Multiwall Carbon Nanotube Inks as Electron Field Emitters

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This thesis is dedicated to the memory of the chemist; John Escritt, former director of the Sports Turf Research Institute and an inspirational Great-Uncle.
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Abstract

The work presented in this thesis is concerned with pure, water-soluble multiwall carbon nanotube inks, in particular their use in the fabrication of inexpensive field emission (FE) cathodes. This work is divided into three parts. Firstly, with the aim of fabricating a transparent FE cathode, nanotube inks are spin-coated onto transparent substrates, which subsequently are subject to laser treatment. An improvement in the FE properties with increasing laser fluence is observed, resulting in threshold fields of less than 6 V/µm (glass substrates) and less than 0.5 V/µm (plastic substrates).

Secondly, with the aim of tailoring the geometric enhancement factor to improve the FE properties, nanotube inks are deposited onto paper substrates of varying surface morphology, via dip-coating. The FE properties are found to dramatically improve with increasing surface roughness of the paper, and a threshold field of less than 1 V/µm is achieved. Additionally, laser treatment is used to improve the threshold field. A 3-terminal device is fabricated with nanotube ink on paper substrates, operating with a gate voltage of 60 V and an anode voltage of 400 V.

Finally, the effect that the work function has upon the FE properties of nanotube ink is investigated. An improvement in the threshold field from 0.42 to 0.25 V/µm is observed after lithium functionalisation was used to reduce the work function from 5.1 eV to 4.5 eV. Additionally, staircase-like current-field characteristics are observed for carboxylic-functionalised carbon fibres and these effects are discussed in terms of resonant tunnelling.
Acknowledgements

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Stephen Lyth

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Publications


Presentations


List of Acronyms and Symbols

\[ \beta = \text{total enhancement factor} \]
\[ \phi = \text{work function} \]
AFM = atomic force microscope
CNT = carbon nanotube
CRT = cathode ray tube
CVD = chemical vapour deposition
E = applied electric field
\( E_F \) = Fermi level
\( E_{th} \) = threshold field
\( E_{vac} \) = vacuum energy level
FE = field emission
FED = field emission display
HPLC = high pressure liquid chromatography
\( i \) = current
ITO = indium tin oxide
LCD = liquid crystal display
Li\(^+\)MWNT = lithium functionalised multiwall carbon nanotube
LiOH = lithium hydroxide
MWNT = multiwall carbon nanotube
\( \sigma \)-MWNT = acid oxidised multiwall carbon nanotube
NDR = negative differential resistance
PDP = plasma display panel
QW = quantum well
\( R_A \) = surface roughness
rpm = revolutions per minute
sccm = standard cubic centimetres per minute
SEM = scanning electron microscope
SWNT = single wall carbon nanotube
TEM = transmission electron microscopy
UV = ultraviolet
WF = work function
Chapter 1: Introduction

1.1 Motivation

The display industry has blossomed over the past decade, with the advent of affordable flat screen televisions, flat panel computer monitors, mobile phone displays and giant outdoor screens on advertisement hoardings. With huge potential markets, the pursuit of replacement technologies (or even niche technologies) is very big business. The battle to produce more energy efficient, brighter, cheaper displays is well funded and widely discussed with innovations such as flexible, transparent and printable devices making headway. Field emission displays (FEDs) may be able to provide one solution to the growing demand for high performance displays.

Carbon nanotubes (CNTs) have already found uses in a wide variety of applications, with many more expected in the future. A vast, international body of work has been published on their application as cold cathodes in FEDs.\textsuperscript{1-4} Their stability, high conductivity, small diameter and extended length make them excellent electron sources when placed in a large electric field. A great number of papers have been published on CNT field emitters fabricated via traditional, high cost, energy intensive techniques.\textsuperscript{5-8} Fewer papers have been published on printed FE cathodes using CNTs. Printing CNTs provides a versatile, low cost, room temperature, simple route for the fabrication FEDs on a wide variety of substrates.

The full potential of pure CNT inks has yet to be realised. At present, CNT inks are understudied and as a result are an under-used material. More research is required in studying their FE properties; for example their use as transparent field emitters, the effect of substrate material, morphology and laser treatment. No research has been carried out exploring work function changes via chemical functionalisation as a route to improve the FE properties of CNTs. This report will address some of these issues.

Global warming is spurring governments, organisations and individuals to reduce their ‘carbon footprint’. In this modern, technological era, it is more important than ever to establish and utilise industrial processes that are efficient in time, energy and materials. This work has been undertaken with energy efficiency as a driving
force and inspiration, and care has been taken to avoid resorting to using complex lithography steps, high temperature processes, high vacuum conditions, and silicon processing.

In this chapter, the key objectives of the report will be outlined. There will be an introduction to the structure, properties and fabrication methods of CNTs. The physics of FE and how to tailor the FE current density will be discussed. Various examples of printed CNT FEDs will be highlighted.

1.2 Objectives

There are several objectives of the current thesis. The first is to explore the possibilities and potential of using CNT ink as a FE cathode material, and to fabricate low cost, simple electron emitters. Secondly, transparent cathodes will be explored. Thirdly, the role that the substrate morphology plays in FE from CNT ink on paper substrates will be examined. Finally, tailoring the work function of CNT inks by simple surface chemical reactions will be explored as a route to improving FE characteristics.

General objectives that will run throughout the work are; to fabricate FE cathodes with threshold fields that are as low as possible (ideally of the order 1 V/µm); to fabricate FE cathodes with high current density (at least 1 mA/cm²) to produce cathodes using simple, scalable techniques with a low carbon footprint; to use the parameters in the Fowler-Nordheim equation (such as geometric field enhancement factor and work function) to improve the emission characteristics; and to fabricate devices using the FE cathodes that have been investigated.
1.3 Electron Field Emission

1.3.1 Introduction

In 1897 whilst experimenting with cathode rays between two very closely spaced spherical platinum electrodes, Robert Wood observed what he described as 'a new form of cathode discharge'. This was the first known observance of the phenomenon known as electron field emission - a quantum tunnelling effect recorded thirty-one years before the advent of quantum mechanics proposed to fully explain it. Even now, over 100 years on, field emission is widely researched and debated in the scientific community and is the main subject of several international conferences every year. In this Section, a description of field emission theory will be presented, and its implications will be discussed in detail.

1.3.2 Theory

Under normal circumstances, electrons are prevented from leaving the surface of a metal by the existence of a difference between the energy of electrons and the vacuum energy level. This is represented in Figure 1.1 as a simple potential energy step. The Fermi energy ($E_F$) is the energy of the electrons in the highest occupied state at absolute zero, i.e. the maximum energy of electrons in the metal. To escape from the surface, electrons must gain sufficient energy to overcome the barrier. This energy is equal to the difference between the vacuum energy ($E_{\text{vac}}$) and $E_F$, and is roughly equivalent to the work function ($\phi$), i.e. minimum energy needed to remove an electron from a metal to a point immediately outside the surface.

![Figure 1.1: Schematic representation of the metal-vacuum interface and of thermionic emission over the barrier. The origin is taken at the Fermi level.](image-url)
One method of overcoming this energy barrier is to thermally excite electrons in the metal. Heating the metal can provide the energy required by the electrons to overcome the electrostatic forces holding them to the substrate. This process is known as thermionic emission and requires temperatures in the region of 2000 to 2700 K for a significant external thermionic current to be observed. By applying an electric field, it is possible to accelerate electrons away from the surface towards, for example a phosphor-coated screen. This is the basic principle of operation of the cathode ray tube in television sets and computer monitors, which are widely used in displays across the world. However, a much more exciting means of overcoming the potential barrier is possible in which quantum mechanics plays a crucial role.

Consider an electron approaching a potential barrier of finite height and width ‘a’ (Figure 1.2). In classical physics, the electron (a particle) would be reflected back from the barrier. However, in quantum mechanics, an electron has wave-like properties and can be described by a wave function, which is a solution to the time independent Schrödinger equation. The probability of finding an electron in a particular region of space is proportional to the square of the wave function. The wave function of an incident electron can be described as a sinusoidal curve, where the frequency of the wave is proportional to the energy of the incoming electron. Upon reaching the barrier, the wave function (and thereby the probability of finding the electron at any given point) will decay exponentially into the classically forbidden region within the potential barrier. At the far side of the barrier, the wave function will revert to a sinusoidal curve with the same frequency (and therefore energy) as the incident curve. This implies that there is a finite probability that the electron will be found at the other side of the barrier, without any energy loss. The phenomenon in quantum mechanics whereby particles can be found in classically forbidden regions is called barrier penetration, or tunnelling.\(^{12}\)
This concept in quantum mechanics is the basis of field emission. Field emission is the emission of electrons from a solid by the application of an intense electric field, via quantum tunnelling of electrons through an approximately triangular potential barrier. When an electric field \((E)\) is applied to the system schematically represented in Figure 1.1, the vacuum potential is assumed to be distorted into a triangular form with a gradient \(-eE\), where \(e\) is the electronic charge (Figure 1.3). This is mathematically expressed in Equation 1.1, where \(x = 0\) is taken at the metal-vacuum interface.

\[
V(x) = \begin{cases} 
0 & x < 0 \\
\phi - eEx & x \geq 0 
\end{cases} 
\]  

\[1.1\]

In simple terms as the electric field increases, the gradient of the vacuum-potential gets steeper, resulting in a thinner triangular barrier. When the barrier becomes
sufficiently thin (less than 1 or 2 nm) there is a significant probability that electrons will be able to quantum mechanically tunnel from near the Fermi level of the metal, through the classically forbidden potential barrier into vacuum. This quantum mechanical tunnelling process under high fields is the very basis of field emission.

In 1928, Fowler and Nordheim wrote their much-referenced paper on field emission in which they applied the new quantum theory to the problem, solving the Schrödinger equation for electrons tunnelling through a triangular potential barrier. Fowler-Nordheim theory assumes that the surface of the emitter is a perfectly smooth metallic plane at absolute zero. They apply the free electron approximation, in which valence electrons have no interaction with the positive ions comprising the crystal lattice of the metal, and therefore can be considered as a free electron 'gas'. The WKB approximation allows the solution of Schrödinger's equation through a general potential barrier to be approximated by a semi-classically expanded function. To further increase the validity of the Fowler-Nordheim model, the image charge potential is considered, whereby a charge distribution is induced on a metallic surface to screen the electric field of a nearby electron. This surface charge distribution mimics the effects of the electron with equal and opposite sign located equivalently in the bulk (i.e. an image charge). The resulting Coulomb potential due to the image charge, superposed with the original triangular barrier, results in an effective lowering of the barrier height, shown in Figure 1.4.

![Figure 1.4: Schematic of the potential at a metal-vacuum interface where image charge barrier lowering is considered. The dark grey line is the triangular potential, the dotted line is the image charge potential, and the black line is the superposition of the two. The origin is taken at the Fermi level.](image)

---

\(^{+}\) G. Wentzel, H. A. Kramers and L. Brillouin
The mathematical derivation of the Fowler-Nordheim equation is involved and complicated, but the final result is relatively simple and is presented in Equation 1.2, where \( J \) is the FE current density, \( F \) is the electric field at the emitting surface and \( \phi \) is the work function. The constants \( a \) and \( b \) are \( 1.54 \times 10^{-6} \text{A(eV)V}^{-2} \) and \( 6.83 \times 10^9 \text{(eV)}^{-3/2} \text{Vm}^{-1} \), respectively.

\[
J = \frac{aF^2}{\phi} \exp\left(\frac{-b\phi^2}{F}\right) \quad [1.2]
\]

This version of the Fowler-Nordheim equation can be modified to include non-planar emitters, by introducing an enhancement factor (\( \beta \)). The enhancement factor is the factor by which the local electric field at the emitting surface exceeds the applied electric field, such that \( F = \beta E \). This modification is presented in Equation 1.3.

\[
J = \frac{a(\beta E)^2}{\phi} \exp\left(\frac{-b\phi^2}{\beta E}\right) \quad [1.3]
\]

This equation is fundamental to Fowler-Nordheim theory and the interpretation of field emission currents. The different variables in the equation will now be discussed in detail.

### 1.3.3 Applied Field (\( E \))

The applied field obviously has a significant impact upon the emitted current density. As \( E \) increases, so the triangular barrier presented to electrons will become thinner, as previously discussed. The transmission probability is critically dependant upon the thickness of the tunnelling barrier, and therefore as the barrier thins a large increase in the tunnelling current will be observed. This crucial dependence upon the applied field is reflected in Equation 1.3, where \( E \) appears in both the squared prefactor and in the exponential term. In experimental investigations, the FE current (or current density) is generally measured with increasing applied electric field. A threshold field \( (E_{th}) \) is usually defined as the applied field where a certain subjective current (or current density) is detected.
1.3.4 Enhancement Factor ($\beta$)

The enhancement factor is the quantity by which the local electric field at the emitting surface exceeds the applied macroscopic electric field. Electric fields cannot penetrate metallic objects (beyond a screening depth of several angstroms). Therefore, placing a metallic object in a uniform electric field causes the electric field to distort in the local vicinity. The distortion results in a concentration of the electric field close to the metallic surface, which is especially pronounced where the radius of curvature of the metal is small (for example at edges or points). Various factors can influence the local electric field such as (i) geometrical effects, (ii) dielectric inhomogeneities or (iii) screening effects. These variations in the local field obviously have a large impact upon the field emission current, in a way analogous to the increase in applied field, as previously discussed. Both the prefactor and the exponential term contain $\beta$, alluding to its significant contribution to the FE current. Figure 1.5 shows how $J$ varies with increasing $\beta$ in the Fowler-Nordheim equation, with all other values set as unity.

![Graph showing variation of field emission current density with increasing $\beta$.](image)

*Figure 1.5: Variation of field emission current density with increasing $\beta$.)*
(i) Geometric Field Enhancement

Metallic protrusions from a substrate can have a profound effect upon the local field at the emitting surface. A completely flat metallic surface, will typically begin to field emit only at electric fields above 1000 V/μm. However, by utilising geometric features (such as Spindt tips or CNTs) emission can be seen at electric fields as low as 0.3 V/μm; an improvement of four orders of magnitude. An example of electric field concentration around a metallic rod-like emitter is shown in Figure 1.6.

Figure 1.6: Simulation of the electric field distribution around a thin metallic rod.

For this simple, idealised rod-like structure, the geometric enhancement factor can be roughly approximated as $h/r$, where $h$ is the height of the rod and $r$ is the radius of the tip. This approximation demonstrates that as the emitter length increases and as the radius of the tip decreases, $\beta$ increases. Therefore, to maximise geometric field enhancement, the emitting feature should have a large aspect ratio, which is precisely why CNTs are so commonly cited as ideal field emitters.

(ii) Dielectric Field Enhancement

Dielectric field enhancement can be seen in materials which have a smooth surface, but comprise of dielectric inhomogeneities in their bulk. This occurs because regions with a low dielectric constant will allow electric field penetration, whereas high dielectric materials will allow field penetration to a lesser extent, or not at all. This leads to local field concentration close to the boundaries between the two materials. This effect is analogous to geometric enhancement; however the vacuum is
replaced by a higher dielectric material. This type of dielectric field enhancement was predicted by Latham to explain vacuum breakdown between flat electrodes at lower-than-expected electric fields. He described relatively insulating contaminants on the surface of metallic electrodes. Filamentary conducting channels form in these at high fields, providing field-line termination points within the insulating region (Figure 1.7), and leading to electric field enhancement in these areas.

Amorphous carbon thin films show dielectric field enhancement due to a dielectric difference between hexagonally and tetrahedrally bonded carbon clusters, the ratio of which can be experimentally controlled. A similar dielectric field enhancement effect has been observed in silicon dioxide layers implanted with silver nanoparticles (Figure 1.8), and in field emitting inks comprising conducting particles in an insulating resin matrix.

Figure 1.7: A schematic representation of the emission regime showing the conducting channels in an insulating contaminant and the associated macroscopic field enhancement.

Figure 1.8: (a) Transmission electron microscope (TEM) image of Ag-SiO$_2$ nano-composites. (b) Simulation of local electric field enhancement within an Ag-SiO$_2$ nano-composite.
To maximise dielectric field enhancement, the difference between the dielectric constants should be large (tending to the extreme case; a metallic emitter in vacuum) and the proximity and distribution of the dielectric clusters should be carefully considered.

(iii) Electric Field Screening

Screening of the electric field due to closely spaced emitters can seriously reduce the local field at the emission site, therefore reducing $\beta$ and the FE current. This concept is demonstrated in Figure 1.9, below. In electrostatic terms, the more densely packed an array of metallic rods becomes, the more it resembles a flat metallic surface. Therefore, as the emitters become more densely packed, the value of $\beta$ tends towards that of a flat metallic surface (i.e. $\beta = 1$). When the emitters are well-spaced, this results in field penetration in the gaps, which leads to a high electric field concentration at the emitting tips. To minimise screening effects, it is important that the emitters are not too densely packed, such that maximal field penetration can occur between them.

We have seen that it is possible to calculate $\beta$ for an idealised metallic rod-like emitter ($\beta = h/r$). However, the vast majority of electron emitters studied are not ideal metallic rods, therefore is it possible to calculate $\beta$ for non-ideal cases? Rearranging Equation 1.3 we can deduce that $\ln(J/E^2)$ varies linearly with $1/E$. 

