could be explained by the Fowler-Nordheim theory. Looking at equation 1.7;
CHAPTER ONE  Introduction

\[ I = \frac{aA\beta^2V^2}{\phi} \exp \left( -\frac{b\phi^2}{\beta V} \right) \]

\[ \log I = \log \left( \frac{aA\beta^2V^2}{\phi} \right) - \frac{b\phi^2}{\beta V} \]  
(1.8).

\[ \log \frac{I}{V^2} = \log \frac{aA\beta^2}{\phi} - \frac{b\phi^2}{\beta V} \]  
(1.9).

Plot,

\[ \log \frac{I}{V^2} \text{ vs } \frac{1}{V} \]

If the plot gives a straight line then the emission can be said that it is most probably Fowler-Nordheim based. It is also possible to extract a value for the enhancement factor, \( \beta \), if \( \phi \) is known, since the gradient of the plot is:

\[ \text{slope} = -\frac{b\phi^2}{\beta} \]  
(1.10).

1.3.2  Hot electron induced emission

The emission mechanism of some carbon thin films generally follow the Fowler-Nordheim model as listed previously. However, when the work function, \( \phi \), is extracted from the Fowler-Nordheim equation, unrealistically small values, up to two orders of magnitude smaller than expected are observed. It is suggested that in such samples the emission point is from the back contact and is controlled by the substrate.

The carbon film acts as a space charge interlayer, where a large enough field penetration can cause significant band bending from the vacuum surface of the substrate. This means that electrons are induced through the back contact by surmounting the heterojunction formed by the Si substrate and semiconducting carbon film. The electrons are known as hot electrons.
when a high internal field accelerates them towards the surface undergoing only a few collisions. In defect free materials they retain the majority of their energy, are not in thermal equilibrium with the host material, and have energy above the bottom of the conduction band. They have a high probability of escaping the vacuum barrier. Fig. 1.14 illustrates an example of hot electron induced emission.

![Diagram of energy levels](image)

**Fig. 1.14.** With the vacuum energy level reduced sufficiently, electrons can jump over the vacuum barrier, not through, as described in the Fowler Nordheim model.

### 1.3.3 Negative electron affinity

The affinity, $\chi$, of a material is defined as the energy required to remove an electron from the bottom of the conduction band, far enough away, i.e. away from image charge effects, to the vacuum level. It is measured in eV and from the conduction band to the vacuum. In certain wide band gap materials, such as hydrogen-terminated (111) diamond [9], the conduction band, $E_C$, lies above (or in practice close to) the vacuum level, $E_{\text{vac}}$. Therefore, the energy of emitted electrons from the diamond film can be greater than that of the vacuum. It now follows that electrons present in the conduction band of such a material would be emitted under the influence of very small external electric fields.

### 1.3.4 Field enhancement factor

The Fowler-Nordheim model was originally designed for a flat emitter, as stated in the assumptions listed previously. Modifications were later made to cater for three-dimensional emitters. Considering a point emitter, for example a sharp spike, the electric field at the tip,
$E_{\text{loc}}$ is greater than that of a point far away, $E_{\text{appl}}$. The local field is said to be enhanced by a factor, $\beta$, and can be expressed as follows.

$$E_{\text{loc}} = \beta E_{\text{appl}}$$  \hspace{1cm} (1.11)

To illustrate how field enhancement factor is calculated, a computer simulation of a single emitter was performed. The Silvaco™ package was used, and is explained in detail in Chapter 4. A single emitter was placed in a vacuum in between flat anode and cathode electrodes. Fig. 1.15 shows the simulation setup. A voltage of 400 V was applied between the anode and grounded cathode. Electric field lines are shown superimposed on the simulation setup.

![Simulation of a single emitter in a vacuum between two flat electrodes. Electric field lines are shown.](image)

The distance between anode and cathode is 10 μm, so therefore the applied field is

$$E_{\text{appl}} = \frac{V}{D}$$
$$= \frac{400 \text{ (V)}}{10 \text{ (μm)}}$$
$$= 4 \times 10^7 \text{ Vμm}^{-1}$$  \hspace{1cm} (1.12)

The simulation package allows the field at the tip of the emitter to be extracted. The local field was found to be $2.3 \times 10^6 \text{ Vcm}^{-1}$. So, using equation 1.11, the enhancement factor, $\beta$, can be shown to be,

$$\beta = \frac{E_{\text{loc}}}{E_{\text{appl}}}$$  \hspace{1cm} (1.13)
Therefore this simulated emitter has an enhancement factor of 5.75.

1.3.5 Field screening

Field enhancement is achieved by carbon nanotubes (and any other tip based structure) in a distortion and grouping of equipotential lines near the tip of the structure. The increasingly dense equipotential lines give rise to a higher electric field than due to \( E = \frac{V}{D} \). When more than one emitter exists, the density of equipotential lines decreases at the tip as the emitters are brought closer together. One can think of it that if only one emitter were present, the equipotential lines would eventually touch the substrate, but as a second emitter draws close to the first, the effective substrate equipotential line moves up. The effect of field screening is important when designing an array of emitters, as if the emitters are too close, the local field drops, therefore the field enhancement drops, therefore the emission drops [10]. Field screening is explored later in the thesis.

1.4 Carbon nanotubes

Carbon nanotubes [11] are tubular carbon molecules with properties that make them potentially useful in extremely small scale electronic and mechanical applications. They exhibit unusual strength and unique electrical properties [12], and are extremely efficient conductors of heat [12]. A nanotube is a rolled up graphene sheet and each end is capped with half a fullerene molecule (C_{60}). They measure only a few nanometers wide, and their length can be millions of times greater than their width, and are composed entirely of sp^3 bonds, similar to graphite [12].
There are two main categories of nanotubes: single-walled (SWNT) made up of a single graphene layer, and multi-walled (MWNT) which contain concentric graphene rings. Additionally, there are a large variety of forms of each of these, identified by a two-digit sequence. The first digit indicates how many carbon atoms around the tube there are, the second digit determines the offset of where the nanotubes wrap around to. If the second digit is a zero, the nanotubes are called "armchair". If both digits are the same, the nanotubes are called "zigzag". Otherwise, they are called "chiral" [12].

In theory, nanotubes which conduct can have an electrical current density greater than 1,000 times higher than metals, such as silver and copper. All nanotubes are expected to be incredible thermal conductors along the tube, but good insulators laterally to the tube.

Nanotubes can be opened and filled with materials such as biological molecules, raising the possibility of applications in biotechnology. They can be used to dissipate heat from tiny computer chips. The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering. Though it is debatable if nanotube materials can ever be made with a tensile strength approaching that of individual tubes, composites may still yield incredible strengths, potentially sufficient to allow the building of such things as artificial muscles, ultrahigh-speed flywheels, and more.

One use for nanotubes that has already been developed, is as electron field emitters [13-15], which could be used as electron sources in thin, high-brightness, low-energy, low-weight displays. This type of display would consist of a group of many tiny emitters, each providing the electrons which are accelerated to hit and illuminate the phosphor of one pixel. These displays are known as Field Emission Displays (FEDs).
1.5 Three terminal devices

Whilst two terminal (i.e. anode and cathode) electron field emission is possible from CNTs, the voltages required to illuminate phosphor screens at a reasonable distance from the CNTs is often in the thousands of volts. For display purposes, we need to be able to address and therefore switch the emission current on and off quickly, safely and without the need of complex driver circuitry.

A common solution to this problem is to design a three terminal device having anode, cathode and gate electrodes in a setup similar to that of Fig. 1.17.

![Diagram of three terminal device](image)

Fig. 1.17. Theoretical three terminal field emission device.

The theory is that the anode, or voltage applied to the phosphor screen, is kept at a constant value, this typically high voltage. The cathode, or voltage to the CNTs is earthed, and it is the gate voltage which is varied.

As the gate electrode is close to the CNT emitters, when a small voltage is applied, a large electric field is produced which extracts electrons from the CNT by process of electron field
emission (see section 1.2). The electrons are then accelerated upwards and drawn to the high voltage applied to the anode. As the gate voltage is low, typically (0-10 V) it can be easily addressed.

1.6 References

1  Image reproduced from www.nationmaster.com/encyclopedia/
2  Image modified from www.atip.org/fpd/
3  Image reproduced from www.mansky.co.uk
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CHAPTER TWO

2 Literature Review of Carbon Nanotubes

2.1 Introduction

This chapter will outline the topics of importance and relevance associated with carbon nanotubes (CNT). We look first at how and when these unique structures were discovered, then look in detail at their properties. The varying methods in which CNT structures are fabricated; arc discharge, laser ablation and chemical vapour deposition (CVD) are discussed. We also review work on CNT-polymer composites before moving onto field emission from CNTs.

Whilst the theory of electron field emission is detailed in Chapter 1, in this literature review we focus on field emission from CNT. The threshold field and field enhancement factors are both detailed for emission from a single CNT, whilst field screening and the effect of orientation are covered for arrays of CNT.

We look at the manner in which CNT field emitters are fabricated into three terminal devices for applications including X-ray sources, and flat screen field emission displays.

2.2 Discovery

Carbon can be found in a variety of everyday materials, from the soft, lightweight three-dimensional lattice of carbon atoms, graphite, which is found in pencils, to the perfectly crystalline, hardest structure known to man, diamond.
The reason why carbon can assume many structural forms is that the carbon atom can form several distinct types of valence bonds [1], enabling the carbon atom to bond with itself in endlessly varied combinations of chains and rings [2].

Until recently there were only two main allotrope forms of crystalline carbon, graphite and diamond. It was Kroto, Smalley and Curl’s experiments on carbon clusters formed by laser vaporisation of graphite that showed a new structure. A distribution of gas-phase carbon clusters was observed, containing mainly clusters of exactly 60 carbon atoms. But it was the discovery of an enclosed cluster, seen in Fig. 2.1, which sparked interest. This structure had unique stability and form. The discovery of $C_{60}$ was published in Nature in November 1985 [3].

![Fig. 2.1. Representation of a $C_{60}$ molecule. [4]](image)

It was found later by Kratschmer and Huffman (K-H) that bulk (90% pure) $C_{60}$ could be produced by the arc evaporation of graphite rods. Iijima of NEC, Japan, was interested in this recent $C_{60}$ discovery and decided to study the soot produced by the K-H technique. The hard, cylindrical deposit formed on the cathode after the arc had been struck, had previously been discarded as a by-product of little use. However, upon study, Iijima discovered tiny carbon fibres consisting of cylinders of graphite closed at each end with caps of precisely six pentagonal rings, essentially a $C_{60}$ cut in half with a rolled up graphite sheet in-between.

These hollow tubes had diameters of between 2.5 nm to 30 nm, and had multiple outer layers. Named nanotubes, these striking results were published in Nature in November 1991[5].

![Fig. 2.2. Representation of a nanotube. Essentially, an elongated fullerene [5]](image)
CHAPTER TWO Literature review of carbon nanotubes

Carbon nanotubes can assume two basic structures, single walled carbon nanotubes (SWNTs) [12] and multi walled carbon nanotubes (MWNTs) [1]. Conceptually, single-wall carbon nanotubes can be considered to be formed by the rolling of a single layer of graphite, or graphene layer, into a seamless cylinder. A multiwall carbon nanotube can similarly be considered to be a coaxial assembly of cylinders of SWNTs, like a Russian doll, one within another; the separation between tubes is about equal to that between the layers in natural graphite. Hence, nanotubes are one-dimensional objects with a well-defined direction along the nanotube axis that is analogous to the in-plane directions of graphite. Fig. 2.3 illustrates SWNT and MWNT.

![Fig. 2.3. Representation of a single walled carbon nanotube (left) [13] and a multiwalled carbon nanotube (right) [14]](image)

2.3 Structure and Properties

2.3.1 Basic structure

Simply put, carbon nanotubes exist as a macro-molecule of carbon, analogous to a sheet of graphite rolled into a cylinder. Graphite looks like a sheet of chicken wire, a tessellation of hexagonal rings of carbon atoms. Sheets of graphite lay stacked on top of one another, but due to the weak π bonds they slide past each other and can be separated easily, which is how it can used for writing, in pencil leads. However, when coiled, the carbon arrangement becomes very strong. In fact, nanotubes have been known to be up to one hundred times as strong as steel and almost two millimetres long. [6] These nanotubes have a hemispherical "cap" at each end of the cylinder. They are light, flexible, thermally stable, and are chemically
inert. They have the ability to be either metallic or semi-conducting depending on the "twist" of the tube, often referred to as chirality.

Nanotubes form different types, which can be described by the chiral vector \((n, m)\), where \(n\) and \(m\) are integers of the vector equation \(R = na_1 + ma_2\). The chiral vector is shown in Fig. 2.4. Imagine that the nanotube is unravelled into a planar sheet as shown in Fig. 2.4. Draw two lines (the blue lines) along the tube axis where the separation takes place. In other words, if you cut along the two blue lines and then match their ends together in a cylinder, you get the nanotube that you started with. Now, find any point on one of the blue lines that intersects one of the carbon atoms (point A). Next, draw the armchair line (the thin yellow line), which travels across each hexagon, separating them into two equal halves. Now that you have the armchair line drawn, find a point along the other tube axis that intersects a carbon atom nearest to the armchair line (point B). Now connect A and B with our chiral vector, \(R\) (red arrow). The wrapping angle \(\Phi\); (not shown) is formed between \(R\) and the armchair line. If \(R\) lies along the armchair line (\(\Phi = 0^\circ\)), then it is called an "armchair" nanotube. If \(\Phi = 30^\circ\), then the tube is of the "zigzag" type. Otherwise, if \(0^\circ < \Phi < 30^\circ\) then it is a "chiral" tube. The vector \(a_1\) lies along the "zigzag" line. The other vector \(a_2\) has a different magnitude than \(a_1\), but its direction is a reflection of \(a_1\) over the armchair line. When added together, they equal the chiral vector \(R\) [7].

The values of \(n\) and \(m\) determine the chirality, or "twist" of the nanotube. The chirality, in turn affects the conductance of the nanotube, it's density, it's lattice structure, and other properties. A SWNT is considered metallic if the value \(n - m\) is divisible by three. Otherwise, the nanotube is semiconducting. Consequently, when tubes are formed with random values of \(n\)
and \( m \), we would expect that two-thirds of nanotubes would be semi-conducting, while the other third would be metallic, which happens to be the case [7]. Given the chiral vector \((n,m)\), the diameter of a carbon nanotube can be determined using the relationship:

\[
d = (n^2 + m^2 + nm)^{1/2} \times 0.0783 \text{ nm}
\]  

(2.1)

Fig. 2.5. is an example of the two extremities of chirality’s; armchair and zigzag.

![Armchair and Zig-zag CNT](image)

Fig. 2.5. Examples of an armchair and zig-zag CNT with their chiral diagram shown.

### 2.3.2 Carbon nanoropes and nanofibres

In 1996, Thess et al. measured the properties of "ropes" of carbon nanotubes produced by pulsed laser ablation of graphite [8]. As shown in Fig. 2.6, ropes are bundles of tubes packed together in an orderly manner. They found that the individual SWNTs packed into a close-packed triangular lattice with a lattice constant of about 17 Å. This was later confirmed by Gao, Cagin, and Goddard in 1997 [9]. In addition, they concluded that the density, lattice parameter, and interlayer spacing of the ropes were dependent on the chirality of the tubes in the mat [9]. Exposed CNT protruding from the end of a carbon nano rope is explored in Chapter 5.

Carbon nanofibres differ from carbon nanotubes in that their diameter is larger (>50 nm). Unlike the concentric rings of rolls of grapheme usually associated with MWCNT, CNF have a herring bone structure of graphene. CNF are explored in Chapter 6.
CHAPTER TWO Literature review of carbon nanotubes

Fig. 2.6. A single nanotube rope consisting of approximately 100 SWNT's. The SWNT pack in a triangular lattice. [8]

2.3.3 Optical properties

2.3.3.1 The Fundamental Gap

The study by Wilder et al. [7] showed that nanotubes of type $n-m=3i$, where $i$ is zero or any positive integer, were metallic. The fundamental gap (HOMO-LUMO) would therefore be 0.0 eV. All other nanotubes, they showed, behaved as a semi-conductor. The fundamental gap, being a function of diameter, was in the order of about 0.5 eV. Their data showed that the energy gap reflected Fig. 2.7 (adapted from [7]). This graph can be modelled by the function:

$$E_{\text{gap}} = 2\gamma_{0}a_c\sqrt{\frac{e}{d}}$$  \hspace{1cm} (2.2)

Fig. 2.7. The Van Hove singularities in metallic and semiconducting CNT. Figure adapted from [7].
Where $y_0$ is the C-C tight bonding overlap energy ($2.7 \pm 0.1$ eV), $a_{cc}$ is the nearest neighbour C-C distance (0.142 nm), and $d$ is the diameter. This shows that the fundamental gap ranged from around 0.4 eV - 0.7 eV, which is in good agreement with the values obtained from one-dimensional relations. They concluded that the fundamental gap of semi-conducting nanotubes was determined by small variations of the diameter and bonding angle, determined by the twist.

In a study published at the same time by Odom, Huang, and Lieber [11], they also agreed that the semiconducting properties of carbon nanotubes were determined by equation 2.2. In addition, they suggested that a gap would exist at the Fermi level in metallic nanotubes. This would be because of the $\pi/\sigma$ bonding orbitals and $\pi^*/\sigma^*$ anti-bonding orbitals mixing due to the curvature in the graphene sheet of a SWNT. They noted, however, that they had not observed any evidence to support this as of the time of publishing (1998). More interesting to note, in the study by Wilder et al. [7], they reported that the conducting nanotubes shows $E_{\text{gap}}$ to range from 1.7 - 2.0 eV, which could be the evidence Odom et al. [11] was predicting.

## 2.4 Fabrication Mechanisms

### 2.4.1 Arc synthesis and purification

The arc synthesis technique consists of two carbon rods, anode and cathode, which are placed inside an evacuated chamber with a constant He supply, which acts as a buffer gas. The rods are approximately 90% pure graphite, and between 5 - 10 mm diameter. Due to the high current needed to strike and sustain the arc, (50 - 100 A), the rods can reach temperatures of about 3000 °C and therefore the cathode needs to be sufficiently water-cooled.

Initially the rods are separated, the power is turned on, and they are slowly moved together until the arc strikes. They are then kept at a constant separation of 1 - 2 mm. To move the rods closer together, and then back apart, a linear feed through is required. However, this doesn’t need to be adjusted to maintain the gap of 1mm, because the arc evaporates carbon from the anode, and onto the cathode, the gap appears to “move” at a rate of a few millimetres per minute.
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To pump

Fig. 2.8 Structure of an arc discharge machine. Two carbon rods are placed 1 mm apart and an arc is struck when up to 100 A is passed. A graphitic compound is seen to form on the cathode as the anode gets consumed [15].

After evaporation, the deposit on the cathode consists of a hard grey outer shell, Fig. 2.9, containing a soft black soot-like structure. It is this black soot, which contains nanotubes.

Fig. 2.9. The compound found to accumulate on the cathode during arcing. The grey outer shell is mainly amorphous carbon, whilst the inner black soot contains nanotubes [16].

It is believed to be a result of carbon vapour condensation and the temperature gradient caused by the He gas that caused the two regions (black and grey) to be formed. Amongst the nanotubes, a quantity of other nano particles, fullerenes and amorphous carbon are produced. As this is not needed, and it is only the nanotubes that we are interested in, a purification stage is required. Removing the graphitic debris has proved difficult. Thomas Ebbesen developed the first successful technique [17]. He showed that nanotubes caps could be selectively attacked by oxidising gases. It was realised that the badly defected nano particles and amorphous carbon could be oxidised much more easily than the otherwise near perfect
structure of the nanotubes. However, 99% of the total material was lost in the process. Although this method left only pure nanotubes, the idea of bulk production was impossible.

A newer method of separating nanotubes by chemical suspension has been developed. The black soot from the arc discharge is mixed in acetone and separated in an ultrasonic bath. The pure nanotubes can be seen to suspend at the surface of the mixture, these can selectively be extracted and dried.

### 2.4.2 Laser ablation

An efficient route for the synthesis of bundles of single walled carbon nanotubes with a narrow diameter distribution employs the laser ablation (or laser vaporization) of a graphite target.

In early reports of laser ablation [18], high yields with up to 70-90% conversion of graphite to single wall nanotubes were reported in the condensing vapour of the heated flow tube (operated at 1200 °C). A Co-Ni/graphite alloy with equal amounts of Co and Ni added to the graphite. Two sequenced laser pulses were used to evaporate a target containing carbon mixed with a small amount of transition metal from the target, see Fig. 2.11 [19].

![Fig. 2.10. Single wall carbon nanotubes produced in a quartz tube heated to 1200°C by the laser ablation method, using a graphite target and a cooled collector for nanotubes [20].](image-url)
FIG. 2.11. SEM image of ropes of single wall CNT produced by laser ablation of graphite from the Thess et al experiments [18].

2.4.3 Catalytic growth by CVD

For over a century it has been known that carbon films can be grown by the catalytic decomposition of a carbon containing gas over a hot surface. P. and L. Schultzenberger first observed this in the 1890's [21]. However the future potential was not known then due to the non-availability of nano scale microscopy at the time.

Work in the 1950's showed filaments could be produced by the interaction of hydrocarbons with transition metals, most effective of which were Fe, Co and Ni. An environment was shown to enhance the carbon growth. Carbon growth in this way was first seen as a serious problem in certain chemical processes, including the operation of gas-cooled nuclear reactors.

The Brodouard equilibrium, [22], shows how a carbon solid is formed by the disproportion of carbon monoxide.

\[
2CO_{(g)} \Leftrightarrow C_{(s)} + CO_{2(g)}
\]  (2.3)

Maximum carbon deposition is achieved in this way at about 550 °C in the presence of metal from the iron subgroup. Growth processes used today to form nanotubes utilise the fact that carbon solid forms when hydrocarbon gas is flowed over transition metal catalysts.

Following previous work and publication [23,24] Chhowalla et al published a study of the growth process of CNT by plasma enhancement chemical vapour deposition (PECVD). The
effect of the Ni catalyst layer, DC bias in order to obtain aligned growth, removal of a-C films, growth temperature and a proposed growth condition were reported.

It was shown that the thickness of the Ni catalyst layer directly influences the dimensions of the grown CNT. Fig. 2.12(a) is a SEM image of the different thicknesses of Ni catalyst after annealing at 750°C. Fig. 2.12(b) is of subsequent CNT growth. It can be seen that the thicker the Ni layer, the larger the diameter of CNT.