Figure 1.9: (a) Field screening effects observed in a densely clustered array of field emitters and (b) an ideal case of well-spaced field emitters with high field concentration at their tips.
By plotting $\ln(J/E^2)$ against $1/E$ (generally known as a Fowler-Nordheim plot) a linearity is observed, with a gradient $-b\phi^{3/2}/\beta$. Therefore, since $b$ is known, $\beta$ can be calculated from the slope of the graph, provided that the work function is known. Plotting FE data in this manner is extremely common and results in linearity for a wide range of emitters of different geometries and materials. This suggests that the Fowler-Nordheim equation describes the FE process well and that the assumptions made in its derivation are realistic.

Multiplying $\beta$ by $E_m$ gives an indication of the local field at the emitting site of a given material during field emission, which should be a few volts per nanometre. This is a good test to apply to experimental results to check the validity of the Fowler-Nordheim equation for a particular sample.

Maximising $\beta$ and minimising screening effects are very effective methods of improving the FE properties of cathodes. However, it is important to differentiate between the total enhancement factor $\beta$ calculated from the slopes of Fowler-Nordheim plots and the purely geometric enhancement factor. The total enhancement factor takes into account all the factors discussed here (geometry, dielectric, screening), and other factors such as surface dipoles may be involved. Therefore, it is unwise to relate $\beta$ to the exact dimensions of field emitters (such as CNTs), as measured by a scanning electron microscope (SEM) or a TEM.

1.3.5 Work Function ($\phi$)

The work function (WF) of a metal plays a fundamental role in the FE properties. A simple schematic representation of how the WF can affect the FE current is shown in Figure 1.10. The dotted lines represent the top of the Fermi level in three different cases (i.e. three differing WFs). At lower WFs, the difference between $E_F$ and $E_{vac}$ is reduced. At $E_F(a)$ in the figure, the barrier thickness is $t_r$. At lower work functions ($E_F(b)$ and $E_F(c)$ in the figure) it is immediately apparent that the barrier thickness is reduced, i.e. $t_1 > t_2 > t_3$. Since the emission current $(i)$ is so critical upon the thickness of the tunnelling barrier, it is apparent that $i_1 < i_2 < i_3$. This qualitatively
shows that the FE current density will increase with decreasing WF, at a given electric field.

Figure 1.10: Schematic of how a reduction in WF increases the FE current. The origin is taken at the Fermi level.

Figure 1.11 shows how the FE current density varies with increasing WF in the Fowler-Nordheim equation, with all other variables and constants set as unity. It is evident that in Fowler-Nordheim theory, as the WF decreases the FE current will increase. Therefore, for efficient FE, low work function materials are desirable.

Figure 1.11: The dependence of the FE current density upon the WF of a material, calculated from the Fowler-Nordheim equation.
1.3.6 Resistance

Another important issue in determining the field emission properties of a material is resistance. Field emission generally involves high currents, and therefore the supply of electrons to the emitting surface must necessarily be large. Resistance limits the supply of electrons to the emitting surface and so limits the amount of current available for FE. This resistance may arise within the film, or at the back contact. A study by Cui et al. showed that in highly resistive amorphous carbon films, the current becomes limited by electron transport through the film, resulting in a saturation of the FE current at high fields, and deviation from Fowler-Nordheim characteristics. For films of lower resistance, this saturation point occurs at a higher FE current. Although resistive materials can limit the current at high fields, this resistance can prove useful for controlling the emission current. Using this concept, ballast resistors have been shown to improve emission site density.

1.3.7 Resonant Tunnelling

Field emission is a quantum mechanical tunnelling effect, resulting in some interesting phenomena observable in field emitting structures, such as Coulomb blockade. Field emission from multilayer cathodes is also predicted to result in resonant tunnelling effects.

A quantum well (QW) is a region of space where the electric potential is lower than its surroundings, and can partially confine an electron in one or two dimensions. According to quantum mechanics, this confinement leads to a quantization of the energy states of the electron, resulting in a discrete energy spectrum of electronic sub bands.

Consider a two-dimensional QW in which several confined electronic energy levels are formed, with walls thin enough for an appreciable electron tunnelling current (Figure 1.12). When the structure is unbiased, no current flows from the contact because there are no electronic states at a low enough energy in the QW for electrons to tunnel into (Figure 1.12(a)), ignoring thermal and inelastic effects. Applying a voltage induces a potential drop across the structure. At some point, the lowest sub-band in the QW will align with and drop below the Fermi energy of the contact. Now, electrons can tunnel into the available sub-band in the QW whilst conserving energy and momentum, and therefore current will flow through the
structure (Figure 1.12(b)). This current will increase with increasing bias until the sub-band in the QW drops below the conduction band in the contact. This cuts off the electron supply available at the resonant energy for tunnelling, and the tunnelling current drops sharply (Figure 1.12(c)). This reduction in tunnelling current with increasing bias is known as negative differential resistance (NDR). If multiple electronic sub bands are present in the QW, a series of NDR peaks can be observed as each sub-band passes the conduction band at the contact.

![Diagram of a QW at different bias conditions.](image)

*Figure 1.12: A QW at (a) zero bias, (b) under resonant tunnelling conditions and (c) under negative differential resistance conditions. $E_1$ is the lowest available sub-band.*

Resonant tunnelling solid-state semiconductor devices have important applications in high frequency oscillators and mixers, and in resonant tunnelling diodes. However, resonant tunnelling in FE has not been widely observed. In 1996, Litovchenko et al. performed a computer simulation of FE from multilayer cathodes of Si-$SiO_2$-$Si-SiO_2$ for different system parameters (Figure 1.13(a)). The results displayed a clear NDR non-linearity in the Fowler-Nordheim characteristics (Figure 1.13(b)) which was shown to be caused by resonant tunnelling of electrons through the sub-bands in the QW. In 1999 the same group observed experimental evidence of resonant tunnelling in FE from the same multilayered structure (Figure 1.13(c)). Similarly, NDR has been seen in the FE characteristics of amorphous carbon-based multilayer structures.
Figure 1.13: (a) Band structure of the layered Si-SiO₂-Si-SiO₂ (b) Theoretical non-linear Fowler-Nordheim plot due to resonant tunnelling and (c) experimental non-linear Fowler-Nordheim plot due to resonant tunnelling from the Si-SiO₂-Si-SiO₂ structure.
1.4 Carbon Nanotubes

1.4.1 Introduction

In this section, a brief history of CNTs will be presented. Their structure and physical properties, the various methods of CNT fabrication, the effects of laser irradiation, and the acid functionalisation of CNTs will be discussed.

1.4.2 History

In 1985, an exciting discovery was made. Up until that point, pure carbon was believed to naturally exist in the forms of graphite, diamond and amorphous, or polycrystalline carbon. The discovery of buckminsterfullerene, or C$_{60}$ (Figure 1.14) showed that pure, stable, isolated molecular carbon structures could be artificially created in the laboratory.$^{36}$

![Figure 1.14: Molecular model of C$_{60}$.]$^{37}$

The importance of this discovery was such that the Nobel Prize for Chemistry was awarded to Kroto, Curl and Smalley in 1996. This hollow, spherical C$_{60}$ molecule is the most stable in a wide range of fullerenes which have varying shapes and sizes.

An important class of the larger fullerenes are carbon nanotubes. These are extended, hollow tubes of graphitic carbon (Figure 1.15), as opposed to the cage-like structure of C$_{60}$. They were observed as early as 1952 as a carbon contaminant in industrial processes,$^{38}$ and recognised in context in 1991 as molecular
microtubules of graphitic carbon. They have recently been the subject of vast amounts of research, with over 14,000 journal papers published on the subject between 1992 and 2007. CNTs have a range of interesting properties which will be properly discussed in the next sections.

![Molecular model of a single wall carbon nanotube](image)

**Figure 1.15: Molecular model of a single wall carbon nanotube.**

### 1.4.3 Structural Properties of CNTs

The structure of a CNT is essentially that of a graphene sheet, rolled up into a hollow tube. However, there are many variations on this theme. Single wall CNTs (SWNTs) have only one graphene layer (Figure 1.15), whilst multiwall wall CNTs (MWNTs) are made up of multiple layers of graphene (Figure 1.16). The diameters can vary *in theory* from 0.4 nm up to an infinite upper limit, but in practice structures with diameters above 100 nm are not considered as nanostructures. The ends can be either capped with spheroid carbon shells, or open. The tubular shape of CNTs lends rigidity to the structure. In the experimental work presented here MWNTs are exclusively used, due to their relatively low cost and ease of manufacture.
A wide range of interesting properties have been demonstrated in CNTs. Their high strength and stiffness, great length, and their ability to be spun into long, strong fibres could lead to applications in materials science. They have extremely good electrical conductivity and thermal conductivity, making them ideal candidates for use in electrical devices and as components in electrical circuits. Nanotubes can be grown over large areas, and at low temperature, making them perfect for large area applications on temperature-sensitive substrates. All of these properties, in combination with their low density (1.4 g/cm$^3$) have led to their popularity as a research topic. Of particular interest in this work are the excellent electron field emission properties of CNTs. Field emission of electrons from CNTs is a large area of research in itself, with one of the earliest discussions of CNT field emission sources notching up over 1200 citations since it was published in 1995.

1.4.4 Fabrication of Carbon Nanotubes

There are three main methods of artificially producing CNTs; (i) arc discharge; (ii) laser ablation; and (iii) chemical vapour deposition, each of which is discussed below.

(i) Arc Discharge:

The arc discharge method was the first used in the discovery of CNTs. A schematic of the process is presented in Figure 1.17. Graphite electrodes are generally drilled
with small holes which are filled with a transition metal catalyst powder such as iron, cobalt or nickel. These electrodes are then vaporized by arc discharge at reduced pressure in an inert atmosphere, or under flowing inert gas. The CNTs form a deposit on the end of the negative electrode, on the walls of the chamber, or as a web-like material draping between surfaces. This method can be used to form both SWNTs, and MWNTs (Figure 1.18). However, MWNTs do not require a catalyst to form.

![Figure 1.17: Schematic of the arc discharge method for producing CNTs.](image)

![Figure 1.18: (a) SWNTs, and (b) to (d) MWNTs, created by arc discharge.](image)

(ii) Laser Ablation:

The laser ablation process is schematically represented in Figure 1.19. A graphitic target, impregnated with a transition metal, is vaporised by a laser beam. This process occurs in a furnace tube, at reduced pressure in an inert atmosphere. A gas flow carries the vaporised material along the tube, where it condenses onto a water-
cooled copper collector. This process is analogous to that of arc discharge, however the CNTs are produced at higher yields, and are of better quality.52

![Figure 1.19: Schematic of the laser ablation method for producing CNTs.](image)

(iii) Chemical Vapour Deposition:

Chemical vapour deposition (CVD) can also be used to grow CNTs. In a typical, generalised process (Figure 1.20) a thin layer of catalyst material (e.g. iron, nickel or cobalt) is deposited onto a silicon substrate. This substrate is placed into a vacuum chamber and heated to around 700°C whereupon the catalyst layer breaks into nanoscale islands due to surface tension effects. Subsequently, a carbon-containing gas (such as acetylene or methane) is introduced into the chamber. This is usually mixed with a background gas such as nitrogen, which lends a degree of control to the CVD growth process.48 Equally, gases such as H₂ or NH₃ can be used to preferentially etch any amorphous carbon that is formed during the growth process.53

![Figure 1.20: Schematic of the CVD method for producing CNTs.](image)

The high temperature and the catalyst act together to crack the carbon gas at the catalyst surface, providing a source of atomic carbon. The resulting carbon is
believed to diffuse through or across the surface of the catalyst particle, precipitating out from the base of the catalyst as a CNT. As the process continues, the CNTs increase in length with the catalyst particle at the tip.\textsuperscript{54} An alternative method of CVD is to conduct the growth with the aid of an ion plasma in parallel electrode configuration. A gas plasma discharge is created between the electrodes, above the substrate surface. The carbonaceous plasma acts as the source of atomic carbon in this case, and the electric field can contribute to the alignment of the resulting CNTs. This process is known as \textit{plasma enhanced CVD}, or PECVD.\textsuperscript{55} Using PECVD, large areas of CNTs can be grown perpendicular to the substrate surface. A SEM image of CNTs grown via PECVD is shown in Figure 1.21.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{CNTs.png}
\caption{SEM image of CNTs grown by PECVD. The image is 5 $\mu$m across and the individual CNTs are around 70 nm in diameter.\textsuperscript{56}}
\end{figure}

The PECVD method of growth gives a high degree of control over the resulting CNTs due to the number of different parameters that can be altered to change the final result. For example, the initial thickness of the catalyst film dictates the morphology, number density and size of the catalyst nanoparticles that are formed. These in turn directly affect the diameter, number density and morphology of the resulting CNTs (Figure 1.22)\textsuperscript{53} since each catalyst particle essentially acts as a mould for its associated CNT.
The pressure and relative concentrations of the process gases have a profound impact upon the resulting CNTs by affecting the supply rate of carbon, and/or the etching rate of amorphous carbon. The growth also is critically dependant upon the temperature of the substrate (Figure 1.23); below 550°C, the temperature is often insufficient to efficiently decompose the carbonaceous gas and promote graphitisation of the CNT walls. However, CNTs grown at very high temperatures (>900°C) become distorted and less well aligned, possibly due to ion damage from the plasma, or accelerated diffusion through/across the catalyst particle.
Three different methods of growing CNTs have been discussed, and each method has its different merits. The MWNTs used in the experimental section of this work are CVD-grown, due to their relatively low cost and commercial availability.

1.4.5 Laser Irradiation of CNTs

The laser irradiation of CNTs at different wavelengths and energy densities can have varying effects upon CNT samples. In theory, at long laser wavelengths the photon energy \((E_\lambda)\) is insufficient to break the C-C bonds in CNTs \((\lambda \geq 198 \text{ nm}, \ E_\lambda \leq 6.3 \text{ eV})\) and therefore CNTs will remain unaltered by laser irradiation. At short laser wavelengths \((\lambda < 198 \text{ nm}, \ E_\lambda > 6.3 \text{ eV})\), the photon energy would be sufficient to break the C-C bonds and introduce defects or dangling bonds, or even wholly decompose the CNT.\(^{57}\) When two photons are incident upon a single C-C bond, multiple-photon excitation may lead to CNT decomposition at longer wavelengths \((\lambda \leq 394 \text{ nm}, \ E_\lambda \geq 3.2 \text{ eV})\).

Additionally, the laser fluence has an impact upon the structural modification of CNTs. At low fluences, the photonic energy of the laser dominates any structural modifications. At high fluences, additional structural modifications are observed, possibly due to thermally assisted bond breaking,\(^{58}\) or by increasing the number of
incident photons per unit area and thereby increasing the likelihood of multiple-photon bond breaking.

The structural decomposition of CNTs to greater and lesser extents by laser irradiation has been observed by several groups; at low energy density and long wavelength, the removal of amorphous carbon and catalyst particles has been observed, whilst the CNTs themselves remain largely unaffected.59,60 The field emission properties of CNTs (such as threshold field and emission site density) have been observed to improve after laser irradiation, attributed to carbon-carbon bond breaking due to multiple photon excitation resulting in dangling bond formation.61

1.4.6 Acid Functionalisation of CNTs

The graphitic surface of CNTs renders them hydrophobic and it is notoriously difficult to obtain stable dispersions in water and other solvents. A simple and common method to form stable, aqueous dispersions is by an oxidative chemical treatment of the CNTs. This is achieved by putting CNTs into a concentrated 3:1 mixture of concentrated nitric and sulphuric acid and then refluxing at an elevated temperature.62 The solution is then washed and filtered, resulting in a pH 7 dispersion of CNTs in water. This process results in the formation of oxygen containing moieties, including carboxylic acid groups, attached to the CNT ends and sidewalls.63 Polar, oxygen containing moieties such as carboxyl groups readily interact with water molecules via hydrogen bonding (see Figure 1.24). Functionalisation via acid treatment also serves to purify CNTs dissolving catalytic particles and removing amorphous carbon.64 After this oxidative treatment, CNTs are also open to further functionality by performing chemistry on the surface functional groups, which has been the subject of intense research.65-68 At high concentrations, these aqueous CNT dispersions are black and ink-like in appearance and in viscosity.
Dispersing CNTs in water or other solvents opens the door to a wide variety of deposition techniques, such as screen printing, spin-coating, spray coating, drop-casting, stamping, inkjet printing and dip coating. These techniques are all cost effective, scalable, have a short processing time and are performed at room temperature. This means that CNTs can be deposited and patterned onto a plethora of substrates; most importantly temperature sensitive substrates such as polymers and even paper.

One of the most common and effective methods of patterning liquid inks over large areas is inkjet printing. In inkjet printing, a series of tiny droplets of ink are ejected from nozzles in a print-head onto a substrate. Each nozzle is typically 20 - 30 μm in diameter, and there may be up to 30,000 individual nozzles in one industrial printer, each of which can deposit up to 40,000 droplets of ink per second. Each droplet of ink forms a dot on the substrate, the position of which is computer controlled. These dots, when viewed from a distance form the image. The minimum size of these individual dots is around 25 μm, with a size variation of less than ± 2 %.69

Recently, acid oxidised CNT inks have been printed using inkjet technology. In 2005, Fan et al.70 experimented with the use of CNT inks in a commercially available desktop inkjet printer. They patterned 3 mm x 3 mm dots onto standard inkjet paper and measured their resistance with increasing layer thickness. They found that once a continuous CNT layer was formed, the resistance was 11600 Ω. They also printed conventional images using the CNT ink (Figure 1.25). The dried
CNT surface was found to remain stable after repeatedly rinsing in water, suggesting that the CNT adhesion to the paper fibres is very strong.