![SEM images of Ni catalyst layers and CNT growth](image)

**Fig. 2.12.** (a) SEM photographs of Ni films with varying thicknesses deposited using magnetron sputtering on 50 nm of ECR SiO₂ after annealing at 750 °C in 20 Torr of H₂ for 15 min. (b) Nanotube growth on varying initial Ni thicknesses. Note that the average diameter for the tubes grown on 0.5 nm Ni film is ~30 nm which increases to ~400 nm for tubes grown on 9 nm Ni films. The average tube height also decreases from ~8 to ~3 mm with Ni thickness. Furthermore the nanotube density decreases from ~10⁷ to 10³ cm⁻² for Ni films thicknesses ranging from 0.5 to 9 nm [25].
Teo et al [26] reported the growth of carbon nanotubes by PECVD, and displayed results by SEM imaging of aligned CNT growth without the usual background deposition of amorphous carbon (a-C). The a-C was almost entirely removed during the growth process by using a mixture of acetylene (C_2H_2) and ammonia (NH_3). Depth-resolved Auger electron spectroscopy showed the removal of all a-C deposition when a ratio of C_2H_2:NH_3 of 1:5 was employed. A diffusion barrier was deposited, typically SiO_2 or TiN to ensure that when a Ni catalyst layer, which was patterned by e-beam lithography, was deposited and annealed to form nano-islands, did not form NiSi_x. A growth temperature of 700°C was used to anneal the Ni catalyst and a 1 kW DC power supply to maintain a bias of -600 V between the substrate and Cu anode (which ensures aligned growth).

2.4.4 Low temperature growth

All examples of nanotube growth seen so far in this thesis have been carried out at high temperatures, upwards of 800 °C. The reaction in which carbon is deposited on metal is exothermic, i.e. releases heat. Taking the heat out of the equation has proved extremely difficult. There has been some success in low temperature growth, this was still at 600 °C, enabling nanotubes to be grown on glass which has a melting point of 666 °C. Young Chul Choi of Korea reported in Journal of Vacuum Science and Technology in February 2000 nanotube growth on Ni coated Si substrates at temperatures of 520 °C [27]. They reported that nanotubes grown at 520 °C were curly in appearance, whereas those grown at temperatures upwards of 600 °C were straight and self aligned.

Room temperature growth of carbon nano-materials has been reported [28]. To date both room temperature grown nanofibres [29] as well as efficient carbon nanotube growth [30] and growth on plastic substrates [32] has been reported.

Hofmann et al reported the growth of carbon nanotubes by PECVD of a mixture of C_2H_2 and NH_3 on catalysed Ni films. The role of the NH_3 was to remove the presence of co-deposited a-C. They reported the growth of CNT at temperatures as low as 120 °C. Fig. 2.13 are SEM images of grown CNT at temperatures of 500, 270 and 120 °C.
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Fig. 2.13. SEM photographs of vertically aligned CNFs grown from e-beam patterned Ni lines at (a) 500 °C, (b) 270 °C, and (c) 120 °C. A tilt angle of 40° was used for imaging [scale bars: (a) and (b) 1 mm and (c) 500 nm] [31].

Fig. 2.14. (a)-(c) SEM photographs of vertically aligned CNFs grown from e-beam patterned single 100 nm wide lines and 100 nm diameter dots of Ni onto Cr covered plastic foil. (d) TEM image of as-grown CNF [scale bars: (a) 1, (b) 5, (c) 100 mm, (d) 15 nm] [32].

2.5  

Field emission from carbon nanotubes

2.5.1  

Field emission mechanisms for CNT

The theory of field emission can be found in Chapter 1 of this thesis. Carbon nanotubes have been increasingly shown to be excellent electron field emitters. Their small, nanometre sized radius together with their long, micrometer sized, elongated shape give rise to a large geometric field enhancement factor, and in turn, to a low threshold field due to the high local field at the tip of the CNT. The local field can be estimated for metallic emitters, to be
approximately 2-3 V/nm\(^{-1}\) at the surface of the emitter from its enhancement factor and the applied field [33 - 35]. The effect of the geometric properties (height, radius etc) of the CNT on its enhancement factor is still not fully understood. This problem is made harder to solve by the fact that the chemical and physical properties of CNTs can be drastically changed by the preparation and purification steps undertaken during synthesis [36 - 39]. However, although the phenomenon of the field enhancement factor is not fully understood in the literature, there have been several attempts at proposals for the mechanisms behind electron field emission from CNT. Many authors show that the emission I-V (or I-E) curves for carbon nanotubes can be shown to follow the well known Fowler-Nordheim emission mechanism, as explained in Chapter 1 of this thesis. It can then be said that carbon nanotubes behave in emission as metallic emitters [40 - 42].

It has been proposed by Obraztov et al that the layers of graphene form sharp bends at the open end of carbon nanotubes, where the atomic structure of the carbon is formed by sp\(^3\)-like atomic bonds instead of the usual sp\(^2\)-like configuration which is typical for graphene [43 - 45]. The change in atomic coordination would lower the height of the potential barrier and is a possible explanation for the low work function (\(\Phi\)) that the authors quote by estimation from the slope of a Fowler-Nordheim analysis plot. However, this mechanism would only be valid for open capped CNT.

Rinzler et al showed that the high efficiency of open capped multiwalled carbon nanotubes and their behaviour under laser irradiation was due to emission from a single carbon chain that unravels at the CNT edge, and produces a high field enhancement factor [46]. This mechanism was not confirmed by experimental results as yet, and, as before, would only be valid for open capped CNT.

If several energy levels contribute together in the electron emission, the level nearest to the Fermi level will be the supplier of the majority of the emitted electrons. However, since the location of this level would be greatly effected by CNT diameter, chirality, and the presence of defects, there will be significant differences in emission characteristics from one CNT to another.

Dean et al suggest complementary mechanisms and shows that the emission characteristics of a CNT is far more complicated than that of a sharp metallic tip with a similar work function of approximately 5 eV [47, 48]. Emission regimes on a single singlewalled CNT were shown to be dependant on the applied field and the temperature. A mechanism similar to resonant tunnelling through an adsorbate was observed under experimental conditions of low electric...
fields and low temperatures. The molecule was found to be water and appeared that this adsorbate-assisted tunnelling is the stable emission model at room temperature. The water will desorb at high applied fields or high temperatures. Other regimes show intrinsic emission from the CNT and show lower emission currents at similar voltages. It is still unclear as to the origin of these intrinsic emission mechanisms but is likely to be enhanced field emission states above the Fermi level or a non metallic density of states.

2.5.2 Fabricating an isolated nanotube for field emission

A single carbon nanotube used as an emission source can be produced in various ways. Wires that are electrochemically etched, tungsten [49], gold [34] and carbon fibres [46] are used as a support for single CNTs. Individual CNTs can be then mounted onto the sharpened tips under an optical microscope which has micromanipulators working in three dimensions. They are used to move the sharpened wire tip support and a separate source of nanotubes [46, 49]. A single CNT can be found to attach itself to the tip of the support by either applying conductive adhesive to the tip of the support [49] or through van der Waals forces alone [34]. It is fairly obvious that an optical microscope has not the resolution to be able to resolve the process of attaching a single CNT to a tip so the process has to be checked by subsequent SEM [34] or transmission electron microscopy (TEM) [49]. Single CNTs have also been attached to probes using low energy electron microscopes with micromanipulators [50].

To manipulate SWNTs into a device, where only one CNT is needed has a number of problems. The small diameter of SWNT’s make it hard to isolate an individual one from carbon ropes, catalytic particles and amorphous carbon that may be present in the CNT sample. One solution is to pick up a group of SWNT in a single fragment of raw material with macroscopic tweezers and fix them onto a tungsten tip [40]. However, the emitting tip is now made up of many single tubes, but, using a probe hole in the counter electrode or phosphor screen can account for this. A second approach is to use well purified SWNT’s to start with to eliminate the presence of unwanted carbonaceous materials by process of oxidation [51]. However, it is not known if the harsh oxidation process damages the morphology of CNT, e.g cap removal and the presence of functionalised groups. Another method is where a tungsten tip is brought close to a mat of SWNT’s under a high resolution optical microscope [52]. Whilst individual tubes will not be resolved optically, when contact is believed to have been achieved a small, (less than 10 V), potential is applied to break the touching CNT from the mat. Care must be taken after attaching the CNT as the tungsten tip has to be examined by SEM or TEM to be sure that a CNT is present. A method has been proposed that eliminates
the need to transfer delicate samples to and from electron microscopy equipment, by manipulating CNT in an SEM [53]. Single CNT can be attached to AFM tips by disassociating residual organic species with the electron beam that are co-deposited onto the sample, or electron beam irradiation. The deposits are mechanically strong [53] and the electron beam enhances the electrical contact between the CNT and AFM tip [54]. AFM probes can also be used as supports to grown single CNT by a CVD process [55 - 57].

2.5.3 Field emission from single CNT

This section is a review of some reported experiments carried out on a single nanotube as an electron source. Reliable estimates of the emission mechanism and work function were made. The first electron field emission from a single carbon nanotube was reported by Rinzler et al [36] who reported FE from an arc discharge produced multi walled carbon nanotube which was mounted on a carbon fibre. They showed that the emission approximated a Fowler-Nordheim behaviour, and currents of 100 nA were seen at an applied field of just 0.12 V\textmu m^{-1} [36].

Studies of open and closed arc discharge produced multi walled nanotubes mounted on gold fibres have been reported [34, 37]. An SEM image of the single CNT on the carbon fibre together with emission current against applied voltage for open and closed CNT is illustrated in Fig. 2.15. The emission at low currents exhibited Fowler-Nordheim behaviour up to emission currents of 20 nA. Strong saturation effects were noticed as the emission current was made to increase. They reported a maximum emission current output of 0.2 mA [34].

![Fig. 2.15. Field emission characteristics for a single open and closed CNT mounted on the apex of an etched gold fibre of diameter 20 \mu m. Note that open CNT require approximately twice the applied voltage to that of closed CNT [34, 37].](image)

Electron field emission has also been possible utilising a scanning anode field emission microscope (SAFEM). Semet et al [54] reported that the emission of individual MWCNT
followed the Fowler Nordheim theory closely. The method of using the SAFEM proved useful in the observation of field emission properties of single CNT, but over a large area. Fig. 2.16 shows the experimental setup of the scanning process.

![Experimental setup](image)

**Fig. 2.16.** (a) Schematic of the method in which a group of CNT can be tested for field emission properties singularly. (b) SEM of the tested array of CNT [35].

This method gave a unique insight to the field emission properties of CNT. Fig. 2.17 shows the emission current distribution for a group of four CNT.

![Current distribution](image)

**Fig. 2.17.** (a) Current distribution for an array of 4 CNT. (b) The corresponding CNT viewed by SEM [58].

### 2.5.4 Field Screening

Nilsson *et al* [59] explored the field emission characteristics of patterned CNT films by the use of a scanning anode field emission apparatus. They initially showed efficient FE properties from the patterned films, but in investigations to the effect of the density of the CNT content highlighted a problem. It was seen that a low density of CNT (SEM of Fig. 2.18 (c)) gave a poor emission site density (Fig. 2.18 (f)) when compared to a higher density of...
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CNT (SEM of Fig. 2.18 (b) with site density in Fig. 2.18 (e)). This was expected, however, Fig. 2.18 (a) is a SEM of a very high density CNT film and its site density (Fig. 2.18 (d) is almost comparable to that of the low density CNT.

Fig. 2.18. Nilsson’s [59] experimental SEM and site density measurements of three different densities of CNT.

They explained this by an electrostatic screening effect provoked by the proximity of neighbouring tubes. The solution of the Poisson equation governs the behaviour of the potential penetration into the CNT deposit. The presence of many tubes per unit area (u.a.) means that there is more charge per u.a. and the charge reduces the potential drop perpendicular to the film. Since it is the local electric field at the emission tip that governs the emission, the distance between the tubes remain a crucial parameter to optimize the field emission performance. The limit of zero distance between the tubes would correspond to a flat metal surface without field penetration. The film depicted in Fig. 2.18 (a) is close to this limit since the CNTs are densely packed. They observed some FE only because there are a few tubes that are branching out of the pattern. Low density films Fig. 2.18 (c) also give poor emission but for another reason. As seen in the SEM image, the CNTs are short, bent, and not protruding out of the substrate. Only very few of them have a sufficient enhancement factor for an adequate emission.
They further went on to show by computer simulation that the distance between the emitter greatly affects the emission output by means of electric field screening. Fig. 2.19 is a representation of their results.

![Simulation output showing the effect of inter-tube separation on field emission performance](image)

Fig. 2.19. Simulation output showing the effect of inter-tube separation on field emission performance [59].

They concluded that for maximum efficiency the optimum distance between CNT emitters had to be approximately twice the height of the tube.

### 2.5.5 Effect of alignment on field emission

Chen and et al [60] reported in 2000, field emission characteristics from aligned high-density carbon nanotubes with different orientations, parallel, 45° and perpendicular to the substrate. Large area uniform CNT were synthesised by dc plasma assisted hot filament CVD. CNT of diameter 100-200 nm were produced and the three different orientations were achieved by changing the angle between the substrate table and applied electric field during deposition. They reported that CNT parallel to the substrate had a lower applied electric field when subjected to field emission testing to that of the CNT which were perpendicular to the substrate. They indicated that electrons can emit from the body of the CNT and not just the
tip, which meant that CNTs could be used as linear emitters. The emission and therefore field enhancement factor from the sides of the CNT were concluded to be from the small radius of the tube. This was an important publication in further understanding the field emission capabilities of carbon nanotubes. Bower et al [61] reported that the emission characteristics of aligned tubes were not significantly different to that of a random array of tubes.

Fig. 2.19 illustrates how alignment of CNT affects their emission characteristics. It can be seen that a random array of SWNT have greater performance than that of aligned MWNT patterned by lithography.

### 2.5.6 Field emission from nanotube composites

The method of preparing nanotubes into a polymer composite is described in Chapter 6. The field emission characteristics of CNT-polymer matrices was investigated in recent publications. FE from CNT-polymer composites has shown that they possess remarkable FE properties and exhibit low turn on fields (<3V\mu m^{-1}) and high peak current densities (4 Acm^{-2}) [62 - 64]. However, when designing for field emission displays (FED), emission over a large area is desirable. Due to the nanolithography process required in order to produce such emitters, large area is still to be shown. For this reason CNT polymer matrices are a viable alternative for next generation FED.
It is only recently that reports of field emission from nanotube polymer composites have been reported. Previous publications highlighted their use in mechanical area. Schadler et al [65] reported the mechanical behaviour of multiwalled carbon nanotubes in an epoxy composite.

Alexandrou et al [66] reported field emission from nanotube polymer composites. They examined single walled nanotubes in ploy (3-octylthiophene). Polymer samples were prepared then spin coated onto n-Si wafers. 33% CNT percentage samples were found to have a lower turn on field (1 V\(\mu\text{m}^{-1}\)) than that of a mat of CNT which had a turn on field of approximately 2.5 V\(\mu\text{m}^{-1}\). They stated that there was an increased field enhancement factor within the polymer samples due to a triple junction of CNT, polymer and vacuum. Fig. 2.20 illustrates the theory that they put forward. Equipotential lines are shown to illustrate where the increased field enhancement factor lies.

![Fig. 2.20. Schematic of the surface potential change due to a triple junction between CNT, polymer and vacuum. Lines are of equipotential.](image)

Poa et al [67] showed field emission from non-aligned carbon nanotube cathodes. Multi walled nanotubes and boron doped multi walled nanotubes were grown by a plasma arc discharge system between two graphite electrodes, whilst the boron doped nanotubes were produced between two boron containing graphite electrodes. The as grown carbon was synthesised by micro filtering and thermal treatment of 500-600 °C for 40 to 50 minutes to remove amorphous carbon and carbon particles and leave nanotubes. Subsequent TEM analysis showed the samples to be approximately 90% pure CNT with diameters of 10 to 50 nm. Boron content was seen to be approximately 1% by EELS K-edge spectra. The CNT were mixed into dissolved polystyrene to achieve concentrations of 11.1%, 14.3%, 20%, 25%, and 33%. The films were subject to a hot pressing treatment to remove any residual solvent and prevent voids in the film. Sheet resistivity was measured by four point probe and
seen to decrease with an increase of CNT concentration, with boron doped samples having a lower resistivity than that of the undoped samples. Fig. 2.21 shows an SEM image of a CNT polymer sample which was physically broken to expose CNT [67].

![SEM micrograph of the MWNT-PS surface at 20% by weight. CNT concentration. Top view shows that the MWNTs are randomly arranged forming tracks across the film. The mechanically bent region exposed the embedded MWNT [67].](image)

Field emission results indicated that the threshold field was controlled by the electric field screening effect at the surface of the samples. A lowest threshold of $1.6 \text{ V} \mu\text{m}^{-1}$ was recorded from the 11.1% sample. Emission properties including current densities were seen to be comparable to that of aligned CVD grown CNT and carbon nanofibres.

### 2.6 Three terminal devices

Whilst effective field emission from carbon nanotubes has proven to be possible, when designing for large area, especially for flat screen displays, thought has to be given to the fact that fast switching of individual pixels is required. Conventionally, this would be difficult due to the high (kV) voltages required on the anode to produce sufficient electric field to allow electron emission. Therefore, placing a third electrode, often designated a gate, close to the emitting surface, would mean that similar electric fields can be achieved at much lower (1-10) voltages, making switching possible even by logic circuits. Although there is increasing research into three terminal devices for field emission utilising CNT, there have been many publications of three terminal devices using other emissive structures.
Takai et al [68] reported electron emission from n-type porous silicon field emitter arrays. They showed that using conventional Si field emitter arrays (FEAs) they could enhance the field emission performance by anodising the tip which would lower the work function, and therefore lower the required gate voltages. The structure which they produced is shown in Fig. 2.22. This is a typical three terminal structure with emitter buried in an insulating layer and a gate electrode as close to the tip as possible.

Another example of a Si FEA device was published by Temple et al [69]. They used anisotropic and isotropic etching to produce arrays of single Si tips. Whilst the fabrication process is not really relevant to this work, they showed a peak emission current of 18 mA for a gate voltage of 150 V for a device with ~6500 tips with a tip density of 1.2x10^6 cm^-2. The highest number of emitters they managed to produce on one sample was as high as ~230,000 with a tip density of 3x10^6 cm^-2.

A method of switching individual emission sites is to use a transistor. Gamo et al [70] reported the growth of a Spindt type FEA with an amorphous silicon thin-film transistor at temperatures as low as 350°C, enabling effective growth on glass substrates. The emission current of the FEA was controlled in the range of 0 to 0.12 μA with the TFT gate voltage from 0 to 15 V.

The use of carbon nanotips as emitters in a three terminal device was reported by Tsai et al [71]. They grew vertically aligned high aspect ratio carbon nanotips by microwave plasma chemical vapour deposition (MPCVD) in a gated device structure with a 4 μm gate aperture. They showed field emission current of ~ 154 μA with a gate voltage of 50 V.

A novel approach using two gates above an emitter to better the electron beam collimation was reported by Dvorson et al [72]. They showed that a comparison between one and two gates reduces the electron spot size, when used with a phosphor screen, by up to a factor of ten. The two gates are defined as an extraction electrode, which is close to the emitter, and a focus electrode to collimate the emitted electron beam.
A self-aligned gated field emission device using carbon nanofibre cathodes was reported by Guillorn et al [73]. They grew vertically aligned carbon nanofibres (CNF) by plasma enhanced chemical vapour deposition (PECVD). Electron beam lithography was used to ensure a well-ordered array of CNFs that were subsequently coated in a SiO₂ insulating layer and a Mo gate. Mechanical polishing and wet chemical etching exposed a circular gate above each emitter. Peak emission current of 25 nA was measured at a gate voltage of 80 V.

### 2.7 Field enhancement factor

Many of the exhaustive studies performed on field emission current-voltage data, (both experimentally and by simulation) have relied upon analysis of the emission current I - voltage V (or field, E) characteristics using the theory of Fowler and Nordheim. The standard analysis often involves a plot of the log (I/V²) versus 1/V (or equally log I/E² against 1/E).

The role of the field enhancement factor, β, is the enhancement of the applied macroscopic field, such that under the action of the local electric field, efficient tunnelling of electrons from the Fermi level through the potential barrier becomes possible. This is defined simply as the local electric field divided by the applied electric field. The interpretation of β, which is a dimensionless quantity, if electric field rather than voltage is used in the analysis, is therefore of great importance.

There have been a number of attempts to model the behaviour of β for a range of nanotube geometries (height h, radius r, singlewall vs. multiwall). Mayer and colleagues [74] have used a transfer matrix technique to compare the field emission behaviour between metallic SWNTs (5,5) (10,10) and (15,15) and a MWNT composed of the three co-centric SWNTs. They observed that the emission from the MWNT is larger than the total current obtained by considering the individual walls separately. They also noted that the emission was improved when the end of the tubes were convex rather than flattops. Moving on from isolated tubes, they further went on to show that the emission behaviour of bundles of open and closed (5,5) tubes depend on two factors; whether the tubes were open or closed and the role of proximity field screening about by neighbouring tubes. Closed tubes were found to emit less current than open tubes and that their FE characteristics are found to be more sensitive to the local electric field. Theoretical investigations of field screening during to neighbouring tubes are important in explaining the FE characteristics such as threshold field and emission site density.
Hu and Huang [76] used a finite-difference time-domain code to calculate self-consistently the electromagnetic field surrounding the MWNTs. The tubes were modelled as cylinders having a half-ellipsoidal tip that has its minor radius equal to the radius of the cylinder section. They also found that higher emission currents were found for open ended tubes than for closed tubes and the emission current is larger for smaller diameter MWNT that large diameter. For tubes 100 – 200 nm in length the spacing between neighbouring tubes should be at least 200 nm to avoid proximity screening. The cathode-anode distance in this case was 2 μm. For a tube of total length 100 nm, consisting of a half-ellipsoidal tip of major radius 40 nm and minor radius equal to the radius of the tube of 10 nm, an enhancement factor of 25 was found.

2.8 Devices

The end result of much of the research listed in this literature review is the hope of creating a prototype field emission display to challenge for the next generation flat screen technology. This next section highlights some of the prototype field emission displays unveiled in recent years. Also, the use of carbon nanotubes as electron sources in X-ray devices has sparked much interest. Such X-ray devices are also described.