Similarly in 2006, Kordás et al.\textsuperscript{71} printed CNT inks onto paper and plastic substrates with 70 µm resolution, using a desktop bubble jet printer (see Figure 1.26). They measured the resistivity of thick CNT layers as ~ 40 kΩ/□ using four point probe measurements. They also printed conventional images using the CNT ink. The dried CNT was found to be remarkably mechanically stable, possibly due to hydrogen bonding between the CNT functional groups and cellulose molecules in the substrates.

Figure 1.25: (left) Images printed using the CNT ink (right) SEM image of the CNTs on paper substrates.

Figure 1.26: Multiple prints of oxidised MWNTs on (a)-(b) plastic and (c)-(d) paper substrates. (e) Image (10 x 10 cm\textsuperscript{2}) printed on paper using water-based MWNT ink.
Several electronic devices have been fabricated using screen-printed CNTs, demonstrating that this simple technique can be applied to create electrochemical sensors, and field emission displays. However these devices generally use un-oxidised CNTs mixed with an organic binder such as ethyl cellulose. After printing the substrates are heated to remove the binder, leaving pure CNTs behind. Using water-based CNT inks has advantages over CNT-binder composites because they can be easily concentrated or diluted, result in a pure CNT residue, and there is no need for a high temperature post-deposition treatment.

1.4.7 Work Function Tailoring of CNTs

In practice, tailoring the WF of CNTs is not a straight-forward process - it is a fundamental property of a material. Examples of how it can be reduced in CNTs are by (i) using low WF coatings, (ii) intercalation of low WF materials, or (iii) chemical functionalisation. Various low WF coatings have been applied to CNTs resulting in an improvement in the FE properties, for example; tetrahedrally bonded amorphous carbon (grown by chemical vapour deposition), thermally evaporated caesium, and barium strontium oxide (deposited by reactive magnetron sputtering). Similarly, caesium and potassium intercalated CNTs have been found to have improved FE properties. However, the methods of depositing these materials are complex with large energy requirements. It is also expected that metals such as caesium and potassium would be extremely susceptible to deterioration in oxygen environments.

Chemical methods of changing the WF of CNTs are much more promising. Chemical procedures are very easy to execute at a large scale, do not require vacuum conditions or high temperatures, use the minimum necessary materials and can be performed in solution. The WF of MWNTs is particularly sensitive to acid oxidative treatments. During the acid oxidisation process, oxygen containing moieties form on the surface of the MWNT, including carboxyl groups. These surface carboxyl groups reduce the \( \pi \)-conjugation of the MWNT and introduce inward-pointing surface dipole moments, leading to a higher WF. Acid oxidisation of CNTs results in an increase in WF from 4.3 eV to 5.1 eV, which would be detrimental to the FE properties. However, further chemical reactions performed via these carboxylic groups can be used to reduce the WF, because the surface dipole is sensitive to the nature of the associated cation. For example, alkali cation...
exchange with lithium can be used to reduce the WF of acid oxidised CNTs from 5.1 eV to 4.6 eV.\textsuperscript{81} This shows that chemistry can be a valuable tool in WF tailoring and it is probable that other functionalities could be found with similar effects upon the WF. Field emission from chemically modified CNTs has not previously been studied in detail with any conclusive observed improvements,\textsuperscript{82} and therefore warrants further investigation.
1.5 Applications of Electron Field Emission from CNT Ink

1.5.1 Introduction

Field emission is an extremely complex phenomenon rooted in quantum mechanics and its interest from a pure physics point of view is sufficient alone to warrant its study. However, there are several technological applications for FE. The main application is for FE cathodes to replace hot, thermionic cathodes with cold tunnelling cathodes in vacuum electronic devices such as microwave amplifiers,83 microscopes,84 X-ray sources,85 and travelling wave tubes.86 Of most relevance to this project is the application of FE sources to displays, specifically FEDs using CNTs as the emitting material. As field emitters, CNTs are ideal candidates. Their chemical inertness, mechanical robustness, unrivalled aspect ratios, plus high electrical and thermal conductivities make them highly suitable for FE applications.

FEDs are potentially rivals for other flat panel displays such as liquid crystal displays (LCD) and plasma display panels (PDPs). Compared to these other technologies, FEDs are considered to have lower power consumption, faster response, higher brightness, larger viewing angles, and very high contrast ratios. So far, FEDs are yet to pose a real challenge to LCD and PDP technology. However, in the long term, FEDs have the potential to take a significant share of the flat screen display market.

1.5.2 Field Emission Displays

Figure 1.27 shows a comparison between a conventional cathode ray tube (CRT) and a generalised FED. In CRTs, electrons are generated by thermionic emission from a hot cathode. Equivalently in FEDs, electrons are generated via FE. In both devices, the electron beam is accelerated towards a phosphor-coated screen where electron bombardment results in light generation. In CRTs, three electron beams are scanned across the phosphor screen to generate an image in red, green and blue. The distance between the cathode and phosphor must be necessarily large to accommodate beam deflection across the whole screen. Therefore CRTs are generally large and bulky. However, in FEDs an image is formed by emitters at individually addressed pixels. Consequently, the distance between the emitter and the front of the display can be very small, with each pixel reliant upon a different group of field emitters. Therefore FEDs are compact, flat-screen devices.
1.5.3 CNT Inks as FED Cathodes

Using printed CNT inks as the basis for FED cathodes is an interesting alternative to growing CNTs in situ by CVD techniques. CNT inks bring about the possibility of directly depositing CNTs at room temperature and pressure, in a controlled manner onto a plethora of pre-patterned substrates with surfaces tailored to enhance geometric field enhancement. Inkjet printing, dip-coating and spin-coating all lend themselves to industrialisation and continuous manufacturing processes with obvious cost benefits over vacuum deposition, thermal evaporation and CVD techniques utilised in other CNT deposition technologies.

Some of the earliest examples of CNT FEDs reported in the literature used CNT pastes and inks. In 1998, Wang et al. fabricated a two-terminal matrix-addressable FED using a CNT/epoxy paste as the emitter. The device operated with a current density of 76 μA/cm² at 7.5 V/μm, and each of the 32 x 32 pixels was 200 μm in diameter (Figure 1.28).
In 1999, Choi et al.\textsuperscript{81} (in collaboration with Sony) fabricated a 4.5 inch fully sealed two-terminal CNT FED display operating with a brightness of 1800 cd/m\textsuperscript{2}, and a current density of 90 \(\mu\text{A/cm}^2\) at 3 V/\(\mu\text{m}\). The FE cathode comprised a CNT/isopropyl alcohol/nitrocellulose paste which was screen printed onto sodalime glass and heated to 415°C to remove the organic binder (Figure 1.29).

A gated, 100 x 100 pixel three-terminal device was fabricated by Wang et al. in 2001. The gated cathode was made from screen-printed CNT/dielectric polymer paste on glass substrates fabricated by a multistage lithography technique (Figure 1.30). The device operated at a gate voltage of 50 V, with the phosphor screen at 500 V, and the leakage current to the gate was 30\% of the current reaching the phosphor screen.
These early devices showed that the printing of CNT pastes was a viable, low cost method of depositing CNTs in working FEDs. As time progressed, more impressive FEDs were fabricated using printed CNT cathodes. In 2001, Uemura et al.\textsuperscript{90} fabricated an experimental 370x260x7 mm CNT segment display (Figure 1.31) operating at 6 kV with a current density of 1000 μA/cm\(^2\) and at peak luminance of 7x10\(^5\) cd/m\(^2\).

In 2002, Lee \textit{et al.} fabricated a 7 inch FED with printed CNT cathodes. The display (Figure 1.32) operated with a brightness of 270 cd/m\(^2\) and a current density of 1000 μA/cm\(^2\) at a gate voltage of 65 V and an anode bias of 4 kV. Full colour video images were obtained.\textsuperscript{91}
More recently, the use of inkjet printing of CNTs has brought FEDs very close to production. A 55 inch surface conduction emission display (SED) made by Canon® has been prototyped and is ready for commercial production, pending litigation (Figure 1.33). The gate voltage is just 10 V, whilst electrons are accelerated towards the phosphor plane by a voltage of around 10 kV.

Figure 1.33: (left) Photograph of a 55 inch SED prototype and (right) a schematic of the SED structure.
1.6 Summary and Conclusions

Field emission of electrons from surfaces can be maximised in a number of different ways, including increasing the applied electric field, changing the emitter geometry, and reducing the work function.

Carbon nanotubes are ideal candidates for FE materials, due to their high aspect ratio, electrical conductivity, strength and versatility. They can also be chemically functionalised to make them soluble in water, and to alter their work function.

Carbon nanotube ink is a promising material for use as cathodes in FEDs, with products just beginning to reach the market. In ink form, CNTs can be deposited and patterned cheaply and quickly over very large areas with uniform thickness and FE properties. If CNT-based FEDs are to compete with PDP and LCD technology, then the printing of CNT cathodes is the best route to fabricating low-cost, large area displays.

Therefore, in the following experimental sections, CNT inks will be widely explored as field emitters. Transparent FE cathodes will be fabricated and characterised. Carbon nanotube inks will be deposited onto paper substrates to gain an insight into morphology tailoring on very cheap, flexible substrates as a route to mass production of large area CNT cathodes. Altering the work function of CNTs by chemical functionalisation as a route to improve the FE characteristics of CNT inks will also be explored.
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Chapter 2: Experimental Techniques

2.1 Introduction

In this chapter, the basic experimental techniques used throughout this work are presented. These include oxygen plasma treatment, acid functionalisation of MWNTs, atomic force microscopy, SEM, profilometry, probe, planar and three-terminal FE characterisation, laser irradiation and optical transmission measurements.

2.2 Substrate Materials

Glass substrates were plain soda-lime glass microscope slides, purchased from Agar Scientific, with dimensions 76 mm x 26 mm x 1.1 mm. Indium-tin-oxide (ITO) coated glass was used as a transparent, conducting substrate and was obtained from Merck. This comprised a 100 nm ITO layer coated onto polished 1.1 mm thick soda-lime glass. The nominal sheet resistance of the ITO layer is 20 Ω/□ and the peak-to-peak roughness was less than 10 nm, confirmed by atomic force microscopy. The optical transparency of these ITO-coated glass substrates is > 90 % at 520 nm. Plastic substrates were commercially available colour laser transparency film obtained from 3M™ and suitable for inkjet printing. The carbon fibre fabric 1071 HCB AvCarb™ was obtained from Ballard Material Products Incorporated. This comprised vacuum baked, carbonized polyacrylonitrile based carbon fibres, grouped and spun into yarns, which are then woven together to form carbon fibre fabric. The individual fibre diameter is 7.5 μm and the electrical resistivity is 1.1 x 10^3 Ωcm. The carbon content of the fibres is > 99.5 % and the thickness of the fabric is 280 to 432 μm. The weave count is around 19 cm⁻¹.

2.3 Substrate Cleaning

Glass and ITO-coated glass substrates were meticulously cleaned before cathode fabrication. The following procedure was performed; substrates were sonicated for 10 minutes in toluene, then in an aqueous solution of Decon 90, and finally in acetone. Substrates were dried by blow drying with nitrogen.
2.4 Oxygen Plasma Treatment

A microwave plasma system (Plasma-Preen, Plasmatic Systems Inc.) was used to treat the surface of substrates at reduced pressure (3 Torr). A process gas (in this case, oxygen) is flowed through the chamber at 3 sccm and a plasma discharge is created using microwaves. This process creates free radicals and ionised gas species within the chamber. These species are free to react at the sample surface, removing residual carbon species from the surface and rendering the surface hydrophilic in preparation for the deposition of water-based materials. Unless otherwise stated, glass and ITO-coated glass substrates were subjected to oxygen plasma treatment for 1 minute, whereas plastic and carbon fibre substrates were exposed for 10 seconds.

2.5 Acid Functionalisation of Multiwall Carbon Nanotubes

For the sake of clarity, acid oxidized MWNTs are herein referred to as o-MWNTs. High purity (>90%) MWNTs grown by CVD were purchased from Nanocyl. These had a nominal diameter of 10 nm. A concentrated H$_2$SO$_4$ (7.5 ml) and H$_2$NO$_3$ (2.5 ml) solution was prepared in a round bottom flask and MWNTs (145 mg) were added. The mixture was sonicated for 10 minutes and then refluxed at 110°C for 40 minutes. The result was diluted with reagent grade HPLC (high pressure liquid chromatography) water and centrifuged for 20 minutes at 8500 rpm to remove large particles and agglomerates from the solution. The centrifuged liquid was then carefully decanted and filtered under negative pressure through a polycarbonate membrane with a pore size of 200 nm. The acid solution was filtered through the membrane, leaving the o-MWNT above. Reagent grade water was added until the filtrate was pH 6-7. The resulting slurry was added to a small quantity of HPLC water, and then sonicated to disperse the tubes. Finally, the mixture was centrifuged at 8500 rpm for 20 minutes and the mixture was again decanted. The final product was a thick, black o-MWNT ink, which was stable over a period of one year. The o-MWNT loading (3.5 mg/ml) was determined by drying and weighing a volume of the o-MWNT ink.
2.6 Atomic Force Microscopy

An atomic force microscope (AFM) was used to study the morphology, surface roughness and phase contrast of several of the samples discussed in this work. A Veeco Dimension 3100 scanning probe microscope in AFM mode, with a Nanoscope IV control system was used in tapping mode. Silicon pyramidal tips with a radius of 10 nm to 20 nm were employed. This system has a resolution of 10 nm in the horizontal plane and angstrom resolution in the vertical direction. The relatively low resolution in the horizontal plane is due to tip convolution effects. A simplified schematic diagram of the system is shown in Figure 2.1.

The tip is made to oscillate at close to its natural frequency (in this case ~300 kHz) and touches the surface periodically at the lower extreme of its deflection. The tip is scanned across the substrate surface by the piezoelectric scanner and as it encounters surface features, the system tries to maintain constant amplitude of oscillation. The movement of the cantilever is detected optically, with a laser beam reflected from the back of the cantilever surface. The reflected beam is measured by a detector comprising four photodiodes. Movement of the laser beam results in a change in the ratio of light intensity received by each different photodiodes. Therefore, the mechanical response of the tip is converted to an electrical signal.

Figure 2.1: Schematic diagram of the main components of an AFM.
which is reconstructed into a topography map as the whole surface is scanned. Phase contrast imaging maps the phase lag between the periodic signal that drives the cantilever and the oscillations of the cantilever. Changes in the phase lag often indicate changes in the properties of the sample surface such as composition, surface adhesion, viscoelasticity or hardness.\footnote{Y. Tison, Veeco Dimension 3100 User Guide, unpublished, 2006}

### 2.7 Scanning Electron Microscopy

A scanning electron microscope (SEM) can provide images of objects in a way analogous to that of optical images, but utilising the small wavelength of electrons relative to photons, providing images with much higher resolution. The SEM used for the work presented here was an FEI Quanta 200, operating between 10 and 30 kV with a maximum resolution of 2 nm. A schematic of a SEM system is shown in Figure 2.2. Electrons are generated by an electron gun, under vacuum conditions. The electron beam is then accelerated and focussed onto the sample surface by a variety of electron lenses. As the beam is scanned across the surface, secondary and backscattered electrons are emitted. These secondary and backscattered electrons are subsequently detected, and the number of electrons and their energy give information about the topology and the elemental composition of the sample. This information is then converted into a digital image.

![Figure 2.2: Schematic diagram of a SEM.](image)

\footnote{Y. Tison, Veeco Dimension 3100 User Guide, unpublished, 2006}
2.8 Surface Profilometry

Surface roughness for samples with large surface features was measured using a Sloan Dektak IIA profilometer. Surface profiles are acquired by moving the sample beneath a diamond tipped stylus with a 12.5 μm radius. Vertical movements of the tip are detected by a linear variable displacement transducer which digitizes the displacement. The data is then displayed as a trace on a screen and the data is stored in the memory of the instrument. The maximum vertical resolution of this system is 0.5 nm and the horizontal resolution is 20 nm.

2.9 Probe Field Emission

The samples were subjected to FE characterisation with a ‘sphere to plane’ configuration, using a 5 mm spherical stainless steel anode at a vacuum of approximately $3 \times 10^{-6}$ Torr. A schematic diagram of the equipment is displayed in Figure 2.3. The anode was adjustable in the vertical direction with a step size of 2.5 μm and in the horizontal plane over a range of 25 mm and therefore FE mapping over large areas was possible. The voltage between the anode and the earthed sample was incremented in 30 V steps (unless otherwise stated) by a computer-controlled high voltage supply (Keithley model 248) up to a maximum of 3000 V. The emission current was recorded as a function of the macroscopic electric field which was calculated by dividing the applied voltage by the electrode gap. The electrode gap was calculated by applying 50 V to the anode and lowering it until current flow was detected, after the measurement was made. The best emitters are likely to emit at 50 V before the anode makes contact with the sample surface, however since the electrode gap during the experiment was generally many hundreds of microns, this error in distance is a very small percentage. Additionally, it is normally straightforward to differentiate between an FE current and an ohmic contact, with experience. A current limit was set at 5 μA to prevent damage to the sample due to resistive heating effects. The threshold field ($E_{th}$) is defined as the macroscopic electric field at which an emission current of 1 nA is detected. At least six widely separated sites were probed on each sample to check the uniformity of emission, and the current was cycled up and down five times at each of these sites to observe conditioning and hysteresis effects. Hysteresis is measured as the
difference in electric field between the upwards and downwards cycle, measured at the threshold field.

Figure 2.3: A schematic diagram of the probe FE characterisation equipment.

2.10 Planar Field Emission

Some samples were subjected to planar FE characterisation to determine current density and emission site density. These measurements were carried out using the same vacuum chamber and voltage supply as the probe FE equipment and the electrical procedure was identical. A schematic diagram (not to scale) of the planar FE cell is presented in Figure 2.4, below. The sample was mounted on the metal cathode, inside a hollow rectangular PTFE spacer. An ITO or phosphor-coated glass slide was then clamped over the top of the PTFE. Contacts were made to the metal cathode and the coated glass anode and the cell was placed in the vacuum chamber. The air outlet hole has the function of ensuring that no residual gas is trapped in the cell. The thickness of the sample and the thickness of the PTFE spacer are measured with a micrometer and therefore the anode-cathode gap can be determined. The area of the entire sample can easily be measured to determine the current density.
2.11 Three-Terminal Field Emission

Three-terminal measurements were carried out using the same vacuum chamber and voltage supply described above, but using an additional gate electrode. A schematic diagram of the three-terminal measurement system is presented in Figure 2.5. During FE characterisation, the anode voltage was varied as described in Section 2.9, whilst the gate voltage was kept constant. The measurement was repeated at different gate voltages.
2.12 Laser Irradiation

Laser irradiation was carried out using single 25 ns pulses from a 248 nm UV excimer laser (Lambda Physik LPX210i). The substrate was placed in a chamber at a vacuum better than $10^{-4}$ Torr, behind a UV transparent window. The number of pulses and the frequency of these pulses could be varied. The laser fluence was varied by using a combination of filters and lenses in the beam path, and measured using an energy density meter. The sample stage could be moved in the horizontal plane by use of a stepper motor. A schematic of the process is presented in Figure 2.6, below.

![Schematic of the laser irradiation process.](image)

2.13 Optical Transmission

A Cary 5000 UV-Vis-NIR spectrophotometer (Varian) was used to perform transmission measurements on transparent samples. This machine has a wavelength range from 175 nm to 3000 nm. Using the dual beam facility, transmission measurements can be made and compared to a reference sample, or to air. A background scan and a zero scan are first performed to calibrate the machine. The sample and the reference are then placed in the path of the light beam, which scans between the desired wavelengths and the transmission is recorded by a photo-detector.
Chapter 3: Transparent Field Emitters

3.1 Motivation

The field of transparent electronics is a growing industry, with possible applications in display technology, sensing, solar cells, touch screens, defrosters, optical coatings and in the military. Recently several groups have studied transparent CNT films,\textsuperscript{1-6} reported transparent thin film transistors,\textsuperscript{7-10} and fabricated transparent field emitters.\textsuperscript{11,12} These transparent field emitters are likely to have specific applications in the display and lighting markets, where high light throughput is a requirement and transparent emitters could have a beneficial impact on device structure and performance.

3.2 Carbon Nanotube Ink on Glass

3.2.1 Introduction

In this section, a method of homogeneously applying pure o-MWNT ink onto glass substrates over large areas to create transparent, electrically conductive films is investigated. Glass substrates were used for their high transparency, low surface roughness, low-cost and wide availability. These substrates are subjected to optical transmission characterisation, AFM, SEM and FE characterisation.

3.2.2 Sample Preparation

Glass microscope slides were cleaved into 25 mm x 25 mm squares and rigorously cleaned according to the procedure outlined in Section 2.3. Subsequently a thin layer of o-MWNTs was spin-coated from a pure o-MWNT ink onto the glass substrates at 2200 rpm, which were then baked at 100°C for 10 minutes to remove residual water. An example of these substrates is shown in the digital photograph in Figure 3.1. The films are largely transparent at visible wavelengths and are brown in colour. The uniformity of the o-MWNT film is homogeneous, except at the corners of the substrate where the films are thicker and appear slightly darker, due to surface tension effects in the spinning process.
3.2.3 SEM and AFM Characterisation

The substrates were imaged at high magnification using a SEM (Figure 3.2). Figure 3.2(a) shows the sample at a 60° tilt. The o-MWNT layer is observed to be uniform over the 12 µm section imaged here and this is true for the whole sample, except at the very corners. Figure 3.2(b) shows the sample at a cleaved edge. Individual o-MWNTs can be observed laying flat on the glass substrate, arranged in a spaghetti-like tangled mat. Towards the cleaved edge, the surface is almost devoid of o-MWNTs. It may be that the o-MWNTs here were dragged away from this half of the substrate due to being intertwined with o-MWNTs that were attached to the other cleaved half. The opposite can be observed in Figure 3.2(c), where o-MWNTs stick out from the substrate edge after the cleaving process. It is difficult to determine the thickness of the o-MWNT films by AFM because these edge effects prevent the formation of definite steps that could be measured by profilometry. From the SEM images we can estimate that the films are 2 to 10 o-MWNTs thick, or 20 to 100 nm, depending on the nanoscale locality.
Figure 3.2: SEM images of o-MWNT films on glass substrates: (a) A low magnification image taken near the centre of the sample, (b) a high magnification image taken close to a cleaved edge, and (c) a high magnification image taken at the opposing cleaved edge.

Figure 3.3 shows AFM images taken at three different scales. The images on the left are topology maps of the substrate while the right hand side shows the phase contrast images. Figure 3.3(a) is markedly similar to the SEM image in Figure 3.2(a), showing correlation between the two techniques. Individual o-MWNTs can be resolved forming a tangled mat over a large scale. At higher magnification (Figures 3.3(c) to 3.3(e)), it is difficult to identify individual o-MWNTs using this technique, because of the complex morphology and intertwining of the o-MWNT layer. The phase contrast images give information about the force between the tip and the sample. The three images in Figure 3.3 have largely uniform phase, which indicates that the o-MWNT layer is uniform in material. The RMS roughness of the samples at
the three different levels of magnification was 9.2, 10.4 and 9.4 nm, respectively. This corresponds well with the nominal diameter of 10 nm of the as-purchased MWNT and is evidence that the acid functionalisation treatment has not significantly altered the MWNT diameter.

Figure 3.3: AFM topology and phase images of o-MWNT on glass at (a),(b) low magnification, (c),(d) medium magnification and (e),(f) high magnification.
3.2.4 Field Emission Characterisation

The FE properties of the substrates were investigated in sphere-plane geometry, with a typical electrode gap of 75 µm. Electrical contacts were made via conductive silver paint applied along the edge of the surface of the sample and the FE results are displayed in Figure 3.4. Figure 3.4(a) shows the current-field characteristics of the samples. The average Eth was 23.1 ± 2.9 V/µm with an average hysteresis of 3.6 V/µm, measured as averages of all the individual current-field curves. It is observed that the emission does not follow classic, smooth FE curves and that the hysteresis between the up and down cycles is large. The statistical error is large and repeatability between current cycles is poor. Some conditioning was also generally observed. A saturation of the FE current is observed at high fields, which may be due to resistance in the o-MWNT film, or possibly due to the contact between the silver paste and the sample (although the silver paste contact was applied to a large area of the sample to minimise contact resistance). Figure 3.4(b) shows the data plotted in Fowler-Nordheim coordinates. Using the slope of this plot, and taking $\phi$ as 5.1 eV, we can calculate $\beta$ as 216 ± 33.

These poor emission properties reflect the low surface roughness and close packing of the o-MWNT mat. Closely packed o-MWNTs result in field screening between individual o-MWNTs and hence a low field enhancement. The individual o-MWNTs are also orientated parallel to the substrate plane, resulting in low geometric field enhancement. However, there is some fine-structure in the o-MWNT layer, such that $\beta$ is not unity. The large hysteresis values may arise from a voltage conditioning effect, whereby adsorbed gas molecules on the o-MWNT surface are removed via ion bombardment, and/or field induced thermal desorption. This results in a change in surface barrier and therefore a difference in the field emission properties at higher fields. The conditioning effects that were observed are likely to be due to micro-arcing between the anode and the sample, resulting in geometric protrusions which locally increase the geometric field enhancement and increase the field emission current at a given electric field.
Due to the poor emission characteristics of the flat o-MWNT films, it was deemed useful to image the surface after emission to see what impact the measurements had on the sample (Figure 3.5). Figure 3.5(a) shows what appears to be the result of electrical arcing between the anode and the sample. At the centre of this feature, the high temperatures caused by the arcing process have caused molten glass to be ejected outwards. Additionally, around the edges of this feature, the o-MWNT layer has been restructured and has partially peeled away from the substrate. This would result in an increase in $\beta$ due to the altered morphology and therefore an improvement in FE properties. This could account for the conditioning effects observed in the FE curves. Figure 3.5(b) shows a low magnification view of several
emission sites, each separated by approximately 1 mm. The areas underneath the probe are optically darker than the surrounding area, and appear lighter in the SEM images (they have a higher secondary electron coefficient), suggesting that they have been physically or chemically altered by the conditioning process.

Figure 3.5: SEM images of the o-MWNT layer after FE characterisation.

The FE characteristics of as deposited o-MWNTs are poor and the emission that does occur is almost certainly due to micro-arcing events leading to increased geometric field enhancement. To improve the FE properties, some kind of post-deposition conditioning is clearly necessary. This will be explored in the next section.

3.3 Laser Treatment of Carbon Nanotube Ink on Glass

3.3.1 Introduction

The emission properties of untreated o-MWNTs on glass substrates are poor, with low $\beta$, large hysteresis and sizable conditioning effects. The conclusions were that a post-deposition treatment could prove useful in improving the emission properties. Specifically, laser irradiation at UV wavelengths is expected to have an impact, since MWNTs absorb strongly in the UV due to the $\pi-\pi^*$ optical transition at 260 nm.\textsuperscript{14} Therefore, in this section o-MWNT layers are irradiated with UV laser pulses of varying fluence and the effects of this on the morphology, FE and optical transmission of the samples are investigated.
3.3.2 SEM Characterisation

Samples were fabricated as previously described, then exposed to single 25 ns pulses from a 248 nm UV excimer laser, over a range of fluences in a vacuum better than $10^{-4}$ Torr. The area of the laser spot was 0.09 cm$^2$. Figure 3.6(a)-(f) shows SEM images of the o-MWNT film after laser treatment at 0, 172, 343, 400, 457 and 571 mJ/cm$^2$. Figure 3.6(a) shows the uniformity of the as-deposited o-MWNT layer, which is consistent with the results previously discussed. After laser irradiation at 172 mJ/cm$^2$ (Figure 3.6(b)) darker spots (~1.5 µm diameter) are observed in the o-MWNT layer. These spots are probably relatively insulating regions, where o-MWNT have been ejected from the surface by the incident laser pulse. Increasing the laser fluence leads to the formation of surface features approximately 500 nm in diameter. These are just visible in Figure 3.6(c) and are prominent in Figures 3.6(d) and 3.6(e). Despite these inhomogeneities in the o-MWNT layer at the submicron scale, at a larger scale this surface modification is uniform over hundreds of microns and seems to be limited only by the Gaussian wavefront of the laser beam. These features are probably glass nodules formed upon melting of the glass substrate as a result of the incident laser pulse. At the highest laser fluences, large patches of o-MWNTs have been completely removed from the substrate surface resulting from the large energy density of the laser wavefront either ejecting, or decomposing the o-MWNT layer. In this case, the large scale uniformity is not maintained. Overall, the morphology of the o-MWNT layer can be seen to have been considerably altered after laser irradiation.
Figure 3.6: SEM images of the o-MWNT layer (a) before laser irradiation and (b) to (f) after laser irradiation with fluences 172, 343, 400, 457 and 571 mJ/cm², respectively.
3.3.3 Field Emission Characterisation

The FE properties of the substrate were investigated in sphere-plane geometry with a typical electrode gap of 75 μm. Electrical contact was made via conductive silver paste applied at the edges of the sample, well away from the emission sites. Figure 3.7(a) shows representative current-field characteristics of o-MWNTs on glass substrates, subjected to UV laser pulses of varying fluence. No significant conditioning effects were observed after laser irradiation - the geometric reconstruction of the o-MWNT by the laser energy is similar in effect to the micro-arcing events previously discussed. It is apparent from these results that laser treatment results in an improvement in $E_{th}$. Some saturation of the FE current is observed at high fields which may be due to the large resistance of the o-MWNT films, limiting the current available at the emitting surface.

Figure 3.7(b) shows the above data plotted in Fowler-Nordheim coordinates. The difference in the slopes for varying laser fluence suggests that the laser irradiation does indeed have a profound effect on $\beta$, as expected from the morphological changes observed in Figure 3.6.
Figure 3.7: Comparison of FE current-field curves for the o-MWNT layer irradiated at varying laser fluences. (b) Corresponding Fowler-Nordheim plots for the above data.

Figure 3.8 shows all four current-field cycles from one emission site for the sample subject to 343 mJ/cm² laser fluence. A fairly wide spread in the data is observed, however at high currents, the ballast resistor effect results in a convergence of the current-field data. The hysteresis values for the first, second, third and fourth cycles
were 1.1, 0.8, 1.1 and 0.8 V/µm and 0.6, 1.3, 2.2 and 1.8 V/µm for two separate emission sites. There is no discernable trend in the hysteresis values with cycle number, and the average value is 1.2 V/µm. By taking the maximum spread of the data and averaging over all the emission sites, a value of 1.4 V/µm is obtained which is very close to the result for hysteresis. Due to the large amount of data analysis required to calculate the hysteresis from individual curves, ‘hysteresis’ will herein be approximated as the maximum spread of data, giving very similar (although slightly overestimated) results. Applying this approximation to the untreated o-MWNTs on glass (Figure 3.4), the hysteresis value is modified from 3.6 V/µm to 3.8 V/µm.

![Figure 3.8: Current-field cycles for o-MWNTs on glass substrates, subject to laser irradiation at 343 mJ/cm².](image)

The threshold fields and enhancement factors extracted from the FE data are plotted versus the laser fluence in Figures 3.9(a) and 3.9(b), respectively. Enhancement factors were calculated using a work function of 5.1 eV. Before laser irradiation, $E_{th}$ is high (23 ± 2.9 V/µm) and $\beta$ is low (240 ± 30). This is due to low surface roughness and screening effects, as previously discussed. The large error indicates that reproducibility across the sample area is poor. At low fluences, as the laser fluence increases, $E_{th}$ improves and $\beta$ increases, peaking at 8 ± 0.6 V/µm and 670 ± 70, respectively. This is due to the laser-induced morphology change in the o-
MWNT layer, observable in Figure 3.6(b)-(e), resulting in increased geometric enhancement and therefore increased \( \beta \). Additionally, the removal or modification of the carboxylic groups due to bond breaking induced by the incident laser energy may contribute to a reduction in WF because of dangling bond formation, or by altering the magnitude of the surface dipoles. The error in \( E_{\text{th}} \) is reduced after laser irradiation, indicating that the reproducibility in emission from site-to-site is improved by the laser irradiation process. At higher fluences, as fluence increases, \( E_{\text{th}} \) increases up to \( 19 \pm 0.6 \text{ V}/\mu\text{m} \) and \( \beta \) decreases down to \( 260 \pm 30 \). This is due to high laser energy densities resulting in the vaporisation and/or removal of o-MWNTs,\(^{15}\) resulting in a lower density of emission sites and therefore a lower total FE current at a given field. This is consistent with Figure 3.6(e) where the modification of the o-MWNT layer at high fluences is observed to be extensive and non-uniform. At lower spatial concentrations of o-MWNTs on the substrate, \( \beta \) would be expected to be increased due to reduced screening effects. However, at some point, the conducting o-MWNT network would be disrupted to such an extent that resistance effects would begin to seriously limit the current supplied through the film available for FE. Therefore the FE current would be limited, and the slope of the FE graph would be reduced, resulting in an associated decrease in \( \beta \).
A numerical summary of the FE characteristics of laser irradiated o-MWNTs is presented in Table 3.10, below. The hysteresis between the up and down cycles is reduced from 3.8 V/µm before laser irradiation to around half that value after laser irradiation. This hysteresis may be due to gas desorption effects, as previously discussed. After laser irradiation, the hysteresis may be reduced due to laser-induced desorption of a large proportion of molecules from the o-MWNT surface before FE measurements are performed.

The local field at the emitting surface (F) can be calculated by multiplying $E_0$ and $\beta$ together. As discussed in Section 1.3.3, this value should be of the order of a few volts per nanometre. The values for local field calculated in this case are largely
constant at around 5 V/nm. This result is slightly higher than predicted, however this may be because the carboxylic groups on the o-MWNT surface result in an increase in the field required extracting an electron from the surface. The value for samples irradiated at 172 mJ/cm² is very high, but this can be attributed to the low data resolution in the Fowler-Nordheim regime in this instance, possibly leading to an over estimate in $\beta$. The value for samples irradiated at 457 mJ/cm² is lower than expected and this may be due to non-linearity observed at the top of the Fowler-Nordheim curve in Figure 3.7(b), resulting in an underestimate of $\beta$.