2.8.1 Flat panel displays

In 1999, Choi et al [77] reported a prototype field emission display in conjunction with Samsung [78]. They used single wall carbon nanotubes mixed in with an organic paste and patterned onto glass substrates. Patterned red green and blue phosphors were used as the anode. Turn on fields of 1 V μm⁻¹ were required for emission, and a peak current of 1.5 mA at 3 V μm⁻¹. A brightness of 1800 Cdm⁻² was seen. Fig. 2.23 is a photograph of their 4.5 inch diagonal fully vacuum sealed FED.
Fig. 2.38. Emitting image of fully sealed SWNT-FED at colour mode with red, green, and blue phosphor columns [78].

Although they only demonstrate two terminal diode-like behaviour, this early publication shows the possibilities of CNT emitters in a closed vacuum flat panel display.

Fig. 2.24. Phosphor screen images showing the emission uniformity of CNT cathodes. Left: a homogeneous $2 \times 2 \text{ cm}$ SWNT cathode. The image was collected at $4.4 \text{ V/µm}$ applied field at $100 \text{ Hz}$, $1\%$ duty cycle. Right: a patterned SWNT structure deposited on ITO glass at room temperature. The CNT line width is $100 \text{ µm}$. The data was collected using $5\%$ duty cycle [79].
Matrix-addressable diode-type field emission displays (FEDs) usually consist of CNT stripes on the cathode glass plate and phosphor-coated indium-tin-oxide (ITO) stripes on the anode plate. Pixels are formed at the intersection of cathode and anode stripes. A 32×32 prototype was first realized using carbon nanotubes as the electron source with a pixel size of 200×200 μm² [79]. Later a 4.5-inch three colour display using SWNT emitters was fabricated [80]. The fully sealed diode display has 128 addressable lines and demonstrates a brightness of 1800 Cdm⁻² at 3.7 Vμm⁻¹ [81].

A diode type FED has a limitation in individually controlling each pixel on the same stripe; a triode structure is needed for the practical applications of FEDs. The triode-type structure inserts a gate electrode between the CNT cathode and the phosphor anode. The gate gap is small (usually less than 10 μm), so that the electrons can be extracted by applying a very low voltage on the gate. A prototype FED using gated CNT field emitters was demonstrated [81], which can address a 100 × 100 matrix over a 1 cm × 1 cm area with a gate voltage of 50 V. A fully sealed 5-inch SWNT-based triode FED exhibited a luminance of 510 Cdm⁻² with 240×120 lines. There is also an under-gate type triode structure, in which gate electrode is under the cathode, on the opposite side of the anode. Fig. 2.25 shows a color image produced by a 9 inch carbon nanotube based FED [80]. Comparing to the commercial LCD and plasma displays, the current CNT based FEDs require further improvement in pixel uniformity and stability.

Fig. 2.25. A color image from a 9-inch CNT-based field emission display reported by Samsung Co. Data taken from [80].

The displays mentioned so far are only small screen sizes, in order to break into the consumer market and to challenge the LCD and PDP market field emission screens need to be upwards of 15” diagonal, widescreen and full colour. There have been a number of prototype field
emission displays since the late 90's. Sony in partnership with Candescent Technologies™ hope to produce a marketable field emission display. In 2001 they demonstrated a 13.2” diagonal full colour field emission display. Fig. 2.26 is a photograph of the screen in demonstration. The display uses CNT as the emission structure and has a pixel resolution of 600 by 800 which means a pixel to pixel pitch of 0.34 mm. The company aims to have field emission displays ranging from 15 to 40 inch diagonal [82].

![Fig. 2.26. Sony and Candescent produced a prototype 13.2" diagonal field emission display capable of full colour SVGA video [82].](image)

Mitsubish are aiming to produce a 10 inch diagonal field emission display by 2005 and a 30 inch by 2007. The largest demonstrated field emission screen was produced by Samsung SDI™. They demonstrated a 30 inch diagonal wide screen display using CNT emitters in 2004 and have a 38 inch screen currently as a demonstration device [82].

### 2.8.2 X-ray sources

X-ray radiation is widely used in medical and industrial applications. A conventional X-ray tube comprises a metal filament (cathode) which emits electrons when resistively heated to over 1000 °C and a metal target (anode) that emits X-rays at wavelengths characteristic of the anode material when bombarded by the accelerated electrons [83]. The use of thermionic cathodes results in several limitations. Field emission is a more attractive mechanism to extract electrons compared to thermionic emission because electrons are emitted at room temperature and emission is voltage controllable. The concept of field emission X-ray tube
has been discussed in the past and devices with low X-ray flux have been demonstrated [84-88]. However, most diagnostic applications require tube current in the order of 10–100 mA and operating voltage in the range of 30–150 KV which was difficult to accomplish for the field emission X-ray tubes.

Yue et al demonstrated a CNT-based X-ray tube which can generate sufficient X-ray flux for diagnostic imaging applications [89]. The device, illustrated in Fig. 2.27, comprises a field emission cathode, a gate electrode, and a metal target in a vacuum chamber with a Be window. The cathode is a SWNT film deposited on a metal substrate. A relatively low voltage is applied between the gate and the cathode to extract electrons from the cathode. The field emitted electrons are accelerated by a high voltage applied between the anode and the gate. A total emission current as high as 30 mA is obtained from a small CNT cathode. The device can readily produce X-ray wave forms with programmable pulse width and repetition rate. Pulsed X-rays with a repetition rate up to 30 kHz have been generated by applying an external triggering voltage on the gate (Fig. 2.27). The X-ray flux is sufficient to image human extremities, as demonstrated in Fig. 2.28.

The CNT-based X-ray sources have several advantages compared to the thermionic X-ray tubes. The life span of the X-ray tubes can potentially be prolonged by eliminating the thermionic cathode. The size of the X-ray source can be reduced significantly. It also has the
ability to produce focused electron beams with very small energy spread and programmable pulse width and repetition rate. This CNT-based cold-cathode X-ray technology can potentially lead to small and portable X-ray sources for industrial and medical applications.

![Image of X-ray signals and image of a humanoid hand]

Fig. 2.28. X-ray generation by CNT-based field emission source [88]. Left: 1 kHz and 50% duty cycle pulsed X-ray signals recorded using an oscilloscope by applying pulsed gate voltage with the same wave form. (The height of the signal is proportional to the photon energy.) Right: X-ray image of a humanoid hand taken using the CNT source on a Polaroid™ film. The X-ray energy is 40 kVp and the image was taken at 40 cm away from the X-ray source without using an image intensifier [89].

2.9 Summary

This chapter has introduced the publication history in the field of research for carbon nanotubes. The extraordinary structure and properties, both physical and electrical, have been discussed in detail. The way in which these structures can be grown has had much research since their realization in 1991. From the literature it can be seen that the growth of CNT by CVD together with the fine patterning of catalyst metal films by electron beam lithography enables single CNTs to be placed entirely at the designer’s discretion. It has also been seen recently that low and room temperature growth of CNT is possible by CVD, opening up the possibility of flexible, plastic substrates. In particular, and of interest to this thesis is their utilization as electron sources for field emission devices. The geometric field enhancement factor which CNT exhibit, together with the ease of growth on a wide number of substrate materials, makes them a promising candidate for the next generation of flat screen displays.
Whilst at present there are no commercially available field emission displays, there has, and continues to be, a growing interest in this field with a number of prototype displays, the most impressive to date being Samsung's 38" CNT based screen displaying full colour video.

### 2.10 References

4. [http://www.hpc.susx.ac.uk/~nickw/c60/c60.jpg](http://www.hpc.susx.ac.uk/~nickw/c60/c60.jpg)
CHAPTER TWO Literature review of carbon nanotubes


CHAPTER TWO Literature review of carbon nanotubes

CHAPTER TWO  Literature review of carbon nanotubes

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82 Data taken from Korea Times online


CHAPTER THREE

3 Experimental

3.1 Introduction

In this chapter the basic techniques implemented in conducting the experimental research are described. The metal deposition of Ni films for nanofibre catalysts (Chapter 6), plasma treatment, catalysis of Ni films (Chapter 6), field emission testing, planar and probe field emission characterisation of nanofibre structures, (Chapter 6), CNT-polymer samples, (Chapter 6) and in-situ field emission within an SEM, field emission from carbon nanoropes, individual CNT, and three terminal field emission from a single CNT, (Chapter 5) are detailed.

3.2 Metal deposition

In order to deposit thin films of metal onto a substrate, we use a thermal evaporator. A wire of the metal to be evaporated is placed in a tungsten crucible. The substrate is placed above this, face down, and a shutter is moved across to cover the wire. A voltage is slowly increased to about 100 V across the crucible, until the wire starts to melt. The shutter is then opened and the metal evaporates up onto the substrate. The thickness of the film is determined by the time the shutter is open. All this is done under a vacuum of about $10^{-6}$ Torr. The evaporator is used to deposit Ni films for the catalysis of carbon nanofibres as seen in Chapter 6.
3.3 Plasma treatment

The equipment used for plasma treatment of Ni films for the catalysed growth of carbon nanofibres, described in Chapter 6, is a (Plasma-Tech DP800) capacitive coupled Plasma Enhanced Chemical Vapour Deposition (PECVD) machine.

PECVD allows for the deposition of a thin film on to a surface at low temperatures, by reactions in a gas plasma which help disassociate the species used for creating the thin film. The reactions are driven to a significant extent by the energy of the charged gas (plasma) particles. Usually, the electrons’ kinetic energy is used to dissociate the input gas.

PECVD requires a pressure between 0.1 to 10 Torr, to allow for a significant gas phase reactions. Thus, the mean free path for neutrals, $\lambda$, is $\leq 1$ mm. The surface temperature is not
used to activate reactions, so it is not a crucial factor in the rate equation, but it does affect film properties. At high growth rates uniformity can be a concern. The PECVD method can be used to deposit carbon films (as described above) using a CH$_4$ gas. By using Ar, O$_2$ or NH$_3$, it is possible to plasma etch the surface of a sample.

In this work two stages of PECVD are utilised. Firstly, Ar is fed into the chamber and a plasma struck between top and bottom electrodes under the bias of an RF power supply to create an Ar ion plasma. This plasma is used to catalyse the surface of Ni films for the growth of carbon nanofibres. Secondly, CH$_4$ is used as the feed gas, and CNF growth carried out at room temperature. A full explanation of the experimental setup is found in Chapter 6.

Gas in

![Fig. 3.2. Schematic of the DP800 PECVD machine](image)

### 3.4 Field emission testing

The equipment used to test the field emission properties of a sample is a planar to probe setup. The sample is fixed to a stage, and a steel ball bearing suspended above as the tip of the probe, connected to a micrometer enabling a sample to anode separation of between 30 – 150 μm. The chamber is then evacuated to approximately 10$^{-6}$ Torr.
A voltage is applied to the anode with the sample held at 0 V. The anode voltage is increased in set steps by a computer program. The parameters the user has to input are:

- Sample name
- Start voltage
- Maximum voltage
- Step size
- Number of cycles
- Separation

As this method uses a ball bearing as a probe, it is ideal for point emission, and by varying the separation a good calculation of the threshold macroscopic field can be acquired.

One problem is that you need to know where 0 μm is, but because the smallest voltage allowed by the equipment is 50 V, the sample (being a good emitter) can start to emit much before the separation is zero. This "unknown" zero, we shall call X. We take a reading at this distance, then increase the anode distance five times in 10 μm steps, taking IV data at each interval. The threshold voltage, when plotted against X, X+10μm, X+20μm ... the gradient can be extracted and threshold field calculated.
For example, Fig. 3.4 shows the threshold voltages for 1nA emission current for the carbon nanofibre sample of Chapter 6. Here the x axis is the distance above the unknown zero.

![Graph showing threshold voltage against anode separation](image)

**Fig. 3.4. Threshold voltage against anode separation for the illustration of how a sample's threshold field is calculated.**

The gradient to the straight line fit is the threshold field, in this case, 5 V μm⁻¹. See Chapter 6 for full sample description.

There is a separate machine for imaging emission from a sample. The machine is in many ways the same as the planar-to-probe one mentioned above; however, in this case we use a phosphor or ITO (indium tin oxide) flat anode to measure the emission current. Fig. 3.5 shows a schematic of the setup. The sample is held on an earthed plate with a PTFE (polytetrafluoroethylene) spacer of known thickness, thus the electric field and therefore threshold field can be accurately calculated. The phosphor screen is then placed on top of this and clamped into place to ensure the separation is as close to the PTFE thickness as possible. This is all inside a vacuum chamber which is pumped down to approximately 10⁻⁶ Torr. There is a CCD camera above the phosphor to allow for image capturing during the emission cycle.
3.5 **SEM**

Scanning electron microscopy (SEM) can detect and graphically display spatially resolved information on the composition and morphology of conductive surfaces. The SEM can achieve powerful magnifications up to $10^5$.

Basically, the SEM works so that a beam of electrons is generated in the electron gun (cathode, located at the top of the column), this beam is accelerated through the anode, condensed by a condenser lens, and focused as a very fine point on the sample by the objective lens. The electron beam hits the sample, producing, among others, secondary and backscattered electrons from the sample. These electrons are collected by a secondary electron or a backscattered electron detector, converted to a voltage, and amplified. The beam scanning the sample surface and the display (CRT) beam are synchronised.

The electrons are ejected from a filament, usually made of tungsten. This filament functions as the cathode. During operation the filament and its heating supply are maintained at a high negative potential by the high voltage supply.
Fig. 3.6. Schematic drawing showing the electron column, the deflection system and the electron detectors.

At the operating temperature, electrons are emitted from the V-shaped filament towards the anode. The anode is positive with respect to the filament - this forms powerful attractive forces for electrons. A hole in the anode allows a fraction of these electrons to continue down the column towards lenses, and on the sample.

3.6 In-situ manipulation

We are able to move two tungsten probes independently, at a resolution of 40 nm, and maximum travel of 5 mm, in three dimensions within a modified SEM chamber. This allows the probes to be positioned with great accuracy above emitter objects for field emission experimentation. Also, the opportunity of three terminal emission, utilising the second probe as a gate becomes possible. A full description of experimental procedure is found in Chapter 5.

3.7 Summary

This chapter has highlighted the experimental procedures undertaken in the research presented in this thesis. Where appropriate, further detail of specific procedures are explained within the relevant chapter.
CHAPTER FOUR

Simulations of field emission properties of a single emitter

4.1 Introduction

This chapter describes the work performed on single tip based emitters. Particular attention was paid to the field enhancement factor, an inherent property of tip based emitters. Firstly, computational simulations of a single, isolated emitter were performed. It was noticed that the location of the anode plane played an important role in defining the field enhancement factor, and therefore, the local electric field. A modified approach to the convention for the applied electric field is defined.

4.2 Simulation

4.2.1 Introduction

The use of computer simulations in the research of electronics has been, and continues to be, a valuable tool in increasing the understanding of device and systems knowledge, and reducing costs. A computer package that, for example, calculates the outcome of boron doping into silicon can solve many situations that would have taken much longer to carry out experimentally in the lab, and as no materials or other laboratory equipment is being used, costs are dramatically reduced.
The simulation package that was available for this work was the commercially available Silvaco™ package, which is a two dimensional simulator used for complex device modeling, process simulation and device performance simulation. We used this package to explore the field enhancement factor of a carbon nanotube. The program allowed us to simulate CNT's of vast ranges of geometries under many changing electrode scenarios. We were able to simulate electric fields at microscopic dimensions with high accuracy, and were also able to determine unrealistically low currents that would normally be undetectable by experimental work as our measurement equipment typically has a maximum resolution in the order of pA.

Many of the experimental studies performed to date on field emission behaviour of carbon nanotubes have relied upon analysis of the emission current I - voltage V (or field, E) characteristic using the well known theory of Fowler and Nordheim [1]. The standard analysis often involves a plot of the log \( \frac{I}{V^2} \) versus \( 1/V \) (or equally log \( I/E^2 \) against \( 1/E \)) and from the slope of the graph a value for the field enhancement factor, \( \beta \), can be extracted. The role of \( \beta \) is the enhancement of the applied macroscopic field such that under the action of the local electric field, efficient tunnelling of electrons from the Fermi level through the potential barrier becomes possible. The interpretation of \( \beta \), which is a dimensionless quantity, if electric field rather than voltage is used in the analysis, is therefore of great importance when considering CNTs as field emitters for a number of applications, including large area flat panel displays.

There have been a number of attempts to model the behaviour of \( \beta \) for a range of nanotube geometries (height \( h \), radius \( r \), single wall vs. multiwall). Mayer and colleagues [2] have used a transfer matrix technique to compare the field emission behaviour between metallic single wall (5,5) (10,10) and (15,15) nanotubes (SWNT) and a multi-wall nanotube (MWNT) composed of the three SWNTs. They observed that the emission from the MWNT is larger than the total current obtained from consideration of the individual walls separately. They also noted that the emission was improved when the end of the tubes were convex rather than flat tops. Moving on from isolated tubes, they further went on to show recently that the emission behaviour of bundles of open and closed (5,5) tubes depended on two factors; whether the tubes were open or closed, and the role of proximity field screening by neighbouring tubes. Closed tubes are found to emit less current than open tubes, and their FE characteristics are found to be more sensitive to the local electric field [2]. Theoretical investigations of field screening due to neighbouring tubes are important in explaining the FE characteristics such as threshold field and emission site density. Nilsson et al [3] compares the threshold field for a mat of tubes and concluded that the optimum nanotube spacing was found to be approximately twice the length of the nanotube.
Hu and Huang [4] used a finite-difference time-domain code to calculate self-consistently the electromagnetic field surrounding the MWNTs. The tubes were modelled as cylinders having a half-ellipsoidal tip that has its minor radius equal to the radius of the cylinder section. They also found that higher emission currents were found for open ended tubes than for closed tubes and the emission current is larger for smaller diameter MWNT than large diameter. For tubes 100 – 200 nm in length the spacing between neighbouring tubes should be at least 200 nm to avoid proximity screening. The cathode-anode distance in this case was 2 µm. For a tube of total length 100 nm, consisting of a half-ellipsoidal tip of major radius 40 nm and minor radius equal to the radius of the tube of 10 nm, an enhancement factor of 25 was found.

In this chapter we explore how FE parameters such as emission current, threshold field and enhancement factor vary for different nanotube parameters (height and radius). We also investigate the role that the position of the anode may play.

### 4.2.2 Simulation of an isolated carbon nanotube

The nanotubes were simulated in two dimensions as having a height, \( h \), and radius, \( r \), vertically aligned with a hemispherical cap on a grounded substrate separated by a distance \( D \) from a flat anode, as shown in Fig. 4.1. In this configuration the nanotube and substrate represent an equipotential surface. The nanotube was simulated with metallic conductivity in order to avoid complications due to field penetration and no account of the presence of localised states, arrangement of capping atoms or the presence of absorbates (e.g. oxygen) is included. Several studies have concluded that the presence of localised states near the apex of the tubes may play an important role in the emission process. Furthermore, the exact bonding arrangements of atoms and the electronic structure obtainable from self-consistent pseudo potential calculations are not included. Such effects should be included to obtain a global interpretation of emission from nanotubes. However, many such simulations are computationally difficult, and are often limited to nanotubes of very small lengths. The nanotubes studied by Mayer et al. [5] consist of only a few hundred atoms and results are often scaled up to more realistic dimensions. The simulations presented in this study therefore represent a grounded metallic cylinder of dimensions \( h \) and \( r \) microns, in the presence of an electrostatic field generated by a potential difference between the substrate, and, an anode located \( D \) away and surrounded by other tubes located a distance, \( W \), away. As a result many of the conclusions drawn are applicable and common to any individual or arrays of tip based emitters.
CHAPTER FOUR  Simulations of field emission properties of a single emitter

Fig. 4.1. Schematic layout of the simulation setup. A hemispherical cap with radius, r, on a cylindrical tube made up of a CNT of height, h, placed on a grounded cathode electrode of width, W, inside a vacuum with an anode electrode suspended a distance, D, above it.

A commercially available simulation package, Silvaco™ [6, 7] was employed in the simulation of metallic nanotubes. To investigate the proximity effects due to neighbouring nanotubes, the separation between the nanotubes is taken as W. Within the Silvaco simulation package, field emission currents were calculated assuming the standard Fowler-Nordheim model with the effects of space charge effects included. The Fowler Nordheim model was originally included for use in MOSFET devices calculating the emission current between Silicon and Silicon oxide layers; therefore, the emission barrier is defaulted to 2 eV. For emission from CNT’s into a vacuum an emission barrier of approximately 5 eV is desirable. This is achieved by modifying the two variables, f.ae, and f.be, which control the way in which the Fowler Nordheim model within the Silvaco package is used (see ref. 7). It is convenient at this stage to define two electric fields; $E_0$ is the macroscopic electric field far from the nanotube and is simply given by applied voltage divided by the anode-substrate separation; $V/D$, and $E_e$ which is the local field calculated from the simulation and is measured at the tip of the nanotube. Within this formulism the field enhancement factor, $\beta_0$, will be given by;

$$\beta_0 = E_e/E_0.$$  \hspace{1cm} (4.1)
An alternative definition for the field enhancement factor will be introduced later in this chapter. During the early phase of the simulation it was observed that the width of the simulation grid played an important role since the boundary conditions are equivalent to mirroring of the simulation area. Such an effect is not an important consideration in device simulation and can improve the resolution of results, however, in the case of an electrostatic calculation in which screening is an important factor; care must be taken to take into account this behaviour.

We assume that the electric field is not a time-varying field and that there are no field sources present, and also that we can solve for the electrostatic field distribution both in the presence and absence of electron emission.

4.2.2.1 Results and Discussion – (variation of emission current with nanotube separation)

Fig. 4.2 shows the variation of the emission current obtained from a nanotube of length 4 μm and radius 200 nm for a simulation work area W, and intertube separations ranging from 1 μm to 32 μm (and with the anode plane located far way – see section 4.2.2.3). It can be observed that as the work area increases the emission current also increases finally becoming similar for tube separations of twice the nanotube height.

The importance of the intertube separation can also be seen in a plot of the variation of voltage required to extract a particular emission current. Fig. 4.3 is the threshold voltage for simulated emission currents of $10^{-20}$ to $10^{-30}$ A. For each emission current, a similar behaviour is observed in which there is an initial decrease in the threshold voltage followed by a levelling off of the current. This behaviour is consistent with the reported experimental result by Nilsson [3]. For all following simulations, a work area of 32 μm is employed to ensure there is no interaction from neighbouring tubes due to the mirroring of the work area which would impede obtaining clear results of an isolated tube.
Fig. 4.2. Electron emission current against applied anode voltage for a CNT of height 4 μm and radius 200 nm. The simulation workarea, W, was varied with values of 1 (■), 2 (●), 4 (▲), 8 (▼), 16 (♦) and 32 μm (◆).

Fig. 4.3. Threshold voltages for emission currents of $10^{-26}$ (■), $10^{-23}$ (●) and $10^{-20}$ (▲) A for all values of W.

In order to prove that the effects of the simulation boundary conditions on emission current seen in Fig. 4.2 are due to the mirroring of the simulation work area, a simple test was performed. It was unclear at first whether the workarea was mirrored or merely repeated. It was important to investigate this further to fully understand how to achieve a truly isolated CNT simulation. Fig. 4.4 shows two simulations A and B. In case A, a CNT was placed in the centre of the workarea as a control simulation because if the workarea is either repeated or mirrored it will make no difference to the result. In case B, we placed a CNT at the right hand side of a workarea of 32 μm, if the workarea was repeated as shown in case B1 (see insert), there would be no difference in emission current from A as the next adjacent tube would still be 32 μm away. If the work area was mirrored, then the next CNT would be next to the original, screening the field and reducing the current as seen in inset B2. As the emission
current of simulation B is lower than that of simulation A, we can conclude that the Silvaco package mirrors the workarea.

![Graph showing possible scenarios](image)

**Fig. 4.4.** Two simulations, A (■) and B (●) showing how the simulation workarea boundary conditions are employed. A is the control, whilst B1 and B2 (insert) are two possible scenarios due to the boundary conditions.

### 4.2.2.2 Variation of field enhancement factor with anode-substrate separation (D) - hemispheres

In the previous section, simulation of emission current was performed where it was assumed that the location of the anode does not influence the emission current. In order to investigate at what stage this assumption breaks down, the emission current against macroscopic electric field from a single tube with length 4 μm and radius 0.20 μm, separated from the neighbouring tube by 32 μm is shown in Fig. 4.5 for anode separations of 6, 20 and 36 μm. The macroscopic field is found by dividing applied voltage by the anode-substrate separation D. If there is no influence of D on the I-E characteristics, the I-E curves should be superimposed upon each other.

Examination of Fig. 4.5 shows that this is the case for the higher values of D, but not for D = 6 μm. This can also be seen in Fig. 4.6 where the threshold field for a emission currents of 10^13 A can be seen for five emitters, similar to that of Fig. 4.5. The lowest threshold fields are observed for the closed electrode separation. Since there is no change in the intrinsic emitter properties, the lower threshold voltage for emission can be explained with an increase in the local electric field.
Fig. 4.5. I-E emission curves for a CNT of height 4 and radius 0.2 μm at values of D of 6 (■), 20 (○) and 36 μm (▲). Emission current can be seen to be higher for a given field for D=6μm, and constant for higher values of D.

Fig. 4.6. Threshold field for an emission current of $10^{-13}$ A for five different distance of the anode position, D, for the simulated emitters.

At this point it is also worth noting that we first varied the voltage for a given geometry and fixed D and observed that the local field varied linearly with anode-substrate separation. This implies that variation of the local field is tied with a variation with D. As a consequence it is important to investigate how the local field is varying as D is changed. This is most easily accomplished by examining the variation of $\beta_0$ with separation. Since this variation is not a priori known for a nanotube of length h and radius r, we first chose to simulate the variation
of the field enhancement factor with D for a grounded hemisphere on a flat plane. Within the 2D nature of the simulation this is equivalent to the simulation of a semicircle on a grounded line. The appendix shows the calculation of the field enhancement factors in terms of the solution to Laplace’s equation for both the 2 and 3D model and gives values of β₀ as 2 and 3, respectively. In both cases, no dependence of β₀ is observed with radius. The results of the 2D simulation shown in Fig. 4.7 for a 1 μm radius hemisphere shows that the predicted value of β₀ = 2 is obtained when the anode-cathode separation is above 4 μm. For a value of D = 2 μm, β₀ has increased to 2.64 and continues to increase reaching a value of 6.71 for D = 1.1 μm. This latter configuration corresponds to a hemisphere-anode plane separation of 0.1 μm. For the 2 μm radius hemisphere a value of β₀ = 2 is obtained when the anode-cathode separation is above 6 μm and the maximum value of β₀ is found to be 21.3 at a relative separation of 0.1 μm. Finally, a similar behaviour is seen in the 4 μm radius hemisphere, whereby a value of β₀ = 2 is found when the anode-cathode separation is above 8 μm and the maximum value of β₀ is found to be 41.7 at a relative separation of 0.1 μm. The results of these simulations clearly indicate that there is an apparent dependence of the β₀ with anode-substrate separation, when D is comparable with the size of the protrusion.

Fig. 4.7. Enhancement factors plotted against anode – cathode separation, D, for two dimensional hemispheres of radius’s 1 (■), 2 (▲) and 4 μm (■). For all three cases an enhancement factor of 2 is seen at high D, increasing as D decreases. Dotted line indicates fit using Eq. 4.4.

The apparent increase in the enhancement factor with reduction in the anode-substrate separation has been shown to be directly related to an increase in the local field experienced
at the surface of the protrusion since there is no change in the applied field as the ratio of \( V/D \) remains constant. Jensen [8] quotes that for a flat anode at potential, \( V \), separated by a distance \( D \) from a hemispherical emitter of radius \( a \), the electric field at the top of the emitter can be expressed as

\[
E = \frac{3V}{(D-a)} \left( \frac{1}{1 + a/D + a^2/D^2} \right)
\]  

(4.2).

The corresponding field enhancement factor in parallel plane electrode geometry is

\[
\beta = \frac{3D}{(D-a)} \left( \frac{1}{1 + a/D + a^2/D^2} \right)
\]  

(4.3).

Taking into account the different geometries between the 3D hemisphere and a 2D semicircle, we find an excellent fit to the data in Fig. 4.7 using a modified version of Eq. 4.3 given by,

\[
\beta_0 = \frac{2D}{(D-a)} \left( \frac{1}{1 + a/D} \right)
\]  

(4.4).

On the basis of (finite element) calculations Edgcome and Valdre [9] have concluded that the enhancement factor for a cylinder of height \( h \) terminated by a half-sphere of radius \( r \) can be expressed as,

\[
\beta_0 = 1.2 \left( 2.5 + \frac{h}{r} \right)^{0.9}
\]  

(4.5).

And that \( \beta_0 \) will increase as the separation between the emitter apex and counter electrode becomes smaller.

Bonard et al. [10] obtained the following expression,

\[
\beta(d) = 1.2 \left( 2.5 + \frac{h}{r} \right)^{0.9} \left[ 1 - 0.033 \left( \frac{d-h}{d} \right) + 0.013 \left( \frac{d-h}{d} \right)^{-1} \right]
\]  

(4.6).
They noted that $\beta$ increases at low value of $(d - h)$ and is observed to plateau off when $d > 1.25h$.

### 4.2.2.3 Variation of field enhancement factor with anode substrate separation ($D$) – nanotubes

In order to examine if this behaviour is also present for nanotubes consisting of a hemispherical cap on a cylindrical shaft, the variation of $\beta_0$ with $D$ for three different nanotubes of length 2, 4 and 6 $\mu$m (and constant radius of 200 nm) was simulated. The results are shown in Fig. 4.8 where it is apparent that two important features are present.

Firstly, at low values of $D$ the value of $\beta_0$ depends on $D$ and is found to increase as $D$ decreases. For a relative anode to tip separation of 0.1 $\mu$m, enhancement factors 24.7, 48 and 68.3 were found for the three nanotubes simulated. Secondly, there exists a regime (approximately given by $D > 3h$) where $\beta_0$ is constant, which we shall call the far anode regime, but in contrast to the simulation of the hemisphere the value of the enhancement factor does not converge to the same value. For the case of $h = 2$, 4 and 6 $\mu$m, the value of $\beta_0$ in the far anode regime are 3.2, 4.3 and 5.9, respectively. It is these far anode values of the enhancement factor that should be used when discussing field enhancement mechanisms and calculating the local electric fields. The increase of the enhancement factor for the three different tubes reflects the length dependence of $\beta_0$. A similar calculation can be performed in which the total length of the nanotube can be held constant but the radius is changed.

![Enhancement factors for 3 emitters of radius 200 nm and heights 2 (■), 4 (●) and 6 $\mu$m (▲) respectively for an emitter tip to anode separation of 0.1 to 150 $\mu$m. Enhancement factors can be seen to decrease with and increasing $D$, and converging to a constant value above separations of $D>3h$.](image)
Fig. 4.9 shows the far anode (50 to 150 µm) enhancement factors for the simulated emitters of Fig. 4.8. Here, it is seen that the values of enhancement factor for the three emitters are tending to 3.2, 4.3 and 5.9, respectively.

The results from this simulation can be found in Fig. 4.10 for a nanotube of length 4 µm and for radii of 50, 100 and 200 nm. It is apparent from the results presented, $\beta_0$ again is seen to increase as the value of $D$ decreases reaching values of 63.4, 54.3 and 48, for a tip to anode separation of 0.1 µm. At the other extreme, for a value of $D$ between 12 and 150 µm, corresponding to the far anode regime, the values of $\beta_0$ for the three nanotubes are 8.0, 6.6 and 4.9, respectively.
The highest values of enhancement is found for all cases with the smallest nanotube radius. The results of the two sets of simulations both highlight the importance of knowing the location of the anode in correctly calculating the enhancement factor. The results also show the general trend that in the far anode regime that the enhancement factor increases for tubes of longer length and smaller radius. This issue is explored in greater detail in the next section.

4.2.2.4 Variation of field enhancement factor with nanotube dimensions (h and r)

The results presented in the two previous sections have highlighted the importance of (i) knowing the location of other tubes in order to exclude the possible effects of proximity-induced field screening and (ii) the location of the anode plane to ensure that it does not play a role in correctly calculating the local field. To test the empirical relationship that $\beta_0$ can be taken as $h/r$, we have assumed that enhancement factor is expressed as a power law dependence on the height/radius ratio of the form $\beta_0 = (h/r)^n$. For $\beta_0 = (h/r)^n$ to be true in this case, $n$ would have to be 1. From the fit to the data presented in Fig. 4.11, a value $n = 0.38$ is found, together with a second gradient of 0.18 for aspect ratios of below 3. From this we conclude that simply regarding $h/r$ would tend to overestimate the value of the local field, and therefore enhancement factor.

Fig. 4.11. Log $h/r$ against Log $\beta$. A gradient of 1 would indicate that the widely used argument that $\beta=h/r$ is true, however, the gradient seen here is 0.38. A gradient of 0.18 is seen to be apparent at aspect ratios below 3 (dotted line).
Based on analytic model for a ellipsoid cylinder, Kosmahl et al. [11] derived an expression for the 2D enhancement factor given by

\[ \beta = \left(1 + \sqrt{\frac{h}{r_c}}\right)^m \]  

(4.7)

where \( h \) is the height of protrusion, \( r_c \) is the radius of curvature given by \( h^2/r \) and \( m = 1 \). The fit to data from the simulation for a power law dependence based on equation 4.7 and \( r_c = \) radius of the nanotube taken gives a slope \( m = 0.94 \). Although the geometry of the spheroid is different from that of a cylindrical shaft capped with a hemisphere, the excellent fit between the simulated data and eq. 4.7 strongly indicates that the functional form of eq. 4.7 is appropriate to describe the data obtained in this study. An alternative equation with a similar functional form is given in eq. 4.8 below

\[ \beta_0 = \left(1 + \sqrt{\frac{h}{a\pi}}\right)^m . \]  

(4.8)

In this case for a value of \( m = 1 \) is obtained with \( a=2.0 \). It is not clear whether there is any significance that can be attached to a value of \( a = 2 \). Using eq. 4.8, we are able to predict the enhancement factor for a range of emitters when in the high D region. Fig. 4.12 illustrates how two emitters of heights 2 and 6 \( \mu m \) with radius 0.2 \( \mu m \), and a hemisphere of radius 4 \( \mu m \), all have an excellent fit to eq. 4.8. The fit is seen by the dotted lines.

Fig. 4.12. Simulation data plotted as points for a CNT of \( h = 6 \mu m \) \( r = 0.2 \mu m \) (■), a CNT of \( h=2 \mu m \) \( r=0.2 \mu m \) (●) and a hemisphere of radius 4 \( \mu m \) (▲). Dotted lines show a fit using Eq. 4.8.
Fig. 4.13 shows the enhancement factors for the three emitters of Fig. 4.12 for an anode to cathode separation of 50 to 150 μm.

Kosmahl [10] go further to predict that the 3D enhancement factor $\gamma$ given by

$$\frac{\gamma}{\beta_0} = \frac{2\sqrt{h/r_e}}{\ln(4h/r_e)}$$  \hspace{1cm} (4.9a)

In the same vein we construct a similar enhancement factor given by

$$\frac{\gamma_0}{\beta_0} = \frac{2\sqrt{h/\alpha r_e}}{\ln(4h/\alpha r_e)}$$  \hspace{1cm} (4.9b)

In relation to variation of the enhancement factor with anode-substrate separation for small separations it is clear that as D decreases the separation between the tip of the nanotube and the anode plane can become much smaller than the length of the nanotube itself. In such a
situation it is convenient to introduce an alternative definition of the normalising electric field, $E_1$, such that

$$E_1 = \frac{V}{(D-h)}, \quad (4.10a).$$

leading to an alternative definition of enhancement factor

$$\beta_1 = \frac{E_1}{V/(D-h)}. \quad (4.10b).$$

Such an approach is valid since the nanotube and substrate represent an equipotential surface. Furthermore electron holography measurements made on nanotubes during emission did not observe a potential drop along the nanotube. As a consequence the field lines are maximised at the tip of the grounded tube. Fig. 4.14 illustrates how the emitter and cathode electrode are at an equipotential, and, furthermore, how the applied electric field can be defined in two manners.

![Diagram](https://via.placeholder.com/150)

**Fig. 4.14.** Schematic of how the surface of the emitter and the grounded cathode electrode are at equipotential 0V (red line). This allows the applied field to be taken as $E$ or $E_1$.

Using the two definitions of field enhancement factor given by eqs. 4.7 and 4.10b, the variation of enhancement factor with anode-substrate for a single unscreened tube of length 4 μm and radius 200 nm is given in Fig. 4.15. Firstly, it is not surprising that at high values of $D$ that the values of $\beta$ converge since as $D \gg h$, the $D - h$ tends to $D$. In the low $D$ regime, the value of $\beta$ is seen initially to increase and then saturate.
Further evidence of this decrease in enhancement factor as D decreases can be seen in Figs. 4.16 and 4.17. Here, enhancement factor is plotted vs. D for three emitters of constant radius 100 nm and heights of 2, 4, and 6 microns (Fig. 4.16) for three emitters of constant radius 50 nm and heights of 2, 4, and 6 microns (Fig. 4.17). As seen in Fig. 4.15, all six emitters of Figs. 4.16 and 4.17 seem to have an enhancement which decreases to unity as the anode electrode approaches the apex of the emitter. It is felt that physically, at this point, the emitter to anode can be considered as a parallel plate configuration due to the macroscopically small D in comparison to the radius of the emitter. It is for this reason that we believe defining the applied electric field as V/(D-h) to be more appropriate when considering the field emission properties of such emitters.
This behaviour has an important physical interpretation in understanding the behaviour of threshold field with anode-substrate separation as reported by Bonard et al. [12]. In order to extract electrons to give a particular current by the application of an electric field, the local electric field, $E_{local}^{th}$ must reach a local threshold electric field. For a given emitter geometry ($h$, $r$ and $D$) with enhancement factor $\beta$, this is accomplished by the application of a suitable applied electric field ($E_{applied}$) such that at the threshold for emission $E_{applied} = E_{applied}^{th}$. This can be expressed in the form that

$$E_{local}^{th} = \beta E_{applied}^{th} \quad (4.11).$$

Since the local threshold field for emission does not possess a dependence of $D$, the behaviour of $\beta$ in which there is an initial increase followed by saturation as $D$ increases would result in an initial decrease in $E_{applied}^{th}$ which is then followed by a levelling off behaviour. This behaviour has been observed experimentally by Bonard et al. [12] where the threshold macroscopic field for emission is observed to decrease from $3 \text{V} \mu \text{m}^{-1}$ for an interelectrode separation of $25 \mu \text{m}$ down to $1 \text{V} \mu \text{m}^{-1}$ at $250 \mu \text{m}$, see Fig. 4.18. Beyond separation the threshold field remains approximately constant at $1 \text{V} \mu \text{m}^{-1}$. From a Fowler-Nordheim study of the emission characteristics, Bonard et al. also concluded that the field enhancement factor increases and then saturated and that the local field was constant with interelectrode separation.
CHAPTER FOUR  Simulations of field emission properties of a single emitter

4.3  Summary

This chapter has dealt with the field emission properties of single tip based emitters. Particular attention was paid to their threshold fields and enhancement factor. It has been seen by simulation that the location of the anode plane plays an important role in further understanding the field emission properties of tip based emitters. An alternative definition to the applied electric field was also introduced.

We have studied the electric field in the vicinity of the tips of metallic nanotubes. Attention was paid to the edge effects of our chosen simulation package to ensure there were no screening effects due to adjacent emitters, which were apparent due to a mirroring of the simulation workspace. The variation of the field enhancement factor as a function of internanotube separation, anode to substrate separation and geometric properties of individual tubes was explored. The location of the anode plane has been shown to become an important factor when the anode to substrate separation approaches and is below three times the height of the tube. Our results imply that the enhancement factor has a dependence on anode to cathode separation, and as a result, alternative definitions for applied field and enhancement factor have been derived.

Fig. 4.18. Experimental work by Bonard et al. Decreasing threshold field and increasing then saturating enhancement factor when D increases [12].
4.4 References

6. Silvaco International, Santa Clara, CA
7. Modifications to the Fowler-Nordheim model had to be performed as this model was originally designed for use in MOSFET devices calculating emission current between Silicon and Silicon oxide layers. Therefore, the emission barrier is defaulted to 2 eV. For emission from CNT's into a vacuum an emission barrier of approximately 4.5 eV is used. This is achieved by modifying the two variables, f.ae and f.be which control the Fowler-Nordheim model within the Silvaco package
CHAPTER FIVE

Field emission from tip based emitters

5.1 Introduction

In order to examine and verify the variations observed in the field enhancement factor seen in the simulations of Chapter 4, which was contrary to previously reported results, experiments were conducted. These consist of first examining the field emission properties of a carbon nanorope exhibiting randomly arranged CNT at the tip, and then comparing with the emission properties of a single CNT. Comparisons of threshold field and enhancement factor are made with the simulation work. Finally, a single CNT is examined for its emission properties when a gate electrode is positioned close to its tip.

5.2 Field emission from tip based emitters – A comparison of theory with experiment

5.2.1 Introduction

From Chapter 4 it was seen how the position of the anode electrode played an important role when calculating the field enhancement factor. It has been shown that the field enhancement factor is independent of the anode to emitter apex when the separation is greater than three times the height of the emitter. It has also been seen that the enhancement factor decreases as the separation decreases when the applied field is defined as $V/(D-h)$, where $V$ is the applied anode voltage, $D$ is the anode to substrate separation, and $h$ is the height of the emitter.
In this chapter we compare experimental results with the theory discussed in the previous chapter. We were interested to see if the theory was applicable to a single emitter, and also to a group of emitters. For this reason we compare the field emission properties of a carbon nanoropes (CNR), (essentially a group of carbon nanotubes) and a single iron tip of comparable dimensions to computer simulations.

5.2.2. Results and discussion

A carbon deposit was prepared on a graphite cathode electrode, in an arc discharge system, in a helium atmosphere at a pressure of 500 Torr. This deposit contained multi-walled carbon nanotubes (MWCNTs) which self-assembled into bundles or ropes of micron dimensions when post-treated by grinding and subjected to ultra-sonic treatment. In a Cambridge Stereoscan 250 Mark III scanning electron microscope (SEM), the CNR had the appearance of high aspect ratio needles that are 1 - 2 mm in length, with an end diameter of approximately 10 microns. The end of the CNRs exhibited protruding MWCNTs of a few microns in length which were randomly spaced, and with diameters of around 100 nm. A CNR, with an end radius of 8 microns was selected, and adhered to a nickel tip by a conducting silver epoxy.

Sample manipulation was made possible by the use of a modified SEM. The SEM was fitted with 2 three-axis piezo slides which had a minimum step of 40 nm and a total travel of 5 mm. Fig. 5.1 is a photograph of the inside of the vacuum chamber of the SEM. The two nano-manipulators can be seen on the left and right sides of the image. Using this setup we were also able to conduct field emission testing in-situ in the SEM. Attaching a sharp Fe probe with an end radius of 5 μm, and connecting this and the earthed sample stage to a high voltage source meter controlled by a computer program, field emission testing was made possible. The main advantage of this setup over a traditional field emission system is that here we have freedom to move both the anode and sample, in three dimensions (together with the tilt and rotate options of the SEM) with an accuracy of 40 nm whilst viewing the setup in real time.
CHAPTER FIVE  Field emission from tip based emitters

Fig. 5.1. Photograph of the setup of the modified SEM. Two piezo electric nano manipulators each having three degrees of movement are located on the left and right of the image. Sharpened iron tips are connected to the manipulators and can be moved with an accuracy of 40 nm.

Fig. 5.2 is an SEM micrograph of the CNR with protruding CNT, and anode electrode, the inset being the anode and cathode experimental setup. An iron tip was electrolytically etched in sodium hydroxide solution to approximately the same dimensions as the CNR for comparison of field emission characteristics associated primarily with geometry.

Fig. 5.2. Scanning electron microscope image of the carbon nanorope and field emission anode. Protruding CNT are clearly visible from the CNR. The inset shows the anode and cathode experimental setup.
Field emission (FE) measurements were performed in a modified Cambridge Stereoscan 250 Mark III SEM configured with a steel probe anode with an end radius of 5 μm and a FE sample stage mounted on the SEM sample stage. The FE testing system was then connected to the sample stage and anode via vacuum feedthroughs. Samples mounted on the earthed stage were tested at different sample to anode separations, measured accurately by the SEM, at a vacuum of better than 10⁻⁵ Torr. A positive voltage was applied to the anode and ramped from 0 V until an emission current of 100 nA was measured and then reduced back to 0 V. This voltage cycle was performed four times for each separate FE test and the threshold field, $E_t$, defined as the applied electric field required to extract an emission current of 100 nA from the sample, recorded. Measurements of emission from both the CNR and the etched iron tip were performed as a function of anode-sample separation. In order to remove any possible effects due to the conditioning of cathodes with time, the testing at different anode-sample separations was not conducted in a sequential manner by increasing or decreasing mode; but in a random sequence. As the I-V measurements were performed in an SEM, accurate measurements of the anode-sample separation could be made. The SEM electron beam and collector voltage were switched off when the FE testing was performed to eliminate any influence on the measurements.