<table>
<thead>
<tr>
<th>Laser Fluence (mJ/cm²)</th>
<th>Threshold Field (V/µm)</th>
<th>Hysteresis at 1 nA (V/µm)</th>
<th>Enhancement Factor ($\beta$)</th>
<th>Local Field (V/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23 ± 2.9</td>
<td>3.8</td>
<td>240 ± 30</td>
<td>5.5 ± 1.4</td>
</tr>
<tr>
<td>172 ± 17</td>
<td>12 ± 2.2</td>
<td>2.0</td>
<td>670 ± 70</td>
<td>8.0 ± 2.3</td>
</tr>
<tr>
<td>343 ± 34</td>
<td>8 ± 0.6</td>
<td>1.4</td>
<td>550 ± 60</td>
<td>4.4 ± 0.8</td>
</tr>
<tr>
<td>400 ± 40</td>
<td>15 ± 0.3</td>
<td>1.9</td>
<td>290 ± 30</td>
<td>4.4 ± 0.5</td>
</tr>
<tr>
<td>457 ± 46</td>
<td>13 ± 1.1</td>
<td>1.7</td>
<td>260 ± 30</td>
<td>3.4 ± 0.2</td>
</tr>
<tr>
<td>571 ± 57</td>
<td>19 ± 0.6</td>
<td>2.1</td>
<td>260 ± 30</td>
<td>4.9 ± 0.1</td>
</tr>
</tbody>
</table>

Table 3.10: Numerical summary of FE properties of o-MWNTs on glass substrates subjected to varying UV laser fluences.

The number of incident laser pulses was also varied and the effect on the FE characteristics was investigated. The laser fluence was held constant at 172 mJ/cm². The results can be seen in Figure 3.11 and Figure 3.12. Both figures demonstrate that the first laser pulse results in a significant improvement in $E_{th}$ from 23 to 12 V/µm, as well as an increase in $\beta$ from 240 to 670. This initial improvement in FE characteristics is due to an initial morphology change in the o-MWNT layer, as previously discussed. However, subsequent laser shots result in a deterioration of $E_{th}$ and $\beta$ back to values comparable to the untreated o-MWNT and increasing the number of shots from 10 to 1000 has little additional effect. These results confirm that the optimum number of laser pulses per emission area is just one. Therefore subsequent work will deal with the effects of just one laser pulse on o-MWNT layers.
Figure 3.11: Comparison of FE current-field curves for the o-MWNT layer irradiated with 0, 1, 10, 100 and 1000 laser pulses. (b) Fowler-Nordheim plots for the above data.
A numerical summary of the emission characteristics of o-MWNTs irradiated with varying numbers of laser pulses is presented in Table 3.13, below. Interestingly, the error in $E_{th}$ is reduced from 2.9 V/µm to 0.3 V/µm as the number of laser pulses is increased; suggesting that laser irradiation increases the uniformity of emission.
across the area of the sample. The degree of hysteresis is initially reduced, but increasing the number of laser pulses results in an increase in hysteresis, close the initial result. The values of local field are equal (within error) at 5 V/nm, except the sample with a local field of 8 V/nm, which has been previously discussed.

<table>
<thead>
<tr>
<th>Number of laser pulses</th>
<th>Threshold Field (V/\mu m)</th>
<th>Hysteresis at 1 nA (V/\mu m)</th>
<th>Enhancement Factor (\beta)</th>
<th>Local Field (V/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23 ± 2.9</td>
<td>3.8</td>
<td>240 ± 30</td>
<td>5.5 ± 1.4</td>
</tr>
<tr>
<td>1</td>
<td>12 ± 2.2</td>
<td>2.0</td>
<td>670 ± 70</td>
<td>8.0 ± 2.3</td>
</tr>
<tr>
<td>10</td>
<td>22 ± 1.2</td>
<td>2.5</td>
<td>240 ± 30</td>
<td>5.3 ± 1.0</td>
</tr>
<tr>
<td>100</td>
<td>25 ± 0.6</td>
<td>4.6</td>
<td>210 ± 20</td>
<td>5.3 ± 0.6</td>
</tr>
<tr>
<td>1000</td>
<td>27 ± 0.3</td>
<td>3.8</td>
<td>200 ± 20</td>
<td>5.4 ± 0.6</td>
</tr>
</tbody>
</table>

Table 3.13: Numerical summary of FE properties of o-MWNT on glass substrates subjected to increasing numbers UV laser pulses.

3.3.4 Optical Transmission

Optical transmission measurements were performed on samples subject to varying laser fluence and number of laser shots. Figure 3.14 shows the percentage transmission at 550 nm as a function of increasing fluence. Before laser treatment, the sample has an optical transmission of 88.7% (compared with glass), and this falls as laser fluence increases, down to a minimum of 82.7%. At the optimum laser fluence for field emission (343 mJ/cm²) the transmission is 85%, which is a minor decrease from the original value. This decrease in transmission as the laser fluence increases is probably due to increased scattering as the o-MWNT layer and the glass is roughened by the laser impulse, as observed in the SEM images.
Figure 3.14: Optical transmission at 550 nm as a function of incident laser fluence.

Figure 3.15 shows the optical transmission at 550 nm, plotted against increasing number of laser pulses. The transmission initially decreases from 88.7% to 72.5% after 10 laser pulses. This decrease in transmission is likely to be due to increased scattering from the roughened sample surface. As the number of pulses increases, the transmission of light through the sample increases, almost back to the original value. This may be because the o-MWNT layer is partially removed by each laser pulse, the additive effects of which result in reduced absorption of light by the o-MWNTs, only observable after many laser pulses.

Figure 3.15: Optical transmission at 550 nm as a function of the number of incident laser pulses.
3.4 Carbon Nanotube Ink on ITO-Coated Glass

3.4.1 Introduction

The laser treatment of o-MWNTs on pristine glass substrates has been discussed. However, laser treating o-MWNTs on glass surfaces coated with thin metallic films is likely to result in substantially different morphological changes, due to the additional effects of the melting of the underlying film. These differences in morphological change could lead to further improvements in the FE characteristics of the o-MWNT layers. Therefore, in this section o-MWNT layers are deposited onto ITO-coated glass substrates and irradiated with UV laser pulses of varying fluence. The morphology changes are investigated with a SEM, the FE characteristics are measured and optical transmission measurements undertaken.

3.4.2 Sample Preparation

ITO-coated (25 x 25) mm² glass slides were oxygen-plasma treated and spin coated with o-MWNT, as previously described. The samples were exposed to single 25 ns pulses from a 248 nm pulsed UV eximer laser over a range of energies. The laser spot size was 0.134 cm², which was used to calculate the incident fluence on the sample surface. Irradiation was carried under a vacuum better than $10^{-4}$ Torr.

An optical image of the sample after irradiation is shown in Figure 3.16. Each row of spots was irradiated with equal laser fluences from 149 mJ/cm² at the top of the image to 335 mJ/cm² at the bottom of the image. At the lowest fluences, the irradiated spots are indistinguishable from the untreated substrate. As the laser fluence increases, the surface becomes brown and more opaque.
3.4.3 SEM Characterisation

SEM images are shown in Figure 3.17. Figure 3.17(a) is an as-spun o-MWNT layer on ITO coated glass. This layer is homogeneous, consistent with previous results on glass substrates. Figures 3.17(b) to 3.17(f) show the sample after laser irradiation with fluences 149, 186, 223, 298 and 335 mJ/cm², respectively. In Figure 3.17(b) it is evident that the incident laser energy has an impact on the physical structure of the underlying ITO substrate and cracks can be seen underneath the o-MWNT layer. This is due to the ITO absorbing strongly at UV wavelengths and therefore absorbing a large portion of the laser energy. This may lead to thermal expansion of the ITO layer which could account for the observed cracks. The o-MWNT layer itself appears thinner than the original layer, suggesting that a portion of the o-MWNTs have been vaporised or ejected from the substrate by the laser pulse. Figure 3.17(c) shows slightly wider cracks in the ITO layer and more damage to the o-MWNT layer. Figure 3.17(d) shows that a large portion of the o-MWNTs have been vaporised or removed entirely from the substrate and much larger cracks appear in the ITO layer. In Figure 3.17(e) no o-MWNTs are observed and they have presumably been entirely removed or destroyed by the laser pulse. The ITO layer has also been partially destroyed and ejected from the surface in large chunks, some of which can
be seen at the edges of the picture. This may be due to a mismatch between the thermal expansion coefficients of ITO and glass, leading to a delamination of the ITO layer. Alternatively, the ITO layer may have been oxidised during the laser treatment. Oxidisation could account for an increase in the volume of the ITO layer and consequent delamination. Figure 3.17(f), taken after the highest laser fluence pulse, shows that the ITO layer has simply melted due to the high temperature.

Figure 3.17: SEM images of the o-MWNT layer (a) before laser irradiation, and (b)-(f) after laser irradiation with fluences 149, 186, 223, 298 and 335 mJ/cm², respectively.
The FE properties of the substrate were investigated in sphere-plane geometry with a typical electrode gap of 180 μm. Surface electrical contacts were made via conductive silver paste applied to edges of the sample. Figure 3.18(a) shows representative current-field characteristics of the o-MWNT on ITO-coated glass, treated with different laser fluences. From this data, we can deduce that laser irradiation does indeed result in an improvement in $E_{th}$. Figure 3.18(b) shows the FE data plotted in Fowler-Nordheim coordinates. The difference in slope for varying laser fluence shows that laser irradiation results in a change in $\beta$, or the work function.

No significant conditioning effects were observed after laser irradiation - the geometric reconstruction of the o-MWNT by the laser energy is similar in effect to the micro-arcing events, as previously discussed. The hysteresis before laser irradiation is around 3 V/μm, which is reduced to around 1.7 V/μm after laser irradiation. This hysteresis may be due to gas desorption effects, as previously discussed. After laser irradiation, this effect may be reduced due to laser-induced desorption of a large proportion of molecules on the o-MWNT surface before FE measurements are performed. Deviation of the FE current from Fowler-Nordheim behaviour is observed at around 1 μA, where the current begins to saturate. This is likely to be due to the resistance of the o-MWNT film limiting the current available at the emitting surface.
The threshold fields and enhancement factors extracted from the FE data are plotted versus the laser fluence in Figure 3.19, and a summary of the numerical results is presented in Table 3.20. Before irradiation, $E_{th}$ is high (18 V/μm) and $\beta$ is low (170) due to low surface roughness and screening effects, as previously discussed. The error in $E_{th}$ before irradiation is 3.7 V/μm which is relatively high, indicating poor reproducibility in emission across the sample. At low fluences, as the laser fluence increases, $E_{th}$ improves to 6 V/μm and $\beta$ increases to 810. This improvement in FE characteristics is due to morphological changes in the o-MWNT.
layer, as observed in Figure 3.17. The error in $E_{th}$ is reduced after laser irradiation, indicating an improvement in the uniformity of emission across the sample area. Another source of field enhancement may be expected at the cracks in the ITO layer, observed at grain boundaries in the SEM images.\textsuperscript{16,17} This cracking may additionally result in an increase in resistance of the ITO layer, however it is assumed that the overlaying o-MWNT network provides electrical contact between the individual ITO grains.

At higher laser fluences, $E_{th}$ deteriorates to 10 V/µm, and $\beta$ is reduced to 350. This is due to the further removal of o-MWNT from the ITO substrate by the laser irradiation process (see Figure. 3.17), resulting in FE from fewer sites. At the highest laser fluences, the incident energy is sufficient to partially remove and then melt the ITO layer. Field emission from the edges of the remaining ITO portions and the metallic islands of the melted ITO layer result in a lower $E_{th}$ and a higher $\beta$ than the original flat, untreated o-MWNT layer. It should also be noted that as o-MWNTs are removed from the surface, the work function (5.1 eV) will change to that of the underlying ITO (4.4 eV)\textsuperscript{16} which would affect the slope of the Fowler-Nordheim plot. At high fluences when the ITO is chemically modified, there will be a further change in work function. The local field, calculated as the product of $E_{th}$ and $\beta$ is calculated as 4.3 V/nm, and is equal for all samples (within error), as expected.

The FE properties presented here are slightly improved compared with those measured for o-MWNT on pristine glass substrates. This may be due to slight differences in the morphology and/or thickness of the initial o-MWNT layer, or more likely due to the additional morphological change due to the cracking of the underlying thin metallic ITO film resulting in an additional source of field enhancement. Using a thin underlying layer could be a simple and useful method of improving FE properties of thin o-MWNT films, and certainly warrants further investigation.
Figure 3.19: Plot of laser fluence versus $E_{th}$ and $\beta$.

<table>
<thead>
<tr>
<th>Laser Fluence (mJ/cm²)</th>
<th>Threshold Field (V/μm)</th>
<th>Hysteresis at 1 nA (V/μm)</th>
<th>Enhancement Factor (β)</th>
<th>Local Field (V/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18 ± 3.7</td>
<td>2.9</td>
<td>170 ± 20</td>
<td>3.1 ± 1.0</td>
</tr>
<tr>
<td>112 ± 11</td>
<td>12 ± 1.8</td>
<td>2.3</td>
<td>310 ± 30</td>
<td>3.7 ± 0.9</td>
</tr>
<tr>
<td>149 ± 15</td>
<td>11 ± 1.9</td>
<td>1.8</td>
<td>440 ± 50</td>
<td>4.8 ± 1.4</td>
</tr>
<tr>
<td>186 ± 19</td>
<td>6 ± 1.3</td>
<td>1.7</td>
<td>700 ± 80</td>
<td>4.2 ± 1.4</td>
</tr>
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<td>223 ± 22</td>
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<td>810 ± 90</td>
<td>5.7 ± 1.8</td>
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<tr>
<td>298 ± 30</td>
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<td>1.8</td>
<td>490 ± 50</td>
<td>4.4 ± 0.7</td>
</tr>
<tr>
<td>335 ± 34</td>
<td>10 ± 2.0</td>
<td>1.8</td>
<td>350 ± 40</td>
<td>3.5 ± 1.1</td>
</tr>
</tbody>
</table>

Table 3.20: Numerical summary of the FE properties of o-MWNT on ITO-coated glass substrates subjected to varying laser fluence.
3.4.5 Optical Transmission

Transmission spectra of the o-MWNT films were measured using pristine ITO-coated glass as a control. Figure 3.21(a) shows transmission spectra at different laser fluences. The transmission (with respect to air) at 550 nm is presented in Figure 3.21(b). Below 300 nm, all the samples strongly absorb the incident radiation. This is expected, since glass, ITO and o-MWNTs all strongly absorb at UV wavelengths. At low laser intensities, the transmission varies slowly as a function of laser fluence. It would be expected that the transmission would increase as o-MWNTs are destroyed or removed from the surface. However, as the laser fluence increases, more light is absorbed by the sample. This decrease in transmission is due to damage of the ITO layer, visible as cracks in the SEM images (Figure. 3.13(b)). This leads to scattering and absorption of incident light in the sample. At the optimum laser fluence for FE (186 mJ/cm²), the transmission is at 98% that of the untreated o-MWNT layer (at 550 nm), which shows that a large improvement in FE characteristics can be achieved without significant reduction in the transmission. At higher laser fluences, the transmission rapidly deteriorates as the ITO surface is modified by the incident laser energy and large surface features increase the amount of scattering from the sample.
Figure 3.21: (a) Transmission with respect to ITO-coated glass versus wavelength at differing laser fluences and (b) transmission versus fluence, measured at 550 nm.
3.4.6 ITO Control Sample

To confirm that these FE characteristics are not solely an effect of the ITO morphology change, pristine ITO substrates were subjected to the same laser irradiation process. The results are plotted in Figure 3.22. The trend here is contrary to the trend in $E_{th}$ observed in Figure 3.19. As laser fluence increases, $E_{th}$ at first increases to 30 V/μm, before slowly improving, finally reaching ~12 V/μm. This marked difference between Figure 3.19 and Figure 3.22 is evidence that the superior FE properties of the o-MWNT coated ITO are indeed due to the o-MWNT coating and not just the morphology change in the ITO layer. At high laser fluences (~350 mJ/cm²) the $E_{th}$ of the laser irradiated ITO substrates tends towards the values in Figure 3.19 (~12 V/μm). This supports the proposal that the o-MWNTs are completely removed at high fluence and that the FE properties at this point are largely due to the change in morphology of the ITO layer observed in Figure 3.17(f). The slight increase in $E_{th}$ at low fluence may be due to the removal of residual organic contaminant on the ITO surface. There is a possibility that laser irradiated pristine ITO-coated glass could be used as a transparent field emitter, without an o-MWNT layer. However, at 12 V/μm the emission occurs at too high a field to be useful, and the optical transmission is low.

![Figure 3.22: Laser fluence versus $E_{th}$ for laser irradiated ITO-coated glass substrates.](image)
3.5 Carbon Nanotube Ink on Plastic

3.5.1 Introduction

In the previous section, the FE characteristics of o-MWNT on glass and ITO-coated glass substrates were found to be improved by laser irradiation up to 186 mJ/cm². Although their FE characteristics compared well with those of other transparent field emitters reported in the literature, they still do not compare well with the best opaque emitters (< 1 V/μm). Therefore, in this section, o-MWNTs are applied onto transparent plastic substrates which have a higher surface roughness than glass, which should result in an improvement in the FE properties. The melting point of plastic is lower than that of glass and therefore a greater impact on the plastic morphology is expected under laser irradiation. Additionally, plastic substrates are flexible, low-cost and widely available. These samples are subjected to SEM and FE characterisation, and the transmission spectra recorded.