While the end of the iron tip was initially jagged relative to the CNR, the initial FE measurement resulted in it becoming smooth (on the nano scale) and geometrically similar (on the micron scale) to the CNR. This change in morphology is attributed to ohmic heating at the tip and melting the iron due to high current densities at the sharp asperities present initially on the end of the tip. No other changes in the morphology of either sample were observed after subsequent FE testing. Fig. 5.2 is an SEM image of the CNR and Fe anode. The inset is a higher magnification of the end of the CNR with protruding CNT clearly visible. The anode-sample separation was accurately measured by the SEM and taken as the distance between the tip of the anode and the tip of the highest protruding CNT.

Fig. 5.3 shows the I-E curves for the carbon nano rope and iron tip as a function of anode to tip separation (D). It is apparent that the CNR has a lower threshold field than that of the iron tip. Furthermore, it is apparent that as D decreases, the turn-on field for both samples increases.
CHAPTER FIVE  Field emission from tip based emitters

Fig. 5.3. Emission current – applied electric field curves for the carbon nanorope and etched iron tip as a function of anode-cathode gap for carbon nanorope, 40(■), 100(○), 200(▲), 400(▼) and iron tip, 40(▲), 100(○), 200(△) and 400 μm(▼).

Values of threshold field, shown in Fig. 5.4, were extracted from the data of Fig. 5.3 and taken for an emission of 100 nA. In this case, the applied electric field, $E_{\text{applied}}$, is defined as the applied voltage divided by the separation, $D$, between the end of the anode and cathode tips, or as $V/(D-h)$ where $h$ is the height of the individual CNTs. Typical $E_T$-D curves are shown in Fig. 5.4. The data in Fig. 5.4 clearly shows that the CNR has a lower value of $E_T$ relative to the iron tip, over the range of electrode gaps tested. Fig. 5.3 also shows that, for both samples, $E_T$ drops with increasing electrode gap, with the rate of decrease reducing with increasing electrode gap.

Fig. 5.4. Threshold field values for 100 nA emission, for the carbon nanorope (○) and etched iron tip (■) as a function of anode-cathode gap.
CHAPTER FIVE Field emission from tip based emitters

The local threshold field, $E_{\text{local}}$, can be expressed as $E_{\text{applied}} \times \beta$, and the reduction of $E_{\text{applied}}$ which subsequently increases with a flattening of D, implies that the enhancement factor must exhibit a dependence with D. Indeed, to maintain electrode geometry independence for values of $E_{\text{local}}$, $\beta$ must increase on D before saturating. In order to test this hypothesis we have simulated; (i) a bare iron tip emitter with a non-planar anode, and (ii) an iron tip emitter with 9 randomly arranged CNT with a non-planar anode.

The commercially available Silvaco™ simulation package was employed to simulate the emission from the experimental setup. The FE properties of a metallic cathode with a semicircular tip of radius of 4 µm (mimicking the etched iron tip), and an identical cathode but with seven metallic randomly positioned spikes with approximate lengths and widths of 2 µm and 100 nm, respectively (mimicking the CNR) were investigated. Fig. 5.5 are screenshots from the simulation package showing the simulated CNR, Fig. 5.5(a), and iron tip Fig. 5.5(b).

Simulated FE measurements were made between the cathodes and an iron anode with a tip radius of 5 µm using anode tip to CNT/iron probe tip gaps of 10, 20, 40, 100, 200 and 400 µm. The I-V curves for the two setups are shown in Fig. 5.6 (a) and (b).
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Fig. 5.6. (a) Field emission I-V curves for the simulated iron tip of Fig. 5.5(a). Anode to tip separations of 400 (■), 200 (●), 100 (▲), 40 (▼), 20 (♦) and 10 μm (▲). (b) Field emission I-V curves for the simulated iron tip with 7 random CNT of Fig. 5.5(b) mimicking the CNR of Fig. 5.2. Anode to tip separations of 400 (■), 200 (●), 100 (▲), 40 (▼), 20 (♦) and 10 μm (▲).

The variation of $E_T$ vs. separation for an undecorated tip and a tip decorated with seven nanotubes is shown in Fig. 5.7. The decreasing trend of threshold field is the same as that of Fig. 5.4. Also, the increasing threshold field as D decreases would suggest that the field enhancement factor is decreasing with a decreasing D, which agrees with the theory and simulation work of Chapter 4.

Fig. 5.7. Simulated threshold field values for the carbon nanoropes (●) and etched iron tip (■) as a function of anode-cathode gap.
5.3 Field emission from a single isolated carbon nanotube – comparing theory with experimental

5.3.1 Introduction

To further reinforce the results observed in section 5.2, field emission was conducted on a single, isolated carbon nanotube. The same modified SEM was used to image, manipulate and also to conduct field emission I-V experiments as in the previous section. The intention of this set of experiments was to extract a set of threshold fields and enhancement factors for a given range of CNT tip to anode distance and see that they follow similar trends demonstrated by simulation, experiment and by previous experimental work by other authors.

5.3.2 Experimental

Field emission (FE) experimentation was performed in a similar manner to that shown in the previous section, utilising nano manipulators to accurately position the anode electrode. See section 5.2 for details.

A CNT-polymer sample was used. To expose a single CNT the sample was physically broken and the broken edge studied in a scanning electron microscope (SEM). An exposed and isolated CNT was found, vertically aligned, with a height of 8 μm and a radius of approximately 40 nm.

Fig. 5.8 is an SEM micrograph of the exposed CNT, prior to a field emission experiment, it can be seen that there are no neighbouring CNTs that would alter the field emission properties by the effect of field screening [1].
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Field emission from tip based emitters

Fig. 5.8. Scanning electron microscope image of a single isolated CNT with height 8 μm and radius 50 nm in a CNT polymer sample. The etched tungsten tip anode can be seen suspended above the CNT at a distance 5 μm away.

Field emission testing was conducted within the SEM chamber at a vacuum of better than 10⁻⁵ Torr. The sample was mounted on the isolated FE stage with silver epoxy and FE was performed at CNT tip to anode separation of 1, 2, 4, 10, 20, 40 and 60 μm and due to the experiments being carried out in the SEM, these separations could be established very accurately. The FE voltage cycling and current/voltage measurements were computer controlled to ensure repeatability of the testing procedure. The applied voltage was increased in 0.5 V steps (smoothed by an RC circuit) until an emission current of 1 μA was measured and then the voltage was reduced to 0 V in similar steps. A limit of 1 μA was employed to ensure that damage to the single CNT due to filament current heating was unlikely. Emission current was plotted against applied electric field for each of the CNT tip-anode separations.

The resulting I-E plots are seen in Fig. 5.9. It can be seen that for a CNT to anode separation of 1 μm, the threshold field, $E_T$, defined here as the applied field required for an emission of 100 nA, is 42 Vμm⁻¹. As the separation is increased to 2 μm the threshold field reduces to 28 Vμm⁻¹. Subsequent increasing of the separation to 4, 10, 20, 40 and 60 μm (60μm being the largest as beyond this, accurate measurements of the distance became difficult as the CNT was no longer resolved at that magnification) gave threshold fields of 20, 9, 5, 4 and 3 Vμm⁻¹ respectively.
Fig. 5.9. Emission current against applied electric field for anode to CNT tip separations of 1 ( ■ ), 2 ( ■ ), 4 ( ▲ ), 10 ( ▼ ), 20 ( ◆ ), 40 ( ▽ ) and 60 μm ( ○ ). A peak emission current of 100 nA was employed to ensure no damage to the CNT.

Fig. 5.10. shows 1/E against ln (I/E^2) Fowler-Nordheim plots, for the seven CNT tip to anode gaps ranging from 1 – 60 μm. All plots fit approximately a straight line curve indicating that the emission mechanism is likely to be of the Fowler-Nordheim emission type with Fermi level tunnelling. A plot of threshold field for an emission current of 100 nA against CNT to anode separation is shown in Fig. 5.11, where it is observed that the threshold reduces asymptotically. This can be explained by the fact that as the anode approaches the tip of the CNT, the tip to anode approximates a parallel plate configuration and the geometric field enhancement factor of the CNT decreases. As the anode electrode is moved away from the CNT tip, the parallel plate approximation diminishes and the geometric properties of the CNT reduces the threshold field required for 100 nA of emission. A plot of the enhancement factor which was extrapolated from the Fowler-Nordheim equation using a work function of 5 eV is also shown in Fig. 5.11.
Fig. 5.10. Fowler-Nordheim analysis and linear fits for the emission characteristics of the CNT to tip separations of 1 (■), 2 (○), 4 (△), 10 (▽), 20 (◆), 40 (□) and 60 µm (●). seen in Fig. 5.9.

Fig. 5.11. Threshold field (■) and extracted enhancement factor (●) against anode to CNT tip separation. The threshold field can be seen to reduce from 42 Vµm⁻¹ at a separation of 1 µm to a value of 4.5 Vµm⁻¹ at a separation of 60 µm, which is accompanied by an increase in enhancement from 120 to 831.

Enhancement is seen to reduce as the anode approaches the tip of the CNT, further suggesting that the system approximates a parallel plate configuration at low D, whereas at higher values of D, enhancement is seen to level out in unison with the threshold field. From this we can deduce that at high D the enhancement factor is dependant on the geometrical properties of the CNT alone and not the location of the anode, as enhancement reaches an asymptotic
value. But at low D the enhancement factor of the single CNT is dependent on its geometrical properties and the location of the anode electrode.

Using an equation, derived in Chapter 4, for the electric field enhancement factor of a single, isolated CNT, when the anode electrode is sufficiently far away of:

\[ \beta \propto 1 + \frac{h}{\sqrt{ar}} \]  

Where α ranges from 1 – 2. It was noticed that this equation gives values for enhancement factor for this experimentation which were two orders of magnitude smaller than those calculations using the Fowler-Nordheim analysis shown in Fig. 5.10. A reason for this could be explained by the fact that the equation was derived from two dimensional simulations, and the enhancement factors seen in Fig. 5.11 are extracted from the Fowler-Nordheim model. However, Eq. 5.1 does produce a similar trend in enhancement as to that of Fig. 5.11.

Whilst the trends of threshold field and enhancement factor of Fig. 5.11 are in contradiction to other reported work on field emission from single CNT [2], we feel that our methodology of the applied electric field, based on anode voltage divided by anode to CNT tip separation, rather than the more commonly used anode to cathode distance (or CNT base/substrate) is more applicable and gives a more realistic insight into the field emission properties of the single CNT emission process. To further analyse the experimental results, using the enhancement factors for the various anode to CNT tip separation, as seen in Fig. 5.11, it is possible to calculate the emission current using the Fowler-Nordheim equation, which is:

\[ I = \frac{aA\beta^2E^2}{\phi} \exp \left( \frac{-b\phi^2}{\beta E} \right) \]  

Where, a and b are constants with values \(1.54 \times 10^{-6} \text{ Ae}V\text{V}^{-2}\) and \(6.83 \times 10^7 \text{ eV}^{3/2}\text{Vcm}^{-1}\) respectively. A is emission area which has been calculated as \(5 \times 10^{-13} \text{ cm}^2\) using the CNT radius of 40 nm. β is enhancement factor which was taken from the data of Fig. 5.11, E is applied electric field in \(\text{Vcm}^{-1}\) and φ is the work function which was estimated at 5 eV. As stated previously, a work function of 5 eV is acceptable. Fig. 5.12 is a plot of emission current against applied electric field using this approach.
Comparing Fig. 5.9 with Fig. 5.12 it is apparent that the rate at which the turn on field reduces as D increases is similar. Also that the values of applied electric field and of emission current obtained both experimentally (Fig. 5.9) and by calculation (Fig. 5.12) are similar. This leads us to the conclusion that whilst the emission process is not necessarily a result of one emission model, the single CNT follows the Fowler-Nordheim tunnelling process very closely and the emission mechanism is more likely to be of the Fowler-Nordheim type.

Extracting the threshold field for a 100 nA emission from Fig. 5.12 and comparing the obtained values to that of the threshold field found experimentally in Fig. 5.11, it is seen that the values calculated by the Fowler-Nordheim equation are very close to that measured experimentally. Fig. 5.13 shows the two sets of threshold fields on one plot.
The two plots of threshold field seen in Fig. 5.13 show broad agreement between the experimentally recorded results and the calculation of emission current from the Fowler-Nordheim equation, as shown in Fig. 5.12.

It is interesting to note the current density obtained from a single CNT. Other reports [2] show current densities in the order of $2 \times 10^7$ Acm$^{-2}$, which lies close to the feasible limit of the CNT emitter due to resistive heating. However, in our results, the current limit of 1 $\mu$A employed to reduce to effects of resistive heating limited the maximum current density to $5.1 \times 10^4$ Acm$^{-2}$ using the CNT diameter of 50 nm, and assuming that the majority of emission is from the tip of the tube.

5.4 Three terminal field emission

5.4.1 Introduction

It has been seen in this thesis, in both the literature review, and in the other results chapters that electron field emission is possible from tip based emitters, i.e. carbon nanotubes, at relatively low applied fields. However, from a device point of view, if these emitters are to be used as the electron sources in field emission displays; individual pixels need to be addressed.

Whilst the turn on fields for a single CNT have been seen previously in this chapter to be as low as 5 V$\mu$m$^{-1}$, a feasible anode to cathode separation from a manufacturing point of view in the millimetre range is required. This means that anode voltages upward of 1000 V are needed for operation. For logic addressing, voltages in the range of 0 – 25 V are desirable. Therefore, a third terminal (gate) is placed microscopically close to the emitter tip enabling high applied fields which controls the flow of emitted electrons towards the now fixed anode field.

This results section looks at the design implications of such an emitter structure, paying attention to physical limitations of a third contact, comparisons between performance and size, and the operation of the gate contact. The results of computer simulations are first described, before in-situ three terminal field emission from a single carbon nanotube.
5.4.2 Simulations of a gated emitter

The field enhancement factor of an emitter is an integral property when considering its field emission performance. The enhancement factor of tip based emitters has been explored previously in this thesis, however, there must be a change in the enhancement factor of an emitter when a typical gated structure is fabricated due to the location of the metal gate contact.

A typical three terminal field emission structure consists of an emitter placed in the well of an insulating layer, with a conductive electrode acting as the gate. Fig. 5.15 illustrates such a structure.

The simulations presented here used the same program used to simulate two terminal field emission as a starting point. Firstly, the emitter was placed in an insulator well (SiO₂ was modelled), an anode voltage was applied, and the field enhancement factor recorded. Secondly, a metal gate contact was placed on top of the oxide and the applied field and local field at the tip of the emitter recorded.

The effect on the size of the well opening and the height above and below the emitter tip was also investigated. A schematic of the setup and parameters is shown in Fig. 5.16.
Fig. 5.17 and Fig. 5.18 show two sets of three simulation outputs highlighting the change in D (5.17) and S (5.18).

Gate heights, D, of 0, 0.5, 1, 1.5, and 2 μm were simulated, then gate widths, S, of 0.5, 1, 1.5 and 2 μm were simulated.

![Figure 5.17](image1.png)

**Fig. 5.17.** Simulation output structures for gate heights, D, of 0 (a), 1 (b), and 3 μm (c). Yellow region is vacuum and blue region is SiO₂.

![Figure 5.18](image2.png)

**Fig. 5.18.** Simulation output structures for gate widths, S, of 0.5 (a), 1 (b), and 1.5 μm (c).
The anode voltage was kept constant at 400 V and the local electric field at the end of the tip was measured, and the enhancement factor calculated. Table 5.1 and Table 5.2 show the measured enhancement factors for all simulated scenarios.

<table>
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<th>Gate D (µm)</th>
<th>Gate S (µm)</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
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Table 5.1. Measured enhancement factors for D = 0 to 2 µm and S = 0.5 to 2 µm. Gate structure was SiO₂ only with no metal electrode.

<table>
<thead>
<tr>
<th>Gate D (µm)</th>
<th>Gate S (µm)</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
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<tr>
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<td>0.3</td>
<td>1.9</td>
<td>5.7</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2. Measured enhancement factors for D = 0 to 2 µm and S = 0.5 to 2 µm. Gate structure was SiO₂ with a metal gate electrode on top.

It can be seen from Tables 5.1 and 5.2, that the enhancement factor of the emitter drops when the gate height is increased. This is due to the higher dielectric constant of silicon oxide compared to that of the vacuum, i.e. there is less field penetration through the oxide than the vacuum. As the gate is moved upwards further, the applied electric field is limited in reaching the emitter tip due to the decrease in field penetration and therefore the enhancement factor drops further.

When the gate is coated with a metal electrode the decrease in enhancement as the gate is raised above the emitter is more substantial than the case of just the oxide. Without the metal electrode the enhancement drops from 45.6 to 21 (for D increasing from 0 to 2 µm, and S of
0.5 µm) whilst with the metal electrode, enhancement drops from 45.6 to 0.29. The same argument of a reduction in field penetration is applicable, but in this case, the metal has a significantly higher dielectric constant than either the vacuum or oxide.

Figs. 5.19 and 5.20 show the decrease of enhancement factor as D increases. Fig. 5.19 is for oxide only and Fig. 5.20 is for oxide with a metal gate contact.

![Fig. 5.19. Enhancement factor against gate height for an oxide only structure. S of 0.5 (■), 1.0 (●), 1.5 (▲), and 2.0 (▼) are shown.](image)

![Fig. 5.20. Enhancement factor against gate height for an oxide with metal electrode structure. S of 0.5 (■), 1.0 (●), 1.5 (▲), and 2.0 (▼) are shown.](image)

It is interesting to see that increasing the gate well width, S, increases the enhancement factor, for all gate heights simulated. As before this is due to the higher dielectric material of the gate, screening field away from the emitter. Also, as before the effect is less with a gate oxide only, compared to that of when the gate metal electrode is present.

Practically, a high gate to emitter electric field is needed. Therefore, the distance, both horizontally and vertically, to the emitter needs to be as small as possible. This would also be beneficial to allow more emitters per unit area, improving resolution of emission and yield of devices. But, limits associated with device fabrication are present when trying to reduce the gate aperture and dimensions.

It has been seen in the results above that in the presence of a gate structure (with metal electrode) level with the height of the emitter, decreases the enhancement factor of the emitter from 45.6 to 28.3. This is the optimum height as the local electric field between the gate and emitter is at its highest. However, if a small gate opening is used, the enhancement drops significantly. Fig. 5.21 illustrates the effect of reducing the gate opening on enhancement factor. The gate is level with the emitter tip.
Fig. 5.21. Effect of reducing the gate width on enhancement factor.

The decrease of enhancement factor with a reducing gate width size, as seen in Fig. 5.21, means that a compromise must be made between gate width and gate voltage to ensure the highest gate to emitter field whilst retaining as high an enhancement factor as possible. Fig. 5.22 is an example of this situation.

Fig. 5.22. Example of the compromise between structure size and enhancement factor. An applied gate voltage of 10 V was used in this case.
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This highlights the importance in designing arrays of three terminal emitters for applications such as field emission displays (FEDs).

5.4.3  Gate effects

Now that the design of a gated emitter structure has been explored, the effect on emission of applying a gate voltage was studied. Similar structures to that seen previously were simulated. An emitter of height 1 μm in a gate well of height 1μm and width 1μm was used. A gold electrode was used as the gate contact which was placed on top of the gate oxide. An anode to emitter tip distance of 20 μm was used. The parameters defining the work function in the Fowler Nordheim model were altered as described in the previous simulation and theory chapter.

The anode voltage was ramped from 0 to 2000 V and the emission current recorded. The gate voltage was fixed at 0.5, 2.5, 5.0, 7.5 and 10 V. The resulting emission plots are shown in Fig. 5.23. An inset is used to highlight the variation observed as a function of gate voltage.

![Emission current against anode voltage with gate voltages](image)

**Fig. 5.23.** Emission current against anode voltage, with gate voltages of 0.5 (■), 2.5 (■), 5 (▲), 7.5 (▼) and 10 V (♦). Inset shows the increasing effect of emission current with the gate voltage.
Fig. 5.24 shows the variation of emission current for an anode potential of 2000 V and varying gate voltages. The emission can be seen to increase as the gate voltage increases.

Whilst the emission currents recorded for the structured simulated are relatively small, $\sim 10^{-14}$ A, these small values have been seen in previous simulations and theory results chapter, and is due to the calculations performed on the device. Also, one would expect the emission current of a single emitter with its geometric enhancement factor decreased by the presence of a gate electrode to be small. However, gate effects were observed, both Figs. 5.23 and 5.24 show an increase in maximum emission current, and Fig. 5.23 shows a reduction in the turn on voltage as the gate voltage is increased.

![Graph showing emission current against gate voltage](image)

**Fig. 5.24. Variation of emission current against gate voltage for an anode voltage of 2000 V.**

### 5.5 Experimental three terminal field emission

#### 5.5.1 Introduction

The effects of the presence of a gate electrode on emission current was investigated experimentally. A single carbon nanotube was used as the emitter. A modified scanning electron microscope with micromanipulators was used to carry out field emission testing.
As a single CNT was used as the emitter, a gate electrode of as small a thickness as possible was needed so as not to affect the emission characteristics.

5.5.2 Manufacturing the gate contact

In order to produce a free standing, microscopically thin metal gate, a FEI Nova 600 dual beam focused ion beam (FIB) was used to mill the end of a tungsten tip. The FIB used had the added benefit of being equipped with an electron column at 52° to the axis of the ion column, allowing two simultaneous fields of view. Firstly, the end of the probe was physically bent so that the end could be lowered into its gate position without the rest of the probe interfering with field emission testing. Next, the sides of the tip were milled by focussed gallium ions accelerated by 30 keV to leave an oblong shape with a width of 500 nm. The tip was then rotated through 90 degrees and a 1 μm diameter hole was etched through the centre of the thin film.

Fig. 5.25 and 5.26 are SEM images of the etched gate contact, with Fig. 5.25 a profile of the contact showing the 500 nm thickness, and Fig. 5.26 a view down the inside of the tungsten tip showing the 1 μm hole.