3.5.2 Sample Preparation

The samples were prepared by spin coating o-MWNTs onto pristine, oxygen plasma-treated acetate sheets at 2200 rpm. These were then baked at 70 °C for 10 minutes to remove residual moisture. The sample was exposed to single 25 ns pulses from a 248 nm UV excimer laser over a range of energies, at a vacuum better than 10⁻⁴ Torr. The laser spot size was 0.293 cm² which was used to calculate the incident fluence on the sample surface.

3.5.3 SEM Characterisation

Because plastic substrates are insulators and the o-MWNT layer is very thin, it is extremely difficult to obtain SEM images of the samples, even at high pressures using an environmental SEM technique. Figures 3.23(a) and 3.23(c) shows images from untreated samples and Figures 3.23(b) and 3.23(d) show those subjected to a laser fluence of 17 mJ/cm². Individual tubes can just be made out in each image. In the untreated sample, the o-MWNT layer can clearly be seen. However, the coverage is not complete and patches of insulating material are observed. These patches show up as 'charging' in the image, where insulating material is charged by incident electrons. Charging changes the secondary electron coefficient by modifying the local accelerating field. These patches are probably protruding from
the surface, which is why the o-MWNTs do not cover them. Due to the large size of these surface features, the samples were deemed unsuitable for AFM studies. After laser treatment, the insulating patches appear as bright spots in the images, suggesting that they have been altered by the laser irradiation process. It is likely that laser irradiation chemically modifies the plastic, resulting in an amorphous or graphitic carbon contaminant layer. Additionally, the surface of the plastic appears rougher after the laser irradiation, suggesting that the process changes the substrate morphology. At higher laser fluences it was impossible to obtain SEM images, due to the insulating nature of the substrates and the sparse distribution of o-MWNTs. However, it is assumed that the o-MWNTs form an interconnecting, conducting network, possibly including the graphitised plastic, since FE is still observed (see next section).

Figure 3.23: SEM images of o-MWNTs on plastic substrates (a),(c) before and (b),(d) after laser irradiation at 17 mJ/cm².
3.5.4 Field Emission Characterisation

The FE properties of the substrate were investigated in sphere-plane geometry with a typical electrode gap of 250 μm. Electrical contacts were made on the surface of the sample edges, using silver paste. Figure 3.24(a) shows representative current-field characteristics of the samples treated with different laser fluences and Figure 3.24(b) shows the data plotted in Fowler-Nordheim coordinates. From these results, it is evident that o-MWNTs on plastic substrates can have very low threshold fields even before laser irradiation, although the hysteresis values are very large. It can also be seen that laser irradiation results in an improvement in $E_{th}$ and a reduction in the degree of hysteresis. The saturation of the FE current observed at high fields is likely to be due to internal resistances in the sample. This saturation is more pronounced than that observed in previous samples on glass and ITO, suggesting that the resistance in these films is greater, as expected from the lower coverage of o-MWNTs observed in the SEM images. The hysteresis is so large as to mask any conditioning effects that may be present.
Figure 3.24: Current-field plots for o-MWNT on plastic substrates subjected to varying laser fluences.

Table 3.25 shows a numerical summary of the FE results. Figure 3.26(a) shows $E_{th}$ as a function of laser fluence and 3.25(b) shows $\beta$ as a function of laser fluence. Before laser irradiation, $E_{th}$ is already very low, at 0.9 V/µm with a large $\beta$ of 10400. These excellent FE properties are attributed to a relatively high surface roughness compared with that of glass, and also to reduced screening effects due to the lower surface coverage, as observed in Figure 3.23(a). Hysteresis values (Table 3.25) are extremely large for untreated samples (2.0 V/µm) and are reduced to 0.3 V/µm at high fluences, which is still large. Again, this hysteresis may be due to gas desorption effects. After laser irradiation, this effect is reduced due to laser-induced molecule desorption from the o-MWNT surface. However, these hysteresis values
are much larger than those previously observed, suggesting that these unusually large values are due to substrate effects. This could be due to the relatively 'soft' nature of the substrate, which may be susceptible to morphological changes under intense electric fields, leading to changes in the o-MWNT layer an in turn affecting $\beta$ and/or $E_{th}$, as a function of $E$. It may be the case that the plastic substrate is carbonised during the laser irradiation, observable as an increase in the secondary electron coefficient in Figure 3.23. If a significant portion of the FE current originates from this carbonised layer, it could account for the hysteresis, which is expected from amorphous carbon layers.\textsuperscript{19}

<table>
<thead>
<tr>
<th>Laser Fluence (mJ/cm\textsuperscript{2})</th>
<th>Threshold Field (V/\mu m)</th>
<th>Hysteresis at 1 nA (V/\mu m)</th>
<th>Enhancement Factor ($\beta$)</th>
<th>Local Field (V/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9 ± 0.1</td>
<td>2.0</td>
<td>10400 ± 2100</td>
<td>9.4 ± 2.9</td>
</tr>
<tr>
<td>17 ± 2</td>
<td>0.8 ± 0.3</td>
<td>1.2</td>
<td>7700 ± 1600</td>
<td>6.2 ± 3.6</td>
</tr>
<tr>
<td>34 ± 3</td>
<td>0.6 ± 0.1</td>
<td>0.6</td>
<td>11900 ± 2400</td>
<td>7.1 ± 2.6</td>
</tr>
<tr>
<td>51 ± 5</td>
<td>0.8 ± 0.2</td>
<td>0.3</td>
<td>12500 ± 2500</td>
<td>10.0 ± 4.5</td>
</tr>
<tr>
<td>103 ± 10</td>
<td>0.7 ± 0.1</td>
<td>0.3</td>
<td>10300 ± 2100</td>
<td>7.2 ± 2.5</td>
</tr>
<tr>
<td>137 ± 14</td>
<td>0.50 ± 0.02</td>
<td>0.3</td>
<td>21300 ± 4300</td>
<td>10.7 ± 2.6</td>
</tr>
<tr>
<td>171 ± 17</td>
<td>0.48 ± 0.09</td>
<td>0.3</td>
<td>12700 ± 2500</td>
<td>6.4 ± 2.5</td>
</tr>
</tbody>
</table>

Table 3.25: Summary of numerical results.

As laser fluence increases, $E_{th}$ starts at 0.8 V/\mu m at low fluences and is reduced to 0.5 at 171 mJ/cm\textsuperscript{2}. Additionally, the statistical error across the sample substrate is reduced from 0.3 V/\mu m to 0.09 V/\mu m. An increase in $\beta$ from 7700 to 21300 is observed. Due to the current rising extremely rapidly after the initial turn-on field, the data resolution in the Fowler-Nordheim regime of the current-field data is very low. Therefore, several of the Fowler-Nordheim curves have very few data points and the calculated values of $\beta$ can only be regarded as estimates.
These significant improvements in the FE properties are attributed to surface modification of the sample, resulting from the laser irradiation process. At low fluences, the o-MWNT form a dense mat, flat on the plastic surface, leading to screening and low geometric enhancement. As fluence increases, the surface of the plastic substrate is physically, and perhaps chemically, modified by the laser energy. This, in turn, results in a change in the o-MWNT layer, affecting $\beta$ and $E_{th}$. Additionally, o-MWNTs are removed from the plastic surface as the laser fluence increases, resulting in a less dense mat of o-MWNTs with increased field penetration and hence reduced field screening between individual o-MWNTs. It is also possible that the emission characteristics are at least partly enhanced due to graphitised surface features. This needs more investigation.
The local field at the emission site (calculated from the product of \( E_{th} \) and \( \beta \)) yields results which are equal within error, but are substantially higher than those previously encountered, and rather larger than expected for emission to occur. Fields this large are predicted to influence the chemical bonds in CNTs, resulting in field evaporation of carbon atoms.\textsuperscript{20}

It is possible that the large values of local field may arise because the resistance of this film is higher than that of those previously measured. This would result in larger values of \( E_{th} \) because the field would need to be higher to register the same current. Larger values of \( E_{th} \) would then result in larger calculated values of applied field. A similar effect has been observed by Smith et al\textsuperscript{21}, where the local field increased dramatically as MWNT loading in a polystyrene matrix was reduced.

However, the overly large values of \( \beta \) calculated from the Fowler-Nordheim curves also need to be explained. It is likely that the FE current in this case is not due solely to the o-MWNTs, which would be expected to result in similar values to those previously observed. More likely, the emission current is partially or wholly due to the polymer substrate, after it has been made conducting by the laser irradiation process. The polymer may have a significantly different work function to that used to calculate \( \beta \), resulting in an overestimate of the enhancement factor.

An alternative explanation is that estimating \( \beta \) from the slope of the Fowler-Nordheim plot may not necessarily be valid for non-ideal, non-metallic emitters. It has already been observed that the local field calculated for o-MWNTs on glass is rather larger than expected for an ideal metallic emitter. It is suggested that the carboxylic group on the MWNT surface disrupts the delocalised \( \pi \)-electron network to such an extent that the MWNT can no longer be considered as purely metallic. This leads to a deviation from the ideal value of \( \beta E_{th} \) (\( \approx 1 \) V/nm) to a larger value (5 V/nm). In this case, \( \beta E_{th} \) is calculated as 10 V/nm, suggesting that the emitter is even more removed from the idealised metallic emitter. If we assume that the emission originates from the plastic substrate, chemically modified by the thermal energy of the laser pulse, then this deviation from the case of an idealised metallic emitter can be justified. If we assume that the values of \( \beta E_{th} \) are overestimates by approximately an order of magnitude, we must also assume that \( \beta \) is overestimated by a similar amount. This would bring the \( \beta \) values down from an average of ~
12000 to an average of around 1200. This lower value is closer to those expected for such a sample.

These very high $\beta$ values could alternatively be attributed to the lowering of the work function under large electric fields, as described in Section 1.3.2. The degree of barrier lowering at a given electric field is given by Equation 1.5, where $\varepsilon_0$ is the permittivity of free space.\(^2\)

$$\Delta \phi = \sqrt{\frac{eF}{4\pi\varepsilon_0}} \quad [1.5]$$

Substituting values into this equation we get that $\Delta \phi = 1.2$ eV at field of $10^9$ V/m, implying that the effective work function at this field is 3.9 eV. According to Equation 1.4, lowering the work function results in a reduction in $\beta$. This effect is demonstrated in Figure 3.27 for three of the above samples. A wide range in $\beta$ is observed when the work function is varied from 5.1 eV to 2.5 eV. At 3.9 eV, $\beta$ is significantly reduced from 21300 to 14200 for samples irradiated at 137 mJ/cm\(^2\). This reduction in $\beta$ at high fields results in more reasonable values. However, it should be noted that this lowering of the effective work function would be applicable to any electron emitter under high fields and therefore the values of $\beta$ reported in this work must still be directly compared to those reported in the literature.

![Figure 3.27: Variation of $\beta$ with changing work function for o-MWNT on plastic substrates subject to laser irradiation at 0, 34 and 137 mJ/cm\(^2\).](image)
Several groups have reported similarly large values of \( \beta \) in their work. Huang et al. reported values of \( \beta \) up to 18800 in FE from branched CNTs grown on carbon cloth. They attributed this to a giant multistage field enhancement effect, whereby the total value of \( \beta \) is a product of the individual enhancement factors of the carbon cloth and the branched CNTs.\(^{23}\) This product rule could explain the high \( \beta \) values reported here, however in Figure 3.23 it is not clear from where such a multistage effect could arise in these samples.

Umnov et al. reported values of \( \beta \) up to 10600 in FE from CNTs, however they observed atomic field evaporation from their samples at high fields.\(^{24}\) Li et al. have reported values of \( \beta \) of \( \sim 25,000 \) from CNTs grown on silicon micro-pillars. Therefore, although the values of \( \beta \) reported in this work seem very large, they are comparable to values reported in the literature.

### 3.5.5 Current Density and Site Density Measurements

Current density (\( J \)) measurements were carried out on the samples, because of their particularly low \( E_{th} \) values. Samples were placed in a planar FE cell, with a sample-anode gap of 970 \( \mu \)m (measured by micrometer) and an emitting area of 0.585 cm\(^2\). The current density measurements are shown in Figure 3.28. The current-field curves are similar in shape to those measured in the probe FE configuration, and \( E_{th} \) is of the same order, as expected. There is a large degree of saturation in the FE current compared to the probe FE experiments on the same samples. This indicates that contact resistances limit the current available at the emitting surface. In the case of probe FE, the total emitted current is limited to the area below the probe and is therefore relatively low. In the planar case, the emitting area is much higher and therefore the total current is higher and more likely to be limited by resistances in the system, especially between the contact and the emission sites. Initially, low current densities were measured; around 3.2 \( \mu A/cm^2 \) at 3 V/\( \mu \)m. This is almost certainly because the FE was limited to just a few small emission sites. To confirm this, the ITO-coated glass was replaced by a phosphor screen to determine the emission uniformity across the substrate.
Figure 3.29 shows digital photographic images of the planar FE cell with a phosphor anode. Figure 3.29(a) shows the cell at zero bias. At 3 V/μm, only a small emission spot is observed. This explains the low current density in the current-field curves. However, once the applied voltage is increased to 4 V/μm, the single emission spot burns out and large areas of the sample begin to emit (Figure 3.29(c)). After reducing the voltage back down to 3 V/μm, the sample still emits fairly uniformly across the substrate (Figure 3.29(d)). After this current conditioning process, the current density was increased to 100 μA/cm² at 1 V/μm. This conditioning process could be routinely applied to samples to improve their emission characteristics. If the laser irradiation process is optimised and the plastic substrate material is altered, it is may be that this conditioning phase could be reduced or completely removed.
3.5.6 Optical Transmission Characterisation

Optical transmission measurements were performed on the samples. Figure 3.30 shows the transmission at 550 nm with respect to air, as a function of increasing fluence. Before laser treatment, the sample has an optical transmission of 80.5%, and this falls as laser fluence increases, down to a minimum of 70.0%. At the highest laser fluence (171 mJ/cm²) the transmission is 70%, which is a decrease of around 10% from the original value. This decrease in transmission as the laser fluence increases is probably due to increased scattering as the o-MWNT layer and the plastic are roughened by the laser impulse. Additionally, the laser pulse may chemically change the plastic surface and hence increase absorption at 550 nm.
3.6 Summary and Conclusions

In this chapter, a study of FE from o-MWNT deposited on various transparent substrates was discussed. Initially, o-MWNT ink was spin-coated onto pristine glass substrates, resulting in a tangled o-MWNT mat. These films were homogeneous across large areas (>20 mm) and found to be very smooth (~10 nm RMS). However, the FE properties of these o-MWNT films were poor, with $E_{th}$ of the order 20 V/$\mu$m. SEM images taken after the emission revealed large damaged features at the emission sites. These poor emission properties reflected the low surface roughness and close tangling of the o-MWNT layer, leading to low geometric field enhancement and large screening effects.

To improve the FE characteristics, it was necessary that the surface roughness be altered such that the local field at the emitting surface could be increased. Therefore, the samples were irradiated with light from a UV laser source in an attempt to alter the morphology of the o-MWNT layer. After laser irradiation at various fluences, the morphology profoundly changed and this was observable by SEM. The FE properties were improved at moderate fluences (8 V/$\mu$m at 343...
mJ/cm²) and deteriorated at the highest fluences as o-MWNTs were completely removed from the surface. Only minor modification of the underlying glass substrate was observed. The experiment was repeated for o-MWNT layers on ITO-coated glass substrates. A similar trend in improvement of FE characteristics was observed (6 V/µm at 186 mJ/cm²), however the peak in emission properties occurred at a lower laser fluence. This difference is attributed to the underlying ITO layer, which is itself affected by the UV laser pulse, resulting in a morphology change in the o-MWNT layer that is different from that of o-MWNTs on pristine glass substrates.

If a thin, metallic ITO layer can result in improved FE properties of laser irradiated films, then the substrate must be important in determining the FE properties. Therefore, the experiment was repeated with o-MWNT on pristine acetate sheets. The FE characteristics of these films before laser irradiation were already much better than those on glass substrates and this improved with increasing fluence to 0.5 V/µm at 137 mJ/cm². These excellent FE characteristics are attributed to the very different morphology of the plastic substrates compared with those of glass substrates. The underlying plastic substrate is also more susceptible to morphological changes under laser irradiation, because it is made of much softer, less stable material with a lower melting point. Current density measurements were carried out on laser irradiated o-MWNTs on plastic substrates because these seem the most promising for practical applications. Low current densities were initially observed; therefore density mapping was undertaken using a phosphor screen. This confirmed that highly localised emission from small areas was limiting the total current density. After conditioning at higher voltages, emission was observed over large areas.

In conclusion, we have determined that laser irradiation can be used to alter the morphology of o-MWNT layers on transparent substrates, resulting in improved FE characteristics. Additionally, it was discovered that the underlying substrate has a significant role to play in this improvement.
3.7 References

Chapter 4: Electron Field Emitters on Paper

4.1 Motivation

In the previous chapter, very flat, smooth layers of o-MWNTs were found to have poor FE properties. Applying a post-deposition laser treatment had the effect of changing the morphology of the o-MWNT layer, resulting in protruding o-MWNT structures with improved FE properties. The initial o-MWNT layers were smooth as a result of the low surface roughness of the underlying substrate. By depositing o-MWNT ink onto substrates with inherent complex morphology, the geometric field enhancement is expected to be increased, without resorting to post-deposition treatments.

In this chapter, the deposition of o-MWNT ink onto paper substrates is investigated as a means to increase the geometric field enhancement by taking advantage of the inherent roughness of the substrate. Paper substrates also have the advantages of low cost, wide availability and flexibility. The field emission characteristics are investigated as a function of the varying morphology of the substrates. Finally, a post-deposition laser treatment is used to further modify the morphology of the samples.