Fig. 5.25. SEM image of the side of the gate contact. Thickness of metal is 500 nm. (Image colours inverted for clarity).
5.6 Field emission experimentation

Field emission testing was carried out in a modified SEM, in which nanomanipulators could be moved in three dimensions with an accuracy of 40 nm positioned both anode and gate electrode. The sample was mounted on the SEM stage which had x, y, z, rotation and tilt movement.

A similar sample was used to that of the two terminal field emission of a CNT seen previously in this chapter. A MWNT – polymer sample was physically broken to expose CNT at the edge. The sample was examined in the SEM until a suitable emitter was found. Gate and anode electrodes were then positioned above it.

Fig. 5.27 and 5.28 show SEM images of the experimental setup. A CNT of height 1.5 μm and radius 40 nm had the gate electrode positioned 1 μm from its tip. The anode electrode was kept 40 μm away from the gate.

The anode voltage was ramped from 0 to 600 V and its current measured. A current limit of 1 μA was employed to ensure minimal damage to both CNT and gate electrode due to current heating, as it was positioned close to the emitter tip. The gate voltage was increased for each
subsequent anode voltage ramp to see if there was any effect on anode current, such as a lowering of threshold voltage.

Fig. 5.27. SEM image showing the second CNT emitter and gate contact positioned 1 μm above it.

Fig. 5.28. SEM image showing the anode and gate electrodes positioned at 1 and 40 μm respectively.

The gate voltage was increased to see if there was any effect on the anode current. Fig. 5.29 shows the I-V characteristics for this emitter for gate voltages, $V_G$, of 0, 5, 10, 15, 20 and 25 V.
Fig. 5.29. Emission characteristics of the gated CNT emitter. Whilst there is emission at $V_G = 0 \, \text{V}$, the application of a voltage at the gate significantly reduces the turn on voltage. Gate voltages of 0 (■), 5 (●), 10 (▲), 15 (▼), 20 (♦) and 25 V (▲) are shown.

It can be seen from Fig. 5.29 that whilst the CNT is emitting at zero gate bias, the application of a gate voltage decreases the threshold voltage for an emission current of 10 nA from 340 V to 140 V for gate bias of 0 and 25 V respectively. Maximum emission current of 1 µA, set by the user, was also reached at lower anode voltages. 450 V with no gate bias compared to 180 V with a gate voltage of 25 V.

In this configuration with the gate electrode 1 µm above the CNT, and with the gate aperture being a 1 µm diameter hole, it is possible to calculate the effective distance of the gate to emitter tip, and therefore, the applied field due to the gate voltage. Fig. 5.30 shows a schematic of the gate emitter configuration.
In this case the gate to CNT distance is 1.4 μm, which is the value to be used from this point forward when calculating gate to CNT tip field. Fig. 5.31 highlights the effect increasing the gate voltage has on emission current.

A Fowler Nordheim analysis was performed on the I-V emission data of Fig. 5.29. The applied field used in this analysis was the anode field, as according to [3, 4]. The resultant plot of Ln(I/E^2) vs. 1/E can be seen in Fig. 5.32.
The straight line fit of the data at high applied anode fields suggest that the emission mechanism follows the Fowler-Nordheim theory. It is apparent that in the case where there is no gate bias (plot ■ of Fig. 5.32.) has a different trend to that of the other straight line fits in the presence of gate bias is observed. This is highlighted further by the calculation of the field enhancement factor, $\beta$, from the Fowler Nordheim fits. Here, a work function of 5 eV was assumed for the emitter. Enhancement for the gate biases used is shown in Fig. 5.33.

![Fig. 5.33. Enhancement factor calculated from by Fowler Nordheim for all gate voltages used. A work function of 5 eV was assumed.](image)

Here, the initial enhancement factor with zero gate voltage is 606. Subsequent increase of the gate voltage increases the enhancement factor to approximately 2000. Only a slight increase of enhancement for gate voltages of between 5 and 25 V is seen (3.57 to 17.8 V$\mu$m$^{-1}$). This sharp increase can be explained by the local field seen at the tip of the CNT due to the gate bias.

It was informative to perform a 2 terminal field emission experiment, i.e. without the gate electrode, to see if there is any difference in performance between this and the case of zero gate bias. The gate electrode was moved out of the way completely, the anode remained in its
position, and the anode voltage increased until an emission of 1 μA was recorded. Fig. 5.34 (a) shows the subsequent I-V plot.

Fig. 5.34. (a) Emission current against anode voltage for the CNT when the gate electrode has been moved away. (b) Fowler Nordheim analysis of the data of (a). Enhancement was calculated to be 795 assuming a work function of 5 eV.
The threshold voltage for an emission current of 10 nA, in this case, is seen to be 230 V, which equates to a threshold field of 5.75 V/μm$^1$, and a peak emission of 1 μA is seen at 280 V, or 7 V/μm$^1$. Fig. 5.34 (b) shows the Fowler Nordheim analysis for this data, where an enhancement factor of 795 is found. Taking the case where the gate electrode is present but with zero bias, we see that the threshold field is higher (8.5 V/μm$^1$) and the enhancement is lower (606). The apparent decrease in threshold field, and increase in enhancement factor seen here can be explained by the removal of the gate electrode.

To investigate this further, it is helpful to analyse the electric field due to the anode with and without the presence of the gate electrode to see if there is a limiting factor, which we shall call the gate screening factor.

Taking the two cases of with and without the gate:

\[ E_1 \quad E_2 \]

\[ \beta_1 \quad \beta_2 \]

Where, \( E_1 \) and \( E_2 \) are applied anode field and \( \beta_1 \) and \( \beta_2 \) are the enhancement factors of the CNT. We can say that the local field at the CNT tip, \( E_L \), can be expressed as:

\[ E_{L1} = \beta_1 E_1 \]  \hspace{1cm} (5.3)

And;

\[ E_{L2} = \beta_2 E_2 \]  \hspace{1cm} (5.4)

Assuming that the enhancement factor calculated from the setup where the gate electrode is removed is that of the CNT alone, and that this enhancement is inherent to the CNT, we can say that,
Armed with a knowledge of the applied voltage, $V_a$, and the enhancement factor, it is possible to calculate the local threshold field, $E_l = \beta V_a/D$, where $D$ is the interelectrode spacing (40 μm). For the case of two terminal measurements, the local field for 10 nA current is 4.566 Vnm$^{-1}$. This is the field that will be required to extract the same current for the unbiased three terminal structure. In such a situation, it is possible to introduce a screening factor $(1-\eta)$, such that

$$E_a\beta(1-\eta) = E_l$$

(5.6).

where $E_a$ is the value of $V_a/D$ in the three terminal arrangement. Using the above values and equation 5.6, allows a value of the screening term, $\eta$, of 0.32 to be calculated. In order to examine whether the value of screening term is affected by the magnitude of the current, a similar analysis was performed at 1 μA current. In the absence of the gated electrode a voltage of 313 V is required, rising to 460 V, in the presence of the metal electrode. Using the same value of the $\beta$ as before (794) and with the aid of Equation 5.6, shows an identical screening factor of 0.32. This shows that nearly a third of the applied electric field (voltage) is screening by the presence of the metallic gate and independent of current (up to 1 μA). If this screening of the field was ignored, a naïve calculation of the local field assuming an applied voltage of 460 V and an enhancement factor of 620, would overestimate the local field at 5.27 Vnm$^{-1}$.

There have been several reports of three terminal devices utilising multiple CNT emitters within the gate [5-8], however, it would be more appropriate to compare the results seen in this section to those utilising single CNT emitters. Gangloff et al [9] reported the fabrication of arrays of individually gated CNT emitters. Their structures involved patterning and etching 800 nm gate apertures through a gate metal and a 1 μm insulator film. Individual CNT were then grown within the gate hole. As stated previously in this section, in order to use as small a gate voltage as possible, the gate electrode must be placed as close to the emitter tip as possible. Gangloff et al used controlled CNT growth to ensure the emitter tip was in line with the gate metal. In their case, the gate to CNT distance was therefore 400 nm. The anode was
positioned 100 μm away and supplied a constant 1 Vμm\(^{-1}\) to collect emitted electrons. The reported results show an emission current of 1 μA (selected to compare to the results in this thesis) obtainable at a gate voltage of 40 V, which is higher than the results obtained in this thesis (25 V). However, if one were to calculate the field supplied by the gate, it is seen in the literature that a gate field of 100 Vμm\(^{-1}\) is required for 1 μA emission [9], comparably higher than that seen previously in the results of this chapter of just 18 Vμm\(^{-1}\).

Examining Fig. 5.28, it is observed that there is a 20 by 20 μm structure to the left of the tested CNT. It is fair to say that the predominant emission is from the gated structure as there is a variation of anode current with gate voltage. However, to rule out the possibility that this large structure was contributing to the total emission current, higher magnification SEM images were taken. Fig. 5.35 (a) and (b) show this structure, 5.35 (b) is of the same magnification of Fig. 5.27, which shows the single CNT. Here, there were no CNT structures observed which could affect the emission results seen above.

![Fig. 5.35. (a) SEM image of the structure to the left of the gated experiment. (b) Higher magnification of (a) and under inspection, no CNT structures which could be emitting under the anode electrode could be observed.](image)

To investigate if the emission current seen at the anode (shown in Figs. 5.29) are from the CNT rather than the gate electrode the computer program running the field emission testing was switched to change and record the gate properties. In this experiment the anode voltage was fixed at 0, 500 and 1000 V, and the gate voltage ramped from 0 to 100 V. The sample was kept at 0 V. Higher values of gate and anode voltage were used here than previously in the hope to rule out significant contribution from gate emission.

Fig. 5.36 shows the gate I-V characteristics for these three anode voltages. Firstly, it is noted that the current recorded is not that of noise as there is a definite trend. This means there is some emission current from the gate. However, the recorded currents are at least 4 orders of
magnitude lower than that seen in Fig. 5.29 for the CNT emitter tested. There is a slight increase in gate current as gate voltage is increased, but as the maximum current does not reach 1 nA, it is conclusive to say that the emission current seen in the previous results are, in majority, from the CNT rather than the gate. It is also worth noting that the slight increase in gate current could be an answer to the slight increase in anode current at low applied anode voltages seen in the previous results.

To further conclude that the gate is not the primary emissive structure, the ratio of gate current and anode current was plotted against anode voltage. Gate voltages of 0, 5, 10, 15, 20 and 25 V were used. The results are shown in Fig. 5.37.

**Fig. 5.36.** Gate current against gate voltage for anode voltages of 0 (■), 500 (●) and 1000 V (▲).

**Fig. 5.37.** Ratio of $I_G$ to $I_A$ against anode voltage for $V_G$ of 0 (■), 5 (●), 10 (▲), 15 (▼), 20 (◆) and 25 V (◀). Ratio can be seen to decrease from between 0.01 – 10 to between $10^{-4}$ – $10^{-5}$ at high $V_A$. 

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A ratio of gate to anode current of >1 would indicate that the gate current is greater than the anode current. Indeed, initially the ratio is greater than 1, however, examining Fig. 5.29 it is seen that the device is not turned on, for all gate voltages. This implies that the high ratio is a result of comparing the inherent background noise of both anode and gate.

At anode voltages greater than 100 V, the ratio of $V_g$ to $V_a$ drops to a low of between $10^{-4}$ and $10^{-6}$, meaning that at high anode voltages, or when the structure is emitting, the anode current is at least 4 orders of magnitude greater than the gate current again indicating that the primary emission structure is the CNT.

5.7 Summary

Based on the simulation results, where it was found that by defining the separation as anode to emitter tip, or (D-h), where h is the height of the emitter, the field enhancement factor decreases as the anode is brought close to the emitter. We were able to experimentally test the field emission properties of an iron tip and of a group of carbon nanotubes at the end of a carbon nano rope. It was found that the threshold field ($E_t$) increases as D decreases. The experimental results were further backed up by a set of simulations, which displayed a similar trend of threshold field. It can also be said that because $E_t$ is increasing, one would expect that the enhancement factor would decrease.

Further evidence to support our claims so far were found when the field emission properties of a single, isolated carbon nanotube were examined. Accurate anode to CNT tip separations down to 1 μm were made possible by manipulating the anode electrode and sample stage within the SEM. It has been shown that as the separation of CNT to anode increases from 1 μm, the threshold field decreases to an asymptotic value dependant on the geometric properties of the CNT, and the enhancement factor increases from unity to an asymptotic value in accordance with the decreasing threshold field. This is due to the CNT tip and anode approximating a parallel plate at low D.

The trends of threshold field and of enhancement factor tie in with the results seen from the carbon nano rope, and of the theory and simulation results sections.

Further analysis on the field emission properties of the single CNT were made possible by calculating an emission current using the Fowler-Nordheim equation. Similar trends and
values of emission current for a given field were seen by calculation when compared with experimental results. The threshold field when extrapolated from the calculated I-E curves exhibited a very good fit to the threshold field for the experimental results. The results from this section support the theory made in previous sections that it is more appropriate to define applied electric field as V/(D-h) when considering field emission characteristics from any tip based emitter.

5.8 References

CHAPTER SIX

Large area field emission

6.1 Introduction

Unlike Chapters 4 and 5, this chapter reports electron field emission over large areas from a number of emitting sites, with possible applications as electron sources for large area field emission displays (FEDs).

Field emission from carbon nanofibres grown at room temperature are shown to exhibit low threshold fields of 5 Vμm⁻¹. The emission mechanism and source of emission is explored.

The mechanism of field emission is explored for carbon nanotube polymer composites (CNT-PmPV). It was found that their conduction is limited by a percolation law which could have implications with regard to the electron field emission from these structures. This percolation theory is investigated experimentally and analytically.

6.2 Room temperature carbon nanofibres

This chapter explains how carbon nanofibres (CNF) were grown by chemical vapour deposition (CVD) of methane (CH₄) on catalysed nickel (Ni) films. Both processes of catalysing the nickel films and growth of the nanofibres were carried out whilst at room temperature (<30°C). Growth mechanisms, SEM micrographs of grown CNF’s and their subsequent field emission properties were investigated. The growth of carbon nanofibres at room temperature for field emission applications enables the use of glass and even plastic substrates, removing the difficulty of scale up when using Si substrates.
Carbon nanofibre growth

Glass substrates were cleaned using a standard three stage chemical bath process of;

Acetone → isopropanol ← methanol ← de-ionised water

10 cm of Nickel wire was thermally evaporated at 2x10⁻⁶ mbar for 20 seconds, half the sample was then masked off to enable a comparison to be made between the Ni layer and subsequent carbon growth. The Ni film was found to be approximately 0.5 µm thick when measured using a Daktak II profile meter.

The Ni film was subsequently treated to an Ar ion plasma of 100 sccm for 30 minutes, with the substrate table monitored to be at room temperature, in a Plasma Technology DP800 capacitively coupled rf plasma enhanced chemical vapour deposition (PECVD) reaction chamber. The sample was placed on the bottom, earthed electrode. A process pressure of 200 mTorr and a rf power of 300 W was used. The reverse power of the plasma was continually adjusted to keep it as close to zero as possible in order to prevent substantial substrate heating. The surface of the film was examined using a Hitachi S4000 cold field emission scanning electron microscope (SEM) and shows the interaction of the Ni with the plasma causes a roughening of the film surface as shown by the circular features of Fig. 6.1.

![Fig. 6.1. SEM image of Ni film, 20 sec Ni evaporation, after Ar plasma treatment.](image1)

![Fig. 6.2. Higher magnification of sample of Fig. 6.1.](image2)

These features are between 3-4 µm in diameter and are surrounded by smaller circular islands of less than 500 nm in diameter as can be observed in the higher magnification image shown in Fig. 6.2. The roughened film possesses numerous round sites, but it is the smaller sites of
Fig 6.2 which we believed would act as growth catalysts for nanofibres, as the larger features are possibly too large in diameter (>3 μm) for catalysed nanofibre growth.

It is known from extensive studies of noble gas ion implantation that "bubbles" may form at sufficiently high dose and ion energies. [1] For example, $10^{17}$ Ar ions cm$^{-2}$ irradiated into a copper foil at 60 keV ion energy, at 20 °C, showed the formation of bubbles [1]. In these studies, the bubbles are believed to be filled with gas molecules which can burst and result in blisters. However, the energies of the Ar ions used in this study would be tens of electron volts not keV and as a result we do not believe that the features observed are bubbles of gas but rather are Ni metal. The formation of the Ni is most likely due to thermal processing experienced by the film via a form of plasma etching though the role of adhesion of the metal to the substrate may also be a contributory factor. It is interesting to note that in the growth of CNTs on plastic substrates, the formation of Ni islands was also attributed to plasma processing rather than adhesion. [2] An example of this effect can be seen in Fig. 6.3.

![Fig. 6.3. Example of how plasma treatment can alter the surface of a material, in this case an Nb single crystal surface. [1]](image)

Nanofibre growth was performed in the same reactor chamber, in which CH$_4$ was introduced at a flow rate of 30 sccm (standard cubic centimetres per minute) and a pressure of 1 Torr. The reverse power of the plasma was again continually adjusted to keep it as close to zero as possible in order to prevent substantial substrate heating. The water cooled substrate table temperature was monitored to be approximately 30°C throughout the deposition. Both the Ar ion treatment and CH$_4$ growth were carried out on the earthed electrode.
6.2.2 Characterisation

A carbon deposition was performed with two samples placed in the chamber at once, one on top electrode, one on the earthed bottom electrode. CH₄ was introduced for 10 minutes at a flow of 30 sccm at 1 torr and a plasma struck and held at a power of 300 W. Carbon structures were only observed from samples placed on the bottom, earthed electrode of the reaction chamber. This is due to the difference in potential between the electrodes. The top, r.f driven electrode will be at a higher negative DC potential relative to the earthed electrode. This in turn means that the average collision energy between positive ions of the plasma and the sample surface is greater on the top electrode than on the bottom. The reason growth was only observed on the earthed electrode could be due to the reduced etching rate of the plasma at the bottom than the top due to the lower energy of collisions.

Fig. 6.4. Carbon nanofibre structures arranged radialy from a central point. The carbon structures were grown on the bottom electrode of the reaction chamber.

Fig. 6.4 is an SEM image of carbon growth in the form of carbon nanofibres from a central Ni particle. The nanofibres are arranged radialy in a star shape which has a diameter of approximately 75 μm. Figure 6.6 is a higher magnification image of the structures. In general, nanotubes grown by a catalyst method should have a Ni particle at the top or bottom of the sample. The structures in Fig. 6.5 do not seem to have a Ni particle at the end (usually denoted by a bright “spot” at the tip of the structure when viewed by SEM) also the tube structures are approximately 300 nm in diameter, which is too large to be a nanotube implying that they are nanofibres rather than nanotubes.
One possible scenario as to how these structures were formed was that it was an effect of film peeling. Film peeling due to surface tension is fairly common, but to get the star shapes seen in Fig. 6.4, 6.7, 6.10, and 6.12 as an effect of peeling is highly unlikely. Had the growth been in one direction only, this might be the case, however the growth has been observed to be in all directions covering the complete 360 degree range, making them near perfect star shapes.

At low growth temperatures, the diffusion of C in Ni is dominated by surface diffusion of C around Ni particles as opposed to C diffusion through the bulk of the metal [2, 3]. The growth mechanism is based on the decomposition and diffusion of carbon through the Ni, similar to that described previously elsewhere in the low temperature growth of nanofibres [3]. At sufficient high C concentration precipitation of the C occurs above the solubility limit resulting in nanofibre growth.

Fig. 6.9 and 6.10 are good examples of how dense these tubes/fibres are. Film peeling usually occurs in one place, not bunched up as observed in this sample. As shown in figure 6.13, once one example had been found by SEM, we found that the sample displayed good uniformity of these structures, the examples here are only 70-80 μm apart when viewed by SEM.
CHAPTER SIX

Large area field emission

Fig. 6.9. High magnification SEM image of the groups of nanofibres seen in the star shape.

Fig. 6.10. A high density of nanofibres. Circled area shows a region with nanofibers seeming to grow on top of each other. This is unlikely an effect of film peeling.

Fig. 6.11. Group of nanofibers.

Fig. 6.12. High density of nanofiber growth which is not possible by film peeling.

Fig. 6.13. Two nanofibre structures seen together, at a distance of 60 μm apart.
CHAPTER SIX Large area field emission

After the previous results showed active growth, we repeated the experiment, altering the deposition power to see the effect on nanofibre growth. New samples were used, cleaned and cut in the same way as previous, evaporation, Ar and CH₄ plasmas were used as in the previous experiment. The ranges of power for the CH₄ plasma used were 50, 100, 200, 300 and 400 W and are shown in table 6.1. Samples were named ARNF 1-5, representing Argon catalysed carbon nanofibre growth.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>CH₄ Plasma Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARNF1</td>
<td>50</td>
</tr>
<tr>
<td>ARNF2</td>
<td>100</td>
</tr>
<tr>
<td>ARNF3</td>
<td>200</td>
</tr>
<tr>
<td>ARNF4</td>
<td>300</td>
</tr>
<tr>
<td>ARNF5</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 6.1. Range of CH₄ plasma power used and location in deposition machine.

The aim of this set of experiments was to prove the repeatability of the previous set, and to clarify the structure further. Fig. 6.14. shows a group of nanofibres, located on sample ARNF5 and had a plasma process of 30 sccm of CH₄ at 1 Torr for 10 mins at 400 W.

Carbon nanofibre growth was apparent at a CH₄ plasma power of 300 W but not at powers of 200 and 100 W. A comparison of Fig. 6.15 (at 400 W) to Fig. 6.5 – 6.12 (at 300 W) highlights that at 400 W denser bundles of CNF are observed, suggesting that the growth mechanism and rate is dependant on plasma power.

Fig. 6.14. SEM image of carbon nanofibres from sample ARNF 5.

Fig. 6.15. Higher magnification SEM image of the structure seen in figure 6.14. A high density of carbon nanofibres can be seen emerging from the centre.

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Fig. 6.16 Cluster of carbon nanofibres from sample ARNF5.

Fig. 6.17. Higher SEM magnification of Fig. 6.16.

Fig. 6.18. High magnification SEM image of the tip of the nanofibre on the right of Fig. 6.17. Diameter of tip ~200nm.

Fig. 6.16 and 6.17 shows how these carbon nanofibres often appear to grow on top of each other; at least three levels can be seen. All these structures show a spherically rounded tip. As seen previously these structures have an end radius of around 100 – 150 nm.

Fig. 6.18 is a high magnification SEM image of one of these tubes. The uniformly rounded tip or cap, can be seen clearly. Due to the tilt of the sample when the SEM analysis was carried out and the fact that the emissive electrons are analogous to light, we see light and dark regions of the fibre of Fig. 6.18, confirming a three dimensional cylindrical shape.

Due to the possible alternative explanation based on thin film peeling to justify the SEM images observed in the experiments performed, we found a situation in which peeling occurs, seen in Fig. 6.19, to highlight the differences. It can be seen how the grey carbon film has peeled away leaving a darker patch at the bottom of the image, and the film curled round to form two tubes, or scrolls.
6.3 Field emission properties

The field emission characteristics of the CNF's were examined using a sphere-to-plane electrode geometry, with a 5 mm stainless steel ball bearing suspended above the sample with a high positive potential applied in a vacuum of around $10^6$ Torr. Although a spherical anode is used, it is assumed that the electric field between the anode and the surface of the sample can be modelled as a parallel plate due to the large radius of the anode with respect to the nanofibre size. The voltage is stepped up and down in 20 V increments by a computer program, and the macroscopic electric field is defined as the applied voltage divided by the anode-cathode separation.

The threshold field, $E_{th}$, is defined as the macroscopic electric field, which gives an emission current of 1 nA. The sample ARNF5 deposited at room temperature displayed excellent emission characteristics with a low threshold field of 5 V$\mu$m$^{-1}$ as shown in Fig. 6.20.

The results show a uniform increase in emission current when the applied electric field is increased with a maximum current of 0.5 $\mu$A observed at a field of 37.5 V$\mu$m$^{-1}$. The probe was moved to a second site on the sample and the same emission experiment was carried out. This time 4 cycles were recorded to highlight any hysteresis and/or conditioning. The results are seen in Fig. 6.21.
CHAPTER SIX  Large area field emission

The four current-voltage characteristics are presented and no significant difference between the two I-E characteristics is present. This implies that there is no need for "conditioning" steps for the onset of stable and reproducible emission, which is in contrast to what has been reported in amorphous carbon (a-C) thin films [4]. In addition, there is no evidence of hysteresis behaviour between the upward and downward cycle of any I-E characteristic. This is an important result since any spread in the I-E characteristic could mean more complicated and expensive drive circuitry for a nanofibre based field emission display.

In order to conclude that the emission of Figs. 6.20 and 6.21 are from the structures seen in this chapter there were two possibilities that we had to consider:

1. The emission could be from the surrounding areas around the nanofibres. This is amorphous carbon which is co-deposited when the fibres were grown.
2. The emission could be from the roughened Ni film as seen in Fig's. 6.1 and 6.2.

Two tests could be carried out to check this. Firstly, it has been reported that amorphous carbon (a-C) films have a threshold of around 20 Vµm⁻¹ [4]. Whilst the nanofibre emission shows an emission threshold field of 5 Vµm⁻¹. We knew that neighbouring star like nanofibre structures were approximately 70 – 80 µm apart, as seen in Fig. 6.13. We were able to move the emission probe away from the site which recorded the data of Fig 6.21. Whilst we did not know if we were indeed above a group of nanofibres in the first place, if when we moved away, repeated the emission cycles, and saw a higher threshold field we could safely say that the lower threshold was that from nanofibres and the higher, from the surrounding amorphous
carbon. Fig. 6.22 shows the emission cycles when the probe was moved 40 μm across from the site which recorded Fig. 6.20 and 6.21.

It can be seen that there is a definite conditioning cycle in the first cycle, and that all four cycles show hysteresis between upward and downward cycles. The threshold field in this case is 30 Vμm⁻¹ and the peak emission current at 40 Vμm⁻¹ is 10⁻⁷ A. The data in Figs. 6.20 and 6.21 show a lower threshold field and higher peak current suggesting the emission in this case is from the amorphous carbon surrounding layer.

To further conclude that the higher quality emission was from the nanofibres, we tested a sample which had its Ni film catalysed, but no carbon growth. As expected, no detectable emission was seen beyond the noise level of the detection apparatus (<0.1 nA). The results can be seen in Fig. 6.23.

To help understand the emission characteristics of the sample ARNF5, we performed a Fowler Nordheim analysis on the IV characteristics seen in Fig. 6.20.

As shown previously the Fowler Nordheim equation is,

\[ I = \frac{aA\beta^2 E^3}{\Phi} \log \left[ -\frac{b\Phi^2}{\beta E} \right] \]  

(6.1)
Where \( a \) and \( b \) are constants with values \( 1.54 \times 10^{-6} \) A eV\(^2\) and \( 6.83 \times 10^5 \) eV\(^{3/2}\) V cm\(^{-1}\) respectively, \( A \) is emission area, \( \beta \) is enhancement factor, \( E \) is applied electric field in V cm\(^{-1}\) and \( \phi \) is the work function which was assumed to be 5 eV. Rearranging equation 6.1 gives,

\[
\log \frac{I}{E^2} = \log \frac{aA\beta^3}{\phi} - \frac{b\phi^2}{\beta E} \tag{6.2}
\]

Therefore, plot \( \log \frac{I}{E^2} \) against \( \frac{1}{E} \) can be used to obtain the gradient, \( m \), which will lead to the calculation of \( \beta \) or \( \phi \). Using the data of Fig. 6.20, the graph of Fig. 6.24 was plotted.

![Graph](image)

**Fig. 6.24. Fowler Nordheim analysis plot of the emission data of Fig. 6.20.**

From the graph of Fig. 6.24 the gradient was extracted and found to be \(-1.8 \times 10^5\).

This gives;

\[
\frac{\phi^2}{\beta} = \frac{1.8 \times 10^5}{6.83 \times 10^{-7}} \tag{6.3}
\]

Therefore;

\[
\beta = \frac{\phi^2}{2.64 \times 10^{-3}} \tag{6.4}
\]

or

\[
\phi = \left(2.64 \times 10^{-3} \beta\right)^{\frac{1}{3}} \tag{6.5}
\]
If it is assumed that the emitting structure is perfectly flat, then it will have a $\beta$ of 1, which gives a work function of 0.19 meV which is electronically too small. If it were assumed that the work function was 5 eV, then the enhancement factor, $\beta$, would be 4200, which is unrealistic as it would imply the local field around the nanofibre structures is 4200 times the applied field, which even at threshold of 5 V $\mu$m$^{-1}$, would imply 21 kV $\mu$m$^{-1}$.

It now needs to be realised from where the emission could be coming. Looking at Fig’s. 6.14 to 6.18 there are four possibilities:

1. Predominately, it would be from the amorphous carbon film surrounding the structures,
2. Emission from the nano fibre structures,
3. A combination of emission from amorphous carbon and nano fibres,
4. There could be a contribution of effects of the junction between the nano fibres, amorphous carbon and the vacuum, analogous of triple junction effects of sp$^2$, sp$^3$ and vacuum of diamond films.

However, as stated previously, the threshold voltage, i.e. the field required to raise the emission current to 1 nA was seen to be 5 V $\mu$m$^{-1}$. If the emission were to be predominately from the amorphous carbon, this threshold field would have been seen to be significantly higher, around 20 V $\mu$m$^{-1}$. Therefore, the emission is most likely to be from the nanofibre structures.

Some caution must be exercised in the FN analysis of the I – E characteristics of Fig. 6.21 since there will be a distribution of field enhancement factors due to the different local work functions, a distribution in nanofibre lengths, radii, and screening due to proximity effects. In addition, a large value of enhancement factor can be inferred in the presence of a shallow I – E characteristic due to a bulk transport limited emission behavior [5]. In this case, despite the apparent linearity of the FN plot, the presence of a bulk limited transport emission process complicates the use of the Fowler-Nordheim analysis.

The possibility of bulk limited conduction was not considered in the original formulation of the Fowler-Nordheim theory of emission from metals due to the high conductivity of the cathode. From Fig. 6.18, we can estimate the radius of curvature, $r$, of the emitter to be about 100 nm and from an enhancement factor of approximately 4200, would suggest an emitting structure of height $h$, 420 $\mu$m based upon the well known approximation of $\beta = h/r$. Such an
emitter structure is not observed in Fig. 6.16, where, an upper emitter length of 25 μm can be seen giving rise to an enhancement factor of 250.

We are able to eliminate space charge limited current (SCLC) effects since the magnitude of the emission current is only $6 \times 10^{-7}$ A. Furthermore, in the high current regime the current is observed, as shown in Fig. 6.25, to follow a power law dependence on voltage (field), $I \propto V^n$, with $n=3.0$. If the emission were to follow a SCLC model, $n$ would ideally be 1.5.

![Log V vs. Log I](image)

**Fig. 6.25.** The fit in the high current regime to the $I-V$ characteristic of Fig. 6.21 assuming $I \propto V^n$ with $n=3.0$.

While a high value of $n=2.5$ was reported for the saturated current density by Rupesinghe et al. [6] and attributed to electron beam interaction from neighboring emitters and hence the onset of a space charge saturation, the level of current in that study was much larger than that observed here. The value of $n$ found in the present study is also significantly different from $n=1.5$ or $n=2$ corresponding to a SCLC in either vacuum or in a thin film semiconductor. [7] We believe that the electron emission from the structure at the low applied field was primarily from the nanofibre structures as the surrounding amorphous carbon film has a much higher threshold field of approximately 20 Vμm$^{-1}$. It is also possible that the nano-scale dielectric inhomogeneities present close to the carbon nanofibres could help to increase the observed enhancement factor [8]. A distribution of enhancement factor Fig. 6.26 can be plotted.
6.4 Field emission properties of carbon nanotube-polymer composites

6.4.1 Introduction

Carbon nanotubes were mixed into a conjugated polymer in the hope that the resultant solution could be spin coated onto a range of substrate materials over a large area for field emission devices.

This section deals with field emission characterisation, where a phosphor screen is used as an anode with a CCD camera utilised to capture the emission images. A range of CNT to polymer concentrations were tested for field emission properties. Analysis of the emission characteristics lead us to believe that the primary emission mechanism is by Fowler-Nordheim tunnelling, however, the transport of electrons through the material is shown to be a limiting factor in the total emission current that can be sourced via these cathodes.

6.4.2 Sample preparation

Samples were prepared at Trinity College Dublin as described in detail elsewhere [9]. In summary, 200 mg of poly(p-phenylenevinylene-co-2,5-dioctyloxy-m-phenylenevinylene)
(PmPV) was dissolved in 10 mL Toluene (20 g/L solution) and 50 mg of arc deposited multi walled carbon nanotube (MWNT) added. The solution was ultra sonically treated with a tip for 2 minutes and left in an ultra sonic bath for 2 hours.

The solution was spun onto 60 nm thick gold on 1 inch square glass substrates at 1000 rpm for 1 minute to achieve a 100 nm thick polymer layer. Five samples were prepared in this way and labelled A-E, together with a 0% CNT concentration sample as a control. The first sample is approximately 6-8 % MWNT, with subsequent samples halved by diluting the first samples solution in equal amount of PmPV. Sample characteristics are listed in Table 6.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% MWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6-8</td>
</tr>
<tr>
<td>B</td>
<td>3-4</td>
</tr>
<tr>
<td>C</td>
<td>1.5-2</td>
</tr>
<tr>
<td>D</td>
<td>0.75-1</td>
</tr>
<tr>
<td>E</td>
<td>0.375-0.5</td>
</tr>
<tr>
<td>PmPV</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6.2. Samples and the concentration of CNT in a PmPV solution.

6.4.3 Field Emission

Electron field emission I-V characteristics performed with a planar phosphor-on-ITO glass anode with a 100 micron PTFE insulator, with a 3 mm radius hole cut in, between the anode and sample. The anode voltage was ramped from 0 to 3000 V in 25 V steps by a computer program. An emission current limit of 10,000 nA was also employed to ensure minimal damage to the samples due to current heating.

Image capturing of the emissive area was performed in the same system with a 2.5" CCD camera focussed on the emission area and connected with image grabbing software. The anode voltage was ramped manually in 250 V steps until emission is seen by an illuminated phosphor screen, then the first image recorded. The voltage was increased manually in 250 V steps and subsequent images were taken until either saturation was observed or a maximum of 4500 V was reached in order to protect both sample and phosphor.
Figures 6.27 and 6.28 show the emission current, \( I \) (A), versus applied field, \( E \) (V\( \mu \)m\(^{-1}\)), for samples A to E together with the 0% CNT concentration PmPV sample.

Fig. 6.27. Samples A (■), B (●) and C (▲), (6 - 8 %, 3 - 4 % and 1.5 - 2% CNT), emission current vs. applied field.

Fig. 6.28. Samples D (■), E (●) and PmPV (▲), (0.75 - 1%, 0.375 - 0.5% and 0% CNT), emission current vs. applied field.

A threshold field for an emission of 10 nA against CNT concentration is shown in Fig. 6.29. It can be seen that the threshold field decreases as the mass fraction of CNT increases.
Fig. 6.29. Threshold field for 10 nA emission vs. nanotube concentration. Fit is to a power law with exponent of -0.13

Image capturing was performed subsequent to I-E trends. A maximum applied voltage of 3500 V was applied. This value was chosen as it caused near full area emission from sample A, as it was assumed that the remaining samples would display poorer emission images than this, it enabled a comparison between samples to be made.

The acquired images are shown in Fig. 6.30, for samples A-E. It can easily be seen that sample A displays near full area emission, with subsequent samples displaying poorer illumination at the same applied voltage.

Fig. 6.30. Emission images for an applied voltage of 3500 V for samples A-E. Black circles indicate the emission area of 3mm radius.
In order to conduct a Fowler-Nordheim analysis, it was important to realise the voltage drop between the sample surface and the anode electrode. For this reason we were able to calculate the voltage drop through the sample at various emission currents. From this it was possible to extract the correct applied voltage for Fowler-Nordheim analysis.

6.4.4 Voltage through film

It can be said that the total voltage in the system, $V_{\text{total}}$, is a sum of the voltage through the vacuum, $V_1$, and the voltage through the sample, $V_2$, and that the emission current is equal to the sample current, $I_{\text{emission}} = I_{\text{sample}}$.

Kilbride et al [9] measured the conductivity of similar CNT polymer samples which were prepared using the same method as employed in this work. From their results which showed conductivity against CNT concentration we were able to extract values of conductivity for the five samples tested here. The conductivities of the samples Kilbride tested [9] were measured in the DC range between -0.15 and 0.15 V and the current in this instance is assumed to be Ohmic. The extracted values of conductivity from [9] for this chapter's samples are listed in Table 6.3. Such low values of conductivity ($10^{-2}$ Sm$^{-1}$ for 8% CNT) are in the range of 2 orders of magnitude smaller than expected for 100% CNT. The low value may reflect the presence of a thick polymer coating resulting in poor electrical connection between tubes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT mass fraction, $p_i$ (%)</th>
<th>$\sigma$ (Sm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6-8</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>B</td>
<td>3-4</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>C</td>
<td>1.5-2</td>
<td>$7 \times 10^{-6}$</td>
</tr>
<tr>
<td>D</td>
<td>0.75-1</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>E</td>
<td>0.375-0.5</td>
<td>$9 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 6.3. Conductivity's and mass fraction of polymer samples A to E.

As we know the conductivity for each sample, we can calculate the voltage drop across the sample,
\[ J = \sigma E \]  \hspace{1cm} (6.6).

\[ \frac{I}{A} = \sigma \frac{V}{d} \]  \hspace{1cm} (6.7).

\[ V = \frac{dl}{\alpha A} \]  \hspace{1cm} (6.8).

Where, \( J \) is current density (Am\(^{-2}\)), \( E \) is applied electric field (Vm\(^{-1}\)), \( A \) is emission area (=2.83x10\(^{-5}\) m\(^2\)) and \( d \) is anode to cathode separation (m) and taken as 100 \( \mu \)m. Table 6.4 shows the voltages through the polymer film for all tested samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (Sm(^{-1}))</th>
<th>Voltage drop (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3x10(^{-3})</td>
<td>1.18x10(^{-3})</td>
</tr>
<tr>
<td>B</td>
<td>1.5x10(^{-3})</td>
<td>2.36x10(^{-3})</td>
</tr>
<tr>
<td>C</td>
<td>7x10(^{-6})</td>
<td>5.50x10(^{-3})</td>
</tr>
<tr>
<td>D</td>
<td>3x10(^{-6})</td>
<td>1.18x10(^{-2})</td>
</tr>
<tr>
<td>E</td>
<td>9x10(^{-7})</td>
<td>3.93x10(^{-2})</td>
</tr>
</tbody>
</table>

Table 6.4. Calculations of the effective voltage drop through each polymer sample for a current of 10 nA.

It can be seen from Table 6.4 firstly that as the conductivity of the samples decreases, the voltage drop through the sample increases. This is to be expected due to Ohm's law; the lower the conductivity, the higher the resistance, therefore, the higher the potential drop. Fig. 6.31 shows the voltage drop using the method above, for all samples, and at 10\(^{8}\), 10\(^{7}\) and 10\(^{6}\) A emission current.
Fig. 6.31. Calculated voltages through polymer samples against CNT mass fraction for an emission current of $10^{-8}$ (■), $10^{-7}$ (●) and $10^{-6}$ (▲).

The highest voltage drop across the sample is seen in Fig. 6.31 to be for the lowest CNT concentration and highest emission current, calculated to be 3.93 V.

For a Fowler-Nordheim analysis we are interested in the voltage between the surface of the sample and the anode electrode. However, in our experimentation we are applying voltages up to a maximum of 3000 V, therefore, as the highest voltage through the sample was seen as 3.93 V which is approximately 0.1% of the applied voltage, and we can say that $V_{\text{sample}}$ is negligible in the subsequent Fowler Nordheim analysis.

Fig. 6.32. Fowler Nordheim analysis for samples A1 (■), B (●), C (▲), D (▼), E (◆). Red lines are linear fits to each data set.
The I-E trends shown in Fig. 6.27 and 6.28 (excluding the 0% CNT sample) were fitted using the Fowler Nordheim model (see Equation 6.1). The work function was assumed to be 5 eV. A plot of Ln(I/E^2) vs. 1/E is shown in Fig. 6.32.

The extracted enhancement factors for each sample were obtained from the Fowler-Nordheim analysis of Fig. 6.32 and are listed below in Table 6.5 with a work function of 5 eV assumed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fowler-Nordheim enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>395</td>
</tr>
<tr>
<td>B</td>
<td>392</td>
</tr>
<tr>
<td>C</td>
<td>349</td>
</tr>
<tr>
<td>D</td>
<td>334</td>
</tr>
<tr>
<td>E</td>
<td>330</td>
</tr>
</tbody>
</table>

Table 6.5. Extracted enhancement factors for samples A-E obtained by Fowler-Nordheim analysis.

The decrease in enhancement factor from 395 for sample A, to 330 for sample E, was expected as the threshold field, E_th, increases from sample A to E. Sample E thus requiring a larger voltage to reach its threshold current as its enhancement and therefore local field is lower than sample A.

Now that both the threshold field and enhancement factors are known, it is possible to calculate the local threshold field for 10 nA emission, F_th, calculated as \( \beta E_{th} \). Fig. 6.33 shows the variation of F_th with CNT loading, p.

![Fig. 6.33](image)

Fig. 6.33. Local threshold field, calculated by \( E_{th} \) times enhancement factor, vs. CNT mass fraction. Fit is to a power law with exponent -0.21.
It is apparent that the local threshold fields for the samples do not vary strongly with mass
fraction, with a typical local field of between 3.3 - 4.8 Vnm⁻¹. The lack of any significant
variation in the local fields for the samples indicates that similar emission conditions are
present in each sample at the PmPV/CNT/vacuum triple junction. This suggests that the
nanotubes in these films experience a similar electrostatic environment, which changes little
with loading. The local threshold field should be independent of nanotube loading, so the
small increase in $F_{th}$ as the nanotube loading decreases reflects the overall resistive nature of
the network. The observation of a power law dependence of both $E_{th}$ and $F_{th}$ can be attributed
to percolation transport through the films and the need to tunnel through the potential barrier
at the front surface.

6.4.5 Percolation analysis

It has been suggested previously [9] that the charge transport in similar CNT polymer samples
are controlled by fluctuation induced tunnelling, and that conductivity through the samples
follow a percolation behaviour.

The lowest filler (CNT in this case) concentration needed for macroscopic conductive
increase, or a formation of an electrical pathway through the sample, is described by the
percolation threshold. It has been seen in the literature that the percolation threshold can be as
low as 0.035% [10].

It has been shown previously, both experimentally and theoretically that the percolation
threshold decreases significantly as the aspect ratio of the CNT increases [11]. This suggests
that the high aspect ratio and local conductivity of CNT make them ideal candidates for fillers
in percolation systems.

According to classical percolation theory, the conductivity of a composite material as the
conductive filler is increased can be expressed by a scaling law,

\[ \sigma \propto (p - p_c)^t \]  \hspace{1cm} (6.9).

Where, $\sigma$ is the conductivity (Sm⁻¹), $p$ is the filler concentration by mass, (%), $p_c$ is the
percolation threshold, (%), and $t$ is an exponent. Equation 6.9 is only valid when ($p>p_c$) and
($p-p_c$) is small.
Fig. 6.34. Conductivity vs. CNT mass fraction. Fit is from Eq. 6.9.

Fig. 6.34 shows the conductivity of all samples. The fit is from Eq. 6.9 values of 0.055 and 1.36 were found for \( p_c \) and \( t \) respectively. These values were calculated by small incremental changes until the best linear fit to the data in Fig. 6.35 was found.

Fig. 6.35. Logarithmic plot of the conductivity vs. mass fraction reduced by the percolation threshold. Linear fit is to Eq. 6.9. and gives 0.055 and 1.36 for \( p_c \) and \( t \) respectively.

A characteristic of fluctuation induced tunneling, (FIT), is that the log of conductivity within the film should vary as \( p^{1/3} \) [9]. In general, whilst it is not possible to assign a field emission ‘conductivity’, if the limiting step for emission is the transport through the film, with emission determined largely by a constant enhancement factor, then \( F_{th} \) should reflect the transport through the film and exhibit a \( p^{1/3} \) dependence. Figure 6.36 clearly demonstrates such a linear variation of the natural logarithm of local threshold field with \( p^{1/3} \).
Fig. 6.36. \( \ln F_0 \) vs. CNT mass fraction, \( p^{1/3} \). Linear relationship indicates fluctuation induced tunnelling, (FIT).

The fit, using Eq. 6.9, to Fig. 6.36 suggests that this plot is indicative of fluctuation induced tunnelling, which is supported by a linear fit of \( (\ln \sigma) \) as a function of \( -p^{1/3} \), suggesting that conductivity is limited by tunnelling through potential barriers between conduction regions.