4.2 Effects of Substrate Morphology on Field Emission

4.2.1 Introduction

The morphology of a surface plays a crucial role in determining its FE properties.\(^1,2\) It is the local electric field at the emission site that governs emission, so geometric field enhancement due to micron and nanoscale protrusions can greatly enhance emission. Therefore, by altering the morphology of an emitter, \(\beta\) and consequently \(E_{th}\) would be expected to vary. In this section, o-MWNTs are deposited onto paper substrates via a straightforward dip-coating process. The field emitting properties of these substrates are investigated as a function of the surface roughness (and thereby the morphology) of the underlying paper substrate.\(^3\) This technique brings about the possibility of directly depositing nanotubes in a controlled manner onto a plethora of pre-patterned substrates with surface morphology chosen to maximise \(\beta\).
4.2.2 Sample Preparation

A variety of paper substrates were obtained from various sources, chosen specifically for their varying micro-scale structure. These were cut into 1 cm² pieces, dipped into o-MWNT ink, removed and baked at 100°C for ten minutes to remove residual moisture.

4.2.3 Surface Roughness

A profilometer was used to measure the average surface roughness (Ra) of the different types of paper, which varied from 1.3 μm to 9.8 μm. Measurements were carried out over a 2 mm scan length, at least 10 times on each sample.

4.2.4 SEM Characterisation

SEM images of the various substrates are presented in Figure 4.1. Figures 4.1(a) to 4.1(c) show the morphology of the paper scaffold with the lowest surface roughness, after the o-MWNT dip-coating process. Figures 4.1(d) to 4.1(f) show the morphology of the paper substrate found to have the largest surface roughness. The difference between the two samples is clear; the low Ra sample has relatively few, widely-spaced surface features and the high Ra sample comprises large, closely packed protruding features. These features are made up of interwoven fibres approximately 25 μm wide. A uniform coating of o-MWNTs is observed on the surface of these fibres at high magnification. Both samples show excellent surface coverage by the o-MWNT ink.
Figure 4.1: SEM images of (a) to (c); low roughness paper substrate ($R_A = 1.3 \, \mu m$) coated with o-MWNT ink and (d) to (f); high roughness paper ($R_A = 4.9 \, \mu m$) substrate coated with o-MWNT ink.
4.2.5 Probe Field Emission Characterisation

The FE properties of the samples were investigated in sphere-plane geometry with a typical electrode gap of 200 μm. Electrical connections were made via top contacts of silver paste, at the edges of the paper substrate. Figure 4.2(a) shows representative current-field characteristics for all the substrates. It is apparent from this graph that the differing paper substrates have very different FE characteristics, with a wide range in $E_r$. Very little hysteresis was observed between the up and down cycles and no conditioning was observed in the first cycle. These are very important properties if the cathodes are to be used in FEDs. Figure 4.2(b) shows the above data plotted in Fowler-Nordheim coordinates. A wide range in the slopes of the graphs is observed, suggesting a wide range in $\beta$. Some saturation is observed in the FE current at high fields. This may be due to the resistance of the films limiting the current available at the emitting cathode. However, this saturation is much less prevalent than previously observed in transparent o-MWNT films, suggesting that the resistances are lower. This is expected, since the films studied here are much thicker than those previously studied, due to the difference in the deposition technique.
A numerical summary of the FE characteristics is presented in Table 4.3, whilst $E_{th}$ and $\beta$ are plotted versus surface roughness in Figure 4.4. A glass slide spin-coated with o-MWNTs was also characterised to represent a ‘flat’ zero-point roughness ($R_A = 23$ nm). A clear trend is observed, where the FE characteristics improve as $R_A$ increases. $E_{th}$ varies widely from 11.6 V/\mu m at low $R_A$ down to 0.8 V/\mu m at high $R_A$, in an approximate inverse linear-log relationship. Equally, a wide range in $\beta$ was observed, from 470 at low $R_A$ to 4700 for high $R_A$ substrates. The very high values of $\beta$ could be partly due to a giant multistage geometric enhancement effect arising
from the product of the separate enhancement factors of the paper substrate and the o-MWNT coating. The statistical error in Eth is reduced from 3.9 V/µm for low RA substrates to 0.2 V/µm for high RA substrates, indicating that the surface roughness of the underlying substrate plays an important role in the uniformity of emission over the area of the substrate. Additionally, a reduction in hysteresis from 1.9 to 0.05 V/µm was recorded with increasing RA. The local field (|3Eth|) remains constant at around 4.8 V/nm within error, as expected.

<table>
<thead>
<tr>
<th>Surface Roughness (µm)</th>
<th>Threshold Field (V/µm)</th>
<th>Hysteresis at 1 nA (V/µm)</th>
<th>Enhancement Factor (β)</th>
<th>Local Field (V/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 ± 0.3</td>
<td>11.6 ± 3.9</td>
<td>1.9</td>
<td>470 ± 50</td>
<td>5.5 ± 2.4</td>
</tr>
<tr>
<td>2.4 ± 0.3</td>
<td>6.0 ± 0.3</td>
<td>0.6</td>
<td>670 ± 70</td>
<td>4.0 ± 0.6</td>
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<tr>
<td>3.4 ± 0.7</td>
<td>7.5 ± 1.8</td>
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<td>4.4 ± 1.1</td>
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</tr>
<tr>
<td>4.9 ± 0.8</td>
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<td>0.2</td>
<td>3900 ± 400</td>
<td>5.9 ±1.4</td>
</tr>
<tr>
<td>9.8 ± 1.0</td>
<td>0.8 ± 0.2</td>
<td>0.05</td>
<td>4700 ± 500</td>
<td>3.8 ± 1.4</td>
</tr>
</tbody>
</table>

*Table 4.3: The surface roughness and FE properties of pure o-MWNT ink on paper substrates.*
These trends are attributed to the varying morphology of the substrates. The low $R_A$ paper is smooth with few, widely spaced, low aspect ratio surface features. This results in low geometric field enhancement and therefore the samples have low $\beta$ and high $E_{th}$. The high $R_A$ paper substrates have very complex morphology with many, closely spaced, high aspect ratio surface features. This results in high geometric field enhancement, and therefore the samples have high $\beta$ and low $E_{th}$.

**4.2.6 Planar Field Emission Characterisation**

Planar FE characterisation was carried out on suitable paper substrates to determine the FE current density. Circular o-MWNT-coated paper samples were used, with an area of 0.196 cm² and the distance from the surface of the substrate.
to the anode was 965 μm. A graph of the results is presented in Figure 4.5. The current density at 1.2 V/μm is 27 μA/cm². This value is comparable to values found in the literature measured under similar conditions (see Section 1.5), and is recorded at a lower applied electric field. However, this current density is low compared to values quoted for some modern devices, but these large current densities are measured at very high applied fields. Additionally, the current density here is limited by resistances between earth and the emitting surface, observed as a saturation of the current at high applied fields.

Figure 4.5: Planar FE current density characteristics for o-MWNT ink on paper.
4.3 Laser Irradiation of Carbon Nanotube Ink on Paper

4.3.1 Introduction

It has already been determined that o-MWNTs deposited onto paper substrates can have excellent FE properties, which can be tailored according to the morphology of the specific paper substrate utilised. In this section, the effects of a post-deposition treatment via excimer laser-processing are investigated.

4.3.2 Sample Preparation

Samples were prepared as previously described, by dip-coating commercially available scientific filter paper (RA = 4.9 µm) into the o-MWNT solution and then baking for 10 minutes at 100°C to remove moisture from the substrate. The sample was exposed to a single 25 ns pulse from a 248 nm pulsed UV excimer laser over a range of energies. The area of the laser spot was 0.18 cm², which was used to calculate the incident fluence on the sample surface. Irradiation was carried out at a vacuum better than 10⁻⁴ Torr.

4.3.3 SEM Characterisation

Figures 4.6(a) to 4.6(f) show SEM images of o-MWNTs on paper substrates irradiated with laser fluences of 0, 28, 56, 83, 111, and 139 mJ/cm², respectively. In Figures 4.6(a) and 4.6(b), the paper is homogeneously coated with an o-MWNT layer and no change in the surface is observed. It is concluded that a laser fluence of 28 mJ/cm² has insufficient energy to affect the o-MWNT layer. In figures 4.6(c) to 4.6(e), portions of the o-MWNT layer have peeled away from the underlying paper substrate, and protrude from the surface almost perpendicularly. These surface features are just a few tens of nanometres thick and tens of microns in length. The uniformity of this surface modification extends over hundreds of microns and seems to be limited only by the Gaussian wavefront of the laser beam. The degree of surface modification increases as the laser fluence increases. Finally, in Figure 4.6(f) a large degree of modification of the o-MWNT layer is observed. Some charging effects are observed at the bottom of the image, where the o-MWNT layer has been completely removed and the underlying insulating paper substrate is exposed to the electron beam. The remaining protruding o-MWNTs form much smaller features with clusters of just a few individual o-MWNTs. Comparing Figures
4.6(a) and 4.6(f) it is clear that the laser irradiation process has a profound impact on the morphology of the surface of these samples. The mechanism behind the formation of the surface features in the o-MWNT layer is likely to be associated with structural defects induced by the laser irradiation process (see Section 1.4.5). Specifically, it is probable that structural defects occur largely at the exposed surface of the o-MWNT layer. This could be a source of thermal stress between the top surface and the underside of the o-MWNT layer, leading to structural reformation (i.e. curling) to restore equilibrium. This scenario fits very well with the features observed in the SEM images, many of which have a uniform radius of curvature over a distance of several microns, indicative of the uniformity of defect formation.
Figure 4.6: SEM images of the paper substrates coated with o-MWNTs and irradiated with laser fluence 0, 28, 56, 83, 111, and 139 mJ/cm², respectively.
4.3.4 Probe Field Emission Characterisation

The FE properties of the laser irradiated o-MWNT on paper substrates were investigated in sphere-plane geometry with a typical electrode gap of 200 μm. Electrical connections were made via top contacts at the edges of the paper substrate. The FE characteristics of the laser irradiated substrates are presented in Figure 4.7. Figure 4.7(a) shows the current-field curves and Figure 4.7(b) shows the data plotted in Fowler-Nordheim coordinates for paper substrates treated with different laser fluences. A large range in $E_{th}$ and the slope gradients are observed, indicating that laser irradiation has a large impact upon the FE properties of the o-MWNT layer.

Although no initial current conditioning occurs in the field emission curves, the hysteresis appears to be slightly larger than that measured for samples without laser irradiation. This may be due to field-dependant shifting of the micron-scale protrusions observed under SEM, whereby the geometric field enhancement is asymmetrically field dependant due to the changing aspect ratios of these features. There is some saturation in the current at high fields, which is likely to be due to resistance in the o-MWNT layer.

This improvement in the FE properties with increasing laser fluence is due to the restructuring of the o-MWNT layer by the incident laser energy, observable in Figure 4.6. The protruding o-MWNT layers are extremely thin and would be expected to have a high field concentration at their tips, contributing to high $\beta$. As the laser fluence increases and more protruding o-MWNT layers are created, more FE sites are created and the emission characteristics improve. At the highest laser fluence, the emission characteristics deteriorate slightly, due to extensive surface damage of the sample, leading to lower o-MWNT coverage and therefore fewer FE sites.
A numerical summary of the FE characteristics is presented in Table 4.8, whilst $E_{th}$ and $\beta$ are plotted against the incident laser fluence in Figure 4.9. Comparing untreated substrates with those irradiated at 28 mJ/cm², it is observed that both have almost identical FE characteristics, with an $E_{th}$ of 4.8 and 4.7 V/µm respectively, and both having a hysteresis of 0.9 V/µm. This is further evidence that a laser fluence of 28 mJ/cm² has insufficient energy to restructure the o-MWNT layer. As the laser fluence increases, $E_{th}$ decreases, the hysteresis decreases and $\beta$. 

Figure 4.7: (a) Current-field curves for substrates subjected to various incident laser fluences and (b) current-field data plotted in Fowler-Nordheim coordinates.
increases, peaking at 111 mJ/cm². Here, $E_{th}$ is 2.1 V/μm and $\beta$ is 2300. The statistical error in $E_{th}$ shows a general decrease as laser fluence increases, indicating that increasing the laser fluence improves the uniformity of emission. At the highest laser fluence (139 mJ/cm²) a slight deterioration in $E_{th}$ is observed, with a higher error, and $\beta$ is reduced to 1900. The local field ($\beta E_{th}$) is approximately constant at 4 V/nm within error, as expected.

<table>
<thead>
<tr>
<th>Laser Fluence (mJ/cm²)</th>
<th>Threshold Field (V/μm)</th>
<th>Hysteresis at 1 nA (V/μm)</th>
<th>Enhancement Factor ($\beta$)</th>
<th>Local Field (V/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.8 ± 0.6</td>
<td>0.9</td>
<td>850 ± 90</td>
<td>4.1 ± 1.0</td>
</tr>
<tr>
<td>28 ± 3</td>
<td>4.7 ± 0.6</td>
<td>0.9</td>
<td>700 ± 80</td>
<td>3.3 ± 0.8</td>
</tr>
<tr>
<td>56 ± 6</td>
<td>2.7 ± 0.6</td>
<td>0.4</td>
<td>1200 ± 130</td>
<td>3.2 ± 1.1</td>
</tr>
<tr>
<td>83 ± 8</td>
<td>2.6 ± 0.5</td>
<td>0.4</td>
<td>1600 ± 180</td>
<td>4.2 ± 1.3</td>
</tr>
<tr>
<td>111 ± 11</td>
<td>2.1 ± 0.1</td>
<td>0.3</td>
<td>2300 ± 250</td>
<td>4.8 ± 0.8</td>
</tr>
<tr>
<td>139 ± 14</td>
<td>2.2 ± 0.4</td>
<td>0.3</td>
<td>1900 ± 210</td>
<td>4.2 ± 1.2</td>
</tr>
</tbody>
</table>

Table 4.8: Summary of the FE properties of α-MWNT ink on paper substrates subjected to laser treatment.

Figure 4.9: $E_{th}$ and $\beta$ of samples subjected to various incident laser fluences
4.4 A Three-Terminal Device Fabricated by Lamination

4.4.1 Introduction

In this section, the o-MWNT-paper cathodes previously discussed are incorporated into three-terminal devices. These devices utilise the flexibility and thin dimensions of the paper cathodes and are fabricated using a simple lamination technique. The purpose of fabricating these devices is a proof of concept that printed o-MWNT-coated paper cathodes can be incorporated into cheap devices, quickly and via very simple methods. If these three-terminal devices can be fully optimised, the route to industrialisation would be fast, utilising only the well-established techniques of printing, metal deposition and plastic lamination.

4.4.2 Device Fabrication

Paper cathodes were prepared by drop-casting an o-MWNT layer onto filter paper. A diagram of the 3-terminal device is schematically represented in Figure 4.10. Commercially available laminate plastic (thickness 60 μm) is sputtered with gold (100 nm) and pierced with holes ~ 50 μm in diameter, using a scanning tunnelling microscopy probe. The o-MWNT coated paper cathode is placed in between the laminate plastic sheets, and fed through a conventional desktop laminator. The laminator heats the sample and bonds the laminate layers to one another, sandwiching the paper cathode in-between. This creates the basic device, in which the o-MWNT coated paper acts as a cathode, the laminate layer acts as a 60 μm spacer, and the gold layer acts as a gate anode. The total thickness of the device is just 230 μm (measured by micrometer) and contact to the o-MWNT layer is made by very thin copper wires.
4.3.3 SEM Characterisation

An SEM image of one of the holes in the gold-coated laminate is shown in Figure 4.11. The gold gate can be seen on the surface of the laminate and around the edge of the hole, which is approximately 50 μm in diameter. The laminate layer is depressed around the edge of the hole as a relic of the piercing process. This could be resolved by using established laser drilling techniques, ion beam drilling, or nano-imprinting. Imaging inside the hole was impossible, due to charging effects arising from the insulating laminate layer, and the underlying paper layer.

Figure 4.11: Typical SEM image of the gated laminate structure.
4.4.4 Two-Terminal Field Emission Characterisation

The FE properties of the structure can be investigated by utilising the gate as an anode and electron collector, i.e. operating it as a two-terminal device. Therefore, the device was placed into the probe FE chamber, a voltage supply was connected to the gold terminal and the o-MWNT layer connected to earth. The voltage was increased and the resulting current measured, as previously described.

Figure 4.12 shows the FE characteristics of the structure. Some hysteresis was observed (perhaps due to charging of the laminate walls inside the hole); however the results are markedly similar to those obtained for similar paper cathodes tested using sphere-to-plane geometry. The working voltage of this structure was around 60 V (1 V/µm) which is remarkably low for such a simplistic device. Assuming that the diameter of the hole is 50 µm and taking the current as 1 mA, the current density for the device is calculated to be 51 mA/cm². This compares very well with those values reported in the literature. A saturation of the FE current at high fields was observed, probably because of a large contact resistance between the copper wires and the o-MWNT layer, or the large resistance of the o-MWNT layer itself.