In this regard, it is possible to explain the electron emission mechanism for CNT-PmPV composites as follows: emission of the electrons from the surface at the nanotube/polymer/vacuum triple junction occurs due to an enhancement of the applied field brought about by the aspect ratio of the nanotube, each of which will have a thin polymer coating. This enhancement factor does not have a strong variation with loading. As the mass fraction of nanotubes increases, a greater density of nanotube-nanotube contacts is made, increasing the overall charge transport of carriers via fluctuation induced tunneling through the tunnel barriers, which result from the polymer coating around each nanotube. Replenishment of the electrons occurring by a percolation controlled charge transport through the disordered nanotube network. Recent studies also suggest that an ability to adjust the nanotube-nanotube interaction may also allow for lower percolation thresholds [12].

6.5 Summary

For field emission from room temperature grown carbon nanofibres, Ni films were subject to an Ar plasma by PECVD and the catalysation of the films by film roughening was seen by
SEM investigation. This catalysation led to the growth of carbon nanofibres by the decomposition of CH$_4$ gas in an rf plasma at 400 W. All experiments were carried out at room temperature, enabling glass substrates to be used.

Field emission testing showed the grown structures had excellent emission characteristics with a low threshold field of 5 V/µm$^1$. Subsequent field emission tests at different locations on the substrate concluded that the initial emission was indeed from the nanofibres rather than the surrounding amorphous carbon which was co-deposited. Further analysis showed that the structures followed the Fowler-Nordheim emission theory and an enhancement factor of between 3000 – 4200 was extracted when work functions of 4 – 5 eV were assumed.

Carbon nanotube polymer composites were examined for their field emission performance. The observations presented in this results section provide insight into the conduction process occurring in the CNT polymer samples tested. A more general conclusion from this work however is that a straight line FN plot of I–V data obtained from these CNT polymer samples does not guarantee that the electron emission process is cold emission.

It has also been seen in this analysis firstly that the CNT-PmPv samples examined follow a percolation law, where the conductance through the sample is dependant on a channel of conduction regions (CNT) and secondly that the samples resistance, when incorporated into the Fowler-Nordheim equation shows that as the resistance is increased from 0 Ω, the emission current falls and saturates. The resistance of the sample is therefore limiting the maximum emission current, and as resistance is the inverse of conductance, and conductance is determined by the flow of electrons through conduction regions in the sample. This is further evidence that CNT-polymer composites field emission performance is limited by a percolation law of conduction.

Finally, it is worth noting that in this chapter, low mass fractions of multiwall nanotubes in spin cast composites were used. In previous studies of electron emission from nanotube polymer composites, considerably higher nanotube concentrations were used. In the study of Alexandrou et al turn-on fields of 3 V/µm$^1$ were reported [13] but from a sample consisting of up to 33 wt. % of single wall nanotubes embedded in to poly(3-octylthiophene), (P3OT). Since single wall nanotubes are expensive to produce, the use of MWNTs at low mass fractions offers the opportunity to reduce cost. Whilst it might be tempting to reduce the value of $E_a$, even further by increasing the nanotube concentration, screening effects occur which effectively render some of the nanotubes redundant. Spin casting allows much large area cathodes to be potentially produced.
6.6 References


CHAPTER SEVEN

Conclusions

The work in this thesis has studied critically the field emission properties of carbon tip based emitters. Particular attention was paid to the geometric enhancement factor, by which, the emitter structure can be altered and increase the local electric field at the apex of its tip. This enhancement means that effective electron emission can be obtained at lower applied electric fields at the anode than from a flat emitter. The application of a third, gate contact in close proximity to the tip of the emitter means that high local gate to tip fields can be achieved at relatively low (<25 V) gate voltages, allowing the possibility of logic switching of individual sites. Further investigation into the field emission properties of tip based emitters was conducted over large area. Firstly, carbon nanofibres were grown at room temperature and examined for their field emission properties, and secondly, a CNT-polymer composite was examined. The benefit of these last two structures is that it opens up the possibility of depositing them over large areas for possible applications in next generation flat panel displays.

7.1 Single emitters

The study of the field emission properties of single emitters first looked at a theoretical simulation of the way in which the emitter alters the applied electric field at its tip by means of a geometric enhancement factor.

It was found that if when calculating the applied electric field, if the distance is taken as the anode to cathode separation, D, minus the emitter height, H, rather than the widely used D, then the enhancement factor is seen to decrease as the anode electrode is brought towards the
tip of the emitter. Whilst this is in contradiction to previous works, the emitter and anode could be assumed to approximate a parallel plate configuration as the anode it brought close to it. In this case, the enhancement factor would decrease as the emitter starts to lose its inherent geometric effect on the field. It was also noticed that as the anode is greater than three times the height of the emitter away (3h), the enhancement appears not to change. It was found that at separations of <3h the enhancement is dependant on h, r and D (being height and radius of the emitter, and anode to emitter gap respectively). At separations >3h, the enhancement is dependant on h and r alone.

Further proof for this theory was found when an isolated carbon nanoropes with seven randomly arranged CNT was examined for its field emission properties in a modified SEM. Micro manipulators allowed accurate positioning of the anode. It was seen that as the anode approaches the emitter, the threshold field increases, an effect of a decreasing enhancement. Also, a single, isolated CNT was tested in the same manner. Again, as the anode approaches the tip, threshold field increases. Also, enhancement factors derived from the Fowler-Nordheim theory showed a decrease as the anode approaches the tip. Enhancement was also seen to saturate at high D as seen in the simulation results.

The method in which the carbon nanoropes and isolated CNT were tested also allowed a gate contact to be brought close to the CNT tip. It was found that at a gate to CNT tip distance of 1 μm, gate voltages of between 0 and 25 V decreased the anode field for an emission of 1 μA.

The way in which we define applied field to explore the enhancement factor and threshold fields of individual emitters, coupled with the technique of positioning anode and gate contacts accurately within an SEM should enable a better understanding into the field emission properties of tip based emitter structures.

7.2 Large area emitters

Whilst Chapters 4 and 5 examined the field emission performance of single emitters, we were interested in the possibility of depositing an emitting material over a large area for the possible use as electron sources in next generation flat panel displays.

One limit on the fabrication process industrially is that CNT and CNF (carbon nanofibres) until recently had to be deposited at temperatures exceeding 700°C. This meant difficult fabrication conditions, and limits on the substrate material. In Chapter 6 we show the growth
of CNF on glass slides, at room temperature. The field emission properties of these structures boasted a low threshold field of 5 V μm⁻¹, which is comparable to that of CNT structures grown at higher temperatures. The process, and field emission characteristics also proved to be repeatable.

The second structures examined in this section were that of CNT-polymer composites. The CNT-polymer solution was spun onto gold coated glass substrates, making large area deposition a possibility. The field emission characteristics were examined using a flat phosphor anode and images were captured illustrating the uniformity of the as spun films. It was also found that the conductivity, and therefore emission performance, of the samples was controlled by percolation limited fluctuation induced tunnelling. This, in turn, suggested that conductivity is limited by tunnelling through potential barriers between conduction regions.

7.3 Future work

There are a number of possible suggestions to extend the work seen in this thesis. This section is intended to give an overview of the possible areas in which one could carry on the research. As in the results chapters, we look firstly at single emitters, then large area emitters.

7.3.1 Single emitters

Possible suggestions for furthering this area of research could be:

- To extend the simulation work, utilising a three dimensional package that would enable us to compare the results of enhancement factor in this work, with that of the enhancement from a three dimensional CNT. Whilst the analysis performed on the two dimensional CNT profile is valid for this work, and for understanding the field emission properties of a single emitter, it would be useful to adapt this for three dimensional arrays of emitters.

- To gain further understanding of the geometric field enhancement factor for tip based emitters. This phenomenon, whilst studied in depth in this work, is still not fully understood. A relationship of emitter height, radius, and now, anode location as reported here, should be able to give rise to a universal equation for enhancement.
• Chapter five, experimental field emission from single tip based emitters, could be extended by the use of the experimental setup. The in-situ field emission within a SEM, coupled with the ability to move two probes independently, has proved invaluable during this work. For this reason I feel it is the setup which could be utilised in other experimentation. Possible suggestions are: using planer anodes, using different gate electrode structures (for example, size and shape of gate aperture).

• Once the most effective gate dimensions and location to emitter/group of emitters has been found by the above method by studying threshold fields, effect of gate bias, maximum emission current, maximum current density, and minimising the gate screening factor, a solid state device could be fabricated for use in a prototype passively addressed field emission display.

• The experimental procedure in finding the most effective gated emitter structure should be tied in with simulation work.

7.3.2 Large area emitters

• In order to sell the idea of room temperature grown carbon nanofibres as possible electron sources for field emission displays, efficient growth on plastic substrates could be advantageous in terms of manufacturing costs.

• Further work in understanding the growth mechanism, together with aligned CNF growth and subsequent field emission testing should be undertaken.

• It should be seen if the method in which the CNF were grown, could give rise to the growth of carbon nanotubes.

• As seen in the literature review, it should be possible to remove the amorphous carbon which is co-deposited with the CNF by means of introducing an ammonia content to the growth plasma.

• The CNT – polymer samples should be investigated further for their field emission properties. Lifetime could be an issue due to the delicate nature of the polymer. However, these structures, due to their self limiting properties (as explained by the
percolation limited charge transport in the results) and ability to be spin coated over large areas, opens the possibility for their use as large area electron sources for possible applications in field emission displays.

### 7.3.3 Field emission displays

The properties of single and arrays of tip based emitters have been explored in depth in this thesis. Investigation of the electric field enhancement factor, coupled with the ability to examine many three terminal device scenarios by means of in-situ field emission within a SEM, and, the deposition of arrays of emitters over a large area opens the possibility that these two distinct pieces of work can be joined to produce field emission devices.

Field emission displays, lighting, vacuum fluorescent devices and vacuum microelectronics are just a few possibilities that could be explored by extending various pieces of work from this thesis. For example, an effective gate configuration, i.e. minimising gate screening and maximising efficiency, could be employed to the CNT–polymer samples.
APPENDIX

Field enhancement factor of a hemisphere in 2D

Using cylindrical symmetry:

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial V}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 V}{\partial \theta^2} = 0$$

Assume that,

$$V(r, \theta) = R(r)S(\theta)$$

$$\Rightarrow \quad \frac{1}{r} S \frac{d}{dr} \left( r \frac{dR}{dr} \right) + \frac{1}{r^2} R \frac{d^2 S}{d\theta^2} = 0$$

$$\Rightarrow \quad \frac{r}{R} \frac{d}{dr} \left( r \frac{dR}{dr} \right) + \frac{1}{S} \frac{d^2 S}{d\theta^2} = 0$$

$$\Rightarrow \quad c_1 = \frac{r}{R} \frac{d}{dr} \left( r \frac{dR}{dr} \right)$$

And,

$$c_2 = \frac{1}{S} \frac{d^2 S}{d\theta^2}$$

$$c_1 = -c_2$$

Require $c_2$ to be negative to ensure that the exponentials for $S$ which must return to original value after a $2\pi$ rotation.
\[ c_2 = -k^2 \]

\[ \Rightarrow \quad \frac{d^2 S}{d\theta^2} = -k^2 S \]

\[ \Rightarrow \quad S = A\cos k\theta + B\sin k\theta \]

Since \( S(\theta + 2\pi) = S(\theta) \), \( k \) must be an integer

\[ \Rightarrow \quad r \frac{d}{dr} \left( r \frac{dR}{dr} \right) = c_1 R, \text{ since } c_1 = -c_2 = k^2 \]

\[ \Rightarrow \quad r \frac{d}{dr} \left( r \frac{dR}{dr} \right) = -k^2 R \]

Which can be solved by \( R = r^n \)

\[ \frac{dR}{dr} = nr^{n-1} \]

\[ \frac{d^2 R}{dr^2} = n(n-1)r^{n-2} \]

\[ r \frac{d}{dr} \left( r \frac{dR}{dr} \right) = r \left[ r \frac{d^2 R}{dr^2} + \frac{dR}{dr} \right] - k^2 R = 0 \]

\[ \Rightarrow \quad r^2 \frac{d^2 R}{dr^2} + r \frac{dR}{dr} - k^2 R = 0 \]

\[ \Rightarrow \quad r^2 n(n-1)r^{n-2} + nr^{n-1} - k^2 r^n = 0 \]

\[ r^n \left[ n^2 - n + n - k^2 \right] = 0 \]

\[ \Rightarrow \quad n^2 = k^2 \]

\[ \therefore \quad n = \pm k \]

In general:

\[ R(r) = \left( r^k + Dr^{-k} \right) \]

But problems arise with the case of \( k=0 \)
$R = \text{constant. There is one solution to a second order one dimensional function.}$

Therefore, $k = 0$ is treated separately.

One solution is a constant for $k = 0$

\[
\frac{d}{dr} \left( r \frac{dR}{dr} \right) = 0
\]

\[\Rightarrow \quad r \frac{dR}{dr} = c
\]

\[\Rightarrow \quad \frac{dR}{dr} = \frac{c}{r}
\]

\[\Rightarrow \quad R = c \ln r + D
\]

For the case of $k = 0, S = A$

\[
\frac{d^2 S}{d\theta^2} = 0
\]

\[\Rightarrow \quad \frac{dS}{d\theta} = b
\]

\[\therefore \quad b\theta + A = S
\]

\[V(r, \theta) = a_0 + b_0 \ln r + \sum_{k=1}^{\infty} \left[ r^k (a_k \cos k\theta + b_k \sin k\theta) \right] + \left[ r^{-k} (c_k \cos k\theta + d_k \sin k\theta) \right]
\]

For a semicircle $(r, \theta)$

\[V(R, \theta) = 0
\]

\[V(r, \theta)
\]

\[\nabla V(r, \theta) \rightarrow -E_0 r \cos \theta
\]
\[ V(R, \theta) = a_0 + b_0 \ln R + \left[ R^1 \left( a_1 \cos \theta + b_1 \sin \theta \right) \right] + \left[ \frac{1}{R} \left( c_1 \cos \theta + d_1 \sin \theta \right) \right] \\
+ \left[ R^2 \left( a_2 \cos 2\theta + b_2 \sin 2\theta \right) \right] + \left[ \frac{1}{R^2} \left( c_2 \cos 2\theta + d_2 \sin 2\theta \right) \right] \\
+ \left[ R^3 \left( a_3 \cos 3\theta + b_3 \sin 3\theta \right) \right] + \left[ \frac{1}{R^3} \left( c_3 \cos 3\theta + d_3 \sin 3\theta \right) \right] + \ldots \]

\[ V(R, \theta) = a_0 + b_0 \ln R + \cos \theta \left[ a_1 R + \frac{c_1}{R} \right] + \sin \theta \left[ b_1 R + \frac{d_1}{R} \right] \\
+ \cos 2\theta \left[ a_2 R^2 + \frac{c_2}{R^2} \right] + \sin 2\theta \left[ b_2 R^2 + \frac{d_2}{R^2} \right] \\
+ \cos 3\theta \left[ a_3 R^3 + \frac{c_3}{R^3} \right] + \sin 3\theta \left[ b_3 R^3 + \frac{d_3}{R^3} \right] + \ldots \]

\[ \therefore \quad a_0 = 0, \quad b_0 = 0, \quad a_1 R + \frac{c_1}{R} = 0 \]

\[ \Rightarrow \quad c_1 = -a_1 R^2 \]

\[ b_1 R + \frac{d_1}{R} = 0 \]

\[ \Rightarrow \quad d_1 = -b_1 R^2 \]

\[ a_2 R^2 + \frac{c_2}{R^2} = 0 \quad \Rightarrow \quad c_2 = -a_2 R^4 \]

\[ b_2 R^2 + \frac{d_2}{R^2} = 0 \quad \Rightarrow \quad d_2 = -b_2 R^4 \]

\[ a_3 R^3 + \frac{c_3}{R^3} = 0 \quad \Rightarrow \quad c_3 = -a_3 R^6 \]

\[ b_3 R^3 + \frac{d_3}{R^3} = 0 \quad \Rightarrow \quad d_3 = -b_3 R^6 \]

\[ \therefore \quad c_k = -a_k R^{2k} \]

\[ d_k = -b_k R^{2k} \]
From $V(r, \theta) \rightarrow -E_0 r \cos \theta$

Therefore the only term involving $\cos \theta$ is:

$$r(a_1 \cos \theta + b_1 \sin \theta) + \frac{1}{r}(c_1 \cos \theta + d_1 \sin \theta) = -E_0 r \cos \theta$$

All other $c_k, d_k, a_k, b_k = 0$ for $(k = 1)$

$$\cos \theta(a_1 r) + \frac{c_1}{r} = -E_0 r \cos \theta$$

$$\Rightarrow \quad a_1 = -E_0$$

$$a_1 r - \frac{a_1 R^2}{r} = -E_0 r$$

$$\Rightarrow \quad c_1 = -a_1 R^2$$

$$= E_0 R^2$$

$$V(r, \theta) = ra_1 \cos \theta + \frac{1}{r} c_1 \cos \theta$$

$$= -E_0 \left( r - \frac{E_0 R^2}{r} \right) \cos \theta$$

$$V(r, \theta) = -E_0 \left( r - \frac{R^2}{r} \right) \cos \theta$$

To check,

When $r = R$, 

$$V(r, \theta) = -E_0 \left( R - \frac{R^2}{R} \right) \cos \theta = 0$$

Correct

When $r \gg R$, 
\[ V(r, \theta) = -E_0 \left( r - \frac{R^2}{r} \right) \cos \theta \]

\[ = -E_0 r \cos \theta \]

Correct

\[ V(r, \theta) = -E_0 \left( r - \frac{R^2}{r} \right) \cos \theta \]

\[ E = -\frac{\partial V}{\partial r} = E_0 \left( 1 + \frac{R^2}{r^3} \right) \cos \theta \]

When \( r = R, \frac{R^2}{r^3} = 1 \)

\[ \therefore \quad E_{r=R} = 2E_0 \cos \theta \]

\[ \therefore \quad \beta = 2 \]

Field enhancement factor of a hemisphere in 3D

Laplace equation in spherical coordinates:

\[ \nabla^2 V = \frac{1}{r^2 \frac{\partial}{\partial r}} \left( r^2 \frac{\partial V}{\partial r} \right) + \frac{1}{r^2 \sin \theta \frac{\partial}{\partial \theta}} \left( \sin \theta \frac{\partial V}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta \frac{\partial^2 V}{\partial \phi^2}} \]

Set

\[ \nabla^2 V = 0 \]

Express \( \nabla^2 \) in polar coordinates

\( V \) depends on \((r, \theta, \phi)\) when expressed in polar coordinates
But due to a hemisphere \( V(r, \theta) \)

\[
V(r, \theta) = \sum_{l=0}^{\infty} \left( A_l r^2 + B_l \frac{1}{r^{l+1}} \right) P_l(\cos \theta)
\]

Where \( P_l(\cos \theta) \) is an associated Legendre polynomial.

The boundary conditions set to the hemisphere are:

\( V(r = R) = 0 \) potential at the surface is 0

\( V(r) |_{R} = -E_0 z \)

Aside, define electric field:

\[
E = \frac{V}{D} = -\nabla V = -\frac{dV}{dz}
\]

\[
\therefore V = -\int dE dz = -E_0 z
\]
First boundary condition,

\[ r = R, \]
\[ V = 0 \]

\[ V(R, \theta) = \sum_{i=0}^{\infty} \left( A_i R^i + B_i \frac{1}{R^{i+1}} \right) P_i \cos \theta \]

Which is 0 for all values of \( i \).

Since \( P_i \cos \theta \) cannot be 0.

\[ A_i R^i = -B_i \frac{1}{R^{i+1}} \]

\[ B_i = -A_i R^{2i+1} \]

\[ V(R, \theta) = \sum_{i=0}^{\infty} \left( A_i r^i + B_i \frac{1}{r^{i+1}} \right) P_i (\cos \theta) \]

\[ = \sum_{i=0}^{\infty} \left( A_i r^i - A_i R^{2i+1} \frac{1}{r^{i+1}} \right) P_i (\cos \theta) \]

\[ = \sum_{i=0}^{\infty} A_i \left[ r^i - \frac{R^{2i+1}}{r^{i+1}} \right] P_i (\cos \theta) \]

Second boundary condition

\[ r^{\prime\prime} \right) R \]
\[ V(r, \theta) = -E_0 z \]
\[ = -E_0 r \cos \theta \]

When \( r \gg R \)

\[ V(r, \theta) = \sum A_i [r' - 0] P_i(\cos \theta) \]
\[ = -E_0 r \cos \theta \]

\[ = \sum A_i r' P_i \cos \theta \]
\[ = -E_0 r \cos \theta \]

\[ = A_0 r^0 P_0 + A_1 r^1 P_1 + A_2 r^2 P_2 + A_3 r^3 P_3 + \ldots \]

Using coefficients from above of \( r^0 \)

\[ A_0 P_0 = 0, \text{ but } P_0 \neq 0, \therefore A_0 = 0 \]

\[ A_1 P_1 = -E_0 \cos \theta \]

But \( P_1 \cos \theta = \cos \theta \)

\[ A_1 \cos \theta = -E_0 \cos \theta \]

\[ \therefore A_1 = -E_0 \]


\[ \therefore \text{All values of } A = 0 \text{ except } A_i \]

Using

\[ V(r, \theta) = \sum A_i \left( r^l - \frac{R^{2l+1}}{r^{l+1}} \right) P_l \cos \theta \]

\( l = 1 \) and \( A_1 = -E_0 \)

\[ V(r, \theta) = A_1 \left( r^1 - \frac{R^3}{r^2} \right) P_1 \cos \theta \]

\[ = -E_0 \left( r - \frac{R^3}{r^2} \right) P_1 \cos \theta \]

\((P_1 \cos \theta = \cos \theta)\)

\[ V(r, \theta) = -E_0 \left( r - \frac{R^3}{r^2} \right) \cos \theta \]

To check,

When \( r = R \),

\[ V = -E_0 (r - r) \cos \theta \]

\[ = 0 \]

Correct

When \( r \gg R \),
\[ V = -E_0 (r - 0) \cos \theta \]
\[ = -E_0 r \cos \theta \]
Correct

\[ E(r, \theta) = \frac{\partial V}{\partial r} \]
\[ = E_0 \left( 1 + \frac{2R^3}{r^3} \right) \cos \theta \]

At surface,

\[ E(r = R, \theta) = 3E_0 \cos \theta \]

Maximum when

\[ \cos \theta = 1 \]
\[ \theta = 0 \]

Max field = 3E₀, field = E₀

\[ \therefore \beta = 3 \]