![Figure 4.12: Two-terminal current-field characteristics of the laminated structure.](image)
4.4.5 Three-Terminal Field Emission Characterisation

The FE characteristics of the gated structure were measured in three-terminal mode, using a spherical probe as the anode. The gate voltage was varied from 0 V to 60 V. Figure 4.13 shows the FE current as a function of the applied voltage at different gate voltages. From 0 V to 40 V (0.7 V/μm), no emission current is observed at the anode. This is because the gate voltage is not sufficient to extract electrons from the cathode. At 60 V (1 V/μm), a FE current of 100 nA is detected with the anode at ~ 400 V, showing that the gate voltage is sufficient to extract electrons from the cathode with sufficient energy to reach the anode. These are remarkably good results from prototype devices that are extremely simple to fabricate. The shape of the emission curve is remarkably similar to that observed in two-terminal measurements on the same sample, and the same resistance-induced saturation of the FE current is observed at high fields.

![Figure 4.13: Emission current versus applied voltage at varying gate voltages.](image)

It is envisaged that a further step may be taken via a second lamination stage (Figure 4.14). This would incorporate a second laminate layer, acting as a second spacer for a phosphor coated anode. If this entire process can be realised, a fully integrated three-terminal device would result from a remarkably simple fabrication process.
4.5 Summary and Conclusions

In this chapter, a study of FE from o-MWNT ink deposited on paper substrates was carried out. Paper substrates were chosen as cheap, flexible, readily available materials, and as established substrates for printing technologies. A study of how substrate morphology affects the FE characteristics was performed by depositing o-MWNT on paper substrates with different surface roughness. As the surface roughness increased (and thereby the surface morphology was modified), $E_{th}$ was found to improve, peaking at 0.8 V/µm at a surface roughness of 9.8 µm. This study showed how straightforward it is to tailor $\beta$ (and thereby the FE properties) of an o-MWNT layer by changing the morphology of the underlying substrate.

Then, paper substrates were irradiated with UV laser light. A study was made of the changing morphology and FE properties of the o-MWNT layer with increasing laser fluence. As fluence increased, the morphology (and thereby $\beta$) of the o-MWNT layer was altered and $E_{th}$ was observed to improve. This showed that a simple post-deposition treatment can be used to improve the emission characteristics of a thin o-MWNT layer on paper substrates.

Finally, paper substrates coated with o-MWNTs were incorporated into a laminate sandwich structure, where a 60 µm plastic layer acted as a spacer between the o-MWNT cathode and a gold anode. This structure showed promising FE results and
emission was observed at a gate voltage of 60 V and an anode voltage of 400 V, and a current density of 51 mA/cm² was achieved. This structure, once optimised may form the basis of a fully operational three-terminal device.

In this chapter it has been shown that it is possible to create cathodes with excellent FE properties by utilising the simplest fabrication materials and techniques. By printing o-MWNT ink onto paper substrate, excellent FE properties have been achieved. Laser irradiation has been shown to improve these FE properties. Finally, by using printing, paper substrates, metal sputtering and plastic lamination, a structure has been fabricated that (once optimised), has the potential to be used as part of an integrated display. This device is thin and light, and very low cost.

4.6 References

Chapter 5: Chemical Derivatisation of Nanotube Ink

5.1 Motivation

In the previous chapters, β was tailored to improve the FE properties of o-MWNT-based cathodes. However, theoretically there is a more fundamental method of improving the efficiency of field emission. Looking to the Fowler-Nordheim equation, it is not just β, but also the work function (WF) of a material which plays a vital role in the FE properties (see Section 1.3.5). If the WF of a material can be reduced, the FE characteristics should be improved. Furthermore, if this WF reduction can be realized via simple, room temperature chemical derivatisation, it could be achieved on a large industrial scale using established chemical engineering techniques. In this chapter, the WF of o-MWNT ink is modified via facile alkali cation exchange. The effects of this WF shift upon the FE characteristics of o-MWNT ink are investigated.

5.2 Work Function Tailoring of Carbon Nanotube Ink

5.2.1 Introduction

The WF of a surface plays a crucial role in determining its field emission properties (see Figure 1.10). The WF of MWNTs is particularly sensitive to acid oxidative treatments. During the acid oxidisation process, oxygen containing moieties form on the surface of the MWNT, including carboxyl groups. These surface carboxyl groups reduce the π-conjugation of the MWNT and introduce inward-pointing surface dipole moments, leading to a higher WF. This WF can be reduced by converting carboxylic surface groups to salts of alkali cations, because the surface dipole is sensitive to the nature of the associated cation. In this section, o-MWNTs are chemically modified via lithium cation exchange. The FE properties of these lithium-functionalised MWNTs are compared with those of o-MWNTs and related to the change in WF.

5.2.2 Lithium Cation Exchange

An o-MWNT ink was prepared as previously described. Lithium cation exchange (schematically represented in Figure 5.1) was achieved by dispersing 4x10^-4 moles of LiOH per mg of o-MWNTs in 2 ml of HPLC grade deionised water. Solutions were
thoroughly mixed in an ultrasonic bath for 30 minutes prior to filtration and then washed with pure water until the filtrate was pH neutral, ensuring the removal of excess hydroxide. Herein, LiOH treated o-MWNTs will be referred to as Li+MWNTs. It should be noted that other, non-carboxylic surface groups will not necessarily interact with Li ions.

![Figure 5.1: Schematic of the cation exchange process](image)

**5.2.3 Sample Preparation**

Carbon fibre fabric was used as a substrate, due to its high conductivity and excellent field emission properties. The as-purchased carbon fibre fabric was extremely hydrophobic and initially little or no wetting between it and the MWNT ink occurred. To render the carbon fibre hydrophilic, it was subject to a 10-second microwave oxygen plasma treatment. This partially oxidizes the carbon fibre surface, resulting in the formation of oxygen containing moieties, including alcohol groups. Polar oxygen containing moieties such as alcohol groups readily interact with water molecules via hydrogen bonding. Therefore, wetting between the MWNT ink and the carbon fibre becomes favourable. Additionally, hydrogen bonding is expected to provide strong adhesion between the carbon fibre and the o-MWNT layer.

After oxygen plasma treatment, a 1 cm$^2$ sample of carbon fabric was dip-coated into the o-MWNT ink and another identical sample into the Li+MWNT ink. The samples were then removed and baked at 100°C for 20 minutes to remove residual water.
5.2.4 SEM Characterisation

Figure 5.2(a) shows SEM images of the pristine carbon fibre at high magnification. This is compared to the same fibre after oxygen plasma treatment in Figure 5.2(b). Evidence of the surface modification by the plasma treatment is observable as inhomogeneity at the nanoscale. After being coated with o-MWNTs, individual o-MWNTs can clearly be seen in Figures 5.2(c) and 5.2(d) as a uniform layer across the whole carbon fibre surface. The o-MWNT layer appears to be well adhered to the carbon fibre, and the coating is continuous. SEM images of carbon fibre coated with Li+MWNTs (not shown) were identical to the o-MWNT-coated carbon fibre.

![Figure 5.2](image)

*Figure 5.2: SEM images of (a) pristine carbon fibre, (b) carbon fibre after oxygen plasma treatment and (c) to (d) o-MWNT coated carbon fibre.*
5.2.5 Field Emission Characterisation

The FE characteristics of the samples were investigated in sphere-plane geometry with a typical electrode gap of 3 mm. Electrical connection was made via back contacts of conductive carbon adhesive tabs. Figure 5.3 shows the current-field curves of the samples. It is apparent from this graph that the different samples have very different FE characteristics, and that Li⁺MWNTs have much improved FE properties as compared with o-MWNTs.

![Figure 5.3: Current-voltage characteristics for pristine, plasma treated, o-MWNT-coated and Li⁺MWNT-coated carbon fibre fabric.](image)

Numerical results are summarised in Table 5.4. The pristine carbon fibre fabric has an $E_{th}$ of 0.42 V/μm with a hysteresis of 0.20 V/μm, and a statistical error of ± 0.03 V/μm. After oxygen plasma treatment, $E_{th}$ is observed to rise to 0.58 V/μm with a larger hysteresis of 0.23 V/μm and larger statistical error of ± 0.15 V/μm. This increase in $E_{th}$ can be attributed to the increase in the WF of the carbon fibre upon plasma treatment. Ago et al. have previously shown that the WF of pristine MWNTs (~ 4.4 eV) is close to that of graphite (~ 4.4 eV) and oxygen plasma treatment increases the WF to 4.8 eV. Since carbon fibres and MWNTs both comprise graphitised carbon, a similar increase in the WF of carbon fibres could be expected. Owing to the porous nature of the carbon fibre fabric, it was not possible to make a
direct measurement of the WF using ultraviolet photoelectron spectroscopy. The slight increase in hysteresis and substantial increase in error across the sample is indicative of the uneven etching of the carbon fibre by the plasma oxidization process (see Figure 5.2(c)).

Coating the plasma treated carbon fibre with o-MWNTs results in a decrease in $E_{th}$ back down to 0.42 V/μm, with a hysteresis of 0.08 V/μm, and a statistical error of ±0.09 V/μm. This significant reduction in hysteresis, error and $E_{th}$, is indirect evidence that FE occurs predominantly from the o-MWNTs themselves. The reduction in $E_{th}$ compared with the plasma treated fibre is attributed to the modification of the surface geometry due to the o-MWNTs, resulting in an overall increase in geometric field enhancement and therefore a higher local field at the emitting sites. However, since the WF of o-MWNTs (5.1 eV) is much larger than that of pristine graphitic carbon fibre (4.4 eV), the beneficial effect of β is offset by the increase in work function.

Coating plasma treated carbon fiber fabric with Li$^+$MWNTs results in a further decrease of $E_{th}$ to 0.25 V/μm with a hysteresis of 0.04 V/μm and statistical error of ±0.02 V/μm. This improvement is attributed to the change in WF from 5.1 eV to 4.5 eV between the o-MWNTs and the Li$^+$MWNTs, respectively. The statistical error is an indicator of the uniformity of emission across the substrate. In this case, the extremely low error suggests that there is very little variation in emission properties across the entire 1 cm$^2$ substrate. It should be noted that the hysteresis for the Li$^+$MWNT coated samples is exceptionally low, indicative of the stability of the emitter during FE.

<table>
<thead>
<tr>
<th></th>
<th>$E_{th}$ (V/μm)</th>
<th>Error (V/μm)</th>
<th>Hysteresis (V/μm)</th>
<th>WF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine carbon fibre</td>
<td>0.42</td>
<td>±0.03</td>
<td>0.20</td>
<td>4.4$^2$</td>
</tr>
<tr>
<td>Plasma treated fibre</td>
<td>0.58</td>
<td>±0.15</td>
<td>0.23</td>
<td>4.8$^2$</td>
</tr>
<tr>
<td>o-MWNT coated fibre</td>
<td>0.42</td>
<td>±0.09</td>
<td>0.08</td>
<td>5.1$^1$</td>
</tr>
<tr>
<td>Li$^+$MWNT coated fibre</td>
<td>0.25</td>
<td>±0.02</td>
<td>0.04</td>
<td>4.5$^1$</td>
</tr>
</tbody>
</table>

Table 5.4: Summary of the FE characteristics of; pristine, plasma treated, o-MWNT-coated and Li$^+$MWNT-coated carbon fibre fabrics.
The current-field data, plotted in Fowler-Nordheim coordinates is presented in Figure 5.5. Table 5.6 shows $\beta$, calculated from the slopes of the Fowler-Nordheim graph, using the respective WFs of the different samples, quoted in Table 5.4. Due to the widely differing WFs of the different samples, the gradients of the Fowler-Nordheim plots seem counterintuitive when compared to the $\beta$ values. For example, the plasma treated carbon fibres have the worst FE characteristics, and the lowest gradient Fowler-Nordheim graph. However, the plasma treated tubes have the highest $\beta$. This counter-intuitive result is due to the large difference in WF between the samples used in calculating $\beta$.

![Figure 5.5: Current-field data plotted in Fowler-Nordheim coordinates](image)

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Slope Gradient</th>
<th>$\beta$</th>
<th>Local Field (V/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine carbon fibre</td>
<td>-15.2 ± 0.6</td>
<td>4100 ± 200</td>
<td>1.7 ± 0.3</td>
</tr>
<tr>
<td>Plasma-treated fibre</td>
<td>-9.7 ± 0.1</td>
<td>7400 ± 100</td>
<td>4.3 ± 1.6</td>
</tr>
<tr>
<td>o-MWNT-coated fibre</td>
<td>-12.6 ± 1.2</td>
<td>6200 ± 600</td>
<td>2.6 ± 0.8</td>
</tr>
<tr>
<td>Li'MWNT-coated fibre</td>
<td>-11.5 ± 0.3</td>
<td>5700 ± 100</td>
<td>1.4 ± 0.3</td>
</tr>
</tbody>
</table>

Table 5.6: Summary of $\beta$ values for the different samples.
For the pristine carbon fibre, $\beta$ is 4100. After plasma treatment this value increases to 7400. This large increase is surprising, since the physical dimensions of the carbon fibre are not affected by the plasma treatment. However, in Figure 5.2, a change in the nature of the carbon fibre surface was observed by SEM. This suggested that dielectric inhomogeneity was introduced to the carbon fibre surface during the oxygen plasma treatment. This would result in variations in the local electric field across the carbon fibre surface, at the nanoscale (see Section 1.3.4). These local field variations could easily account for the high $\beta$. However, the current-field characteristics did not improve. This is likely to be because the resistivity of the carbon fibre surface was increased during plasma treatment, leading to a limited current through the sample in FE conditions and therefore a high value of $E_{th}$.

After coating the carbon fibre with o-MWNTs, $\beta$ is reduced to 6200. Ignoring the plasma treated fibre (due to the dielectric inhomogeneity effects), this value is compared with that of the pristine carbon fibre. The increase between $\beta$ for the pristine carbon fibre and the o-MWNT-coated carbon fibre is due to the application of the o-MWNTs. The surface of pristine, individual carbon fibres is relatively smooth (see Figure 5.2). However, the surface of fibres coated with o-MWNTs has a more complex morphology, due to the high aspect ratio of individual o-MWNTs and the manner in which they protrude from the surface. This complex morphology leads to local field enhancement at the emission sites and therefore a high $\beta$ compared with that of pristine carbon fibre. The error in $\beta$ for o-MWNTs is very large compared to that of the other samples. This is due to non-linear behaviour observed in the current-field characteristic and Fowler-Nordheim plots of o-MWNT-coated carbon fibre. These non-linear curves will be discussed in detail in Section 5.3.

Coating carbon fibres with Li$^+$-MWNTs, results in a $\beta$ of 5700 which agrees with that of o-MWNTs, within error. This similarity between the two values is expected, since $\beta$ is largely determined by the morphology of an emitting surface and the two samples have identical morphology. This shows that the cation exchange reaction has a minimal effect upon $\beta$ and that the improvement in the FE characteristics is solely due to difference in WF between o-MWNTs and Li$^+$-MWNTs.
The local field (Table 5.6) in this set of samples varies widely, unlike in previous experiments. This is due to the fundamental differences in the nature of conduction in these different materials. For carbon fibre the local field is 1.7 V/nm, which is very close to the expected value (≥ 1 V/nm). This implies that the carbon fibre acts as a simple metallic emitter under FE conditions. For plasma treated carbon fibre, the local field is 4.3 V/nm, which is much closer to the values observed from o-MWNTs in the previous chapters. This suggests that there may be some similarity between the two - the obvious comparison being that both are carbonaceous materials with chemical functionalities on the surface. In this case, the surface moieties may result in a deviation from simple metallic properties of the material, possibly due to the nature of the surface dipole and/or the disruption of the conducting π electron network at the graphitic surface of the carbon fibre or the MWNT. The local field for FE from Li⁺MWNTs is 1.4 V/nm, again much closer to the ideal result expected for a metal under FE conditions. This may be due to the fact that the size of the dipole in the Li⁺MWNT surface moieties is smaller than that in the o-MWNT moieties, such that the π electron network is disrupted to a lesser extent and therefore that Li⁺MWNTs can be considered to act more as ideal metallic emitters than o-MWNTs.
5.3 Staircase Field Emission Characteristics

5.3.1. Introduction

In the previous section, o-MWNTs were deposited onto carbon fibre substrates and the FE properties were investigated. Close analysis of the o-MWNT FE characteristics revealed unexpected staircase-like increases in the current-field curves and non-linearity in the Fowler-Nordheim plots. In this section, these staircase-like emission characteristics are analysed in more detail.

5.3.2. Staircase Field Emission Curves

Samples were prepared and the FE characteristics were probed as described in Section 5.2. Figure 5.7(a) shows FE current-field characteristics from the upwards part of 5 current cycles and Figure 5.7(b) shows this data plotted in Fowler-Nordheim coordinates. The emission curves show staircase-like current-field characteristics, which are repeatable over the five successive voltage cycles. The emission current rises in steps of approximately one order of magnitude and the width of the steps is roughly constant at ~ 0.047 V/μm. The Fowler-Nordheim graph shows a similar staircase-like form. The stepped nature of the FE characteristics is highlighted in the derivative plot of the data, presented in Figure 5.8, where a very distinct staircase is observed.
Figure 5.7: (a) Current-field curves for o-MWNTs deposited on carbon fibre substrates (upwards cycle only) and (b) the same data plotted in Fowler-Nordheim coordinates.
Figure 5.8: Derivative plot of the FE characteristics presented in Figure 5.8(a).

Figure 5.9(a) shows FE current-field characteristics from the downwards part of the same five current cycles and Figure 5.9(b) shows this data plotted in Fowler-Nordheim coordinates. These curves also have atypical stepped shapes, however they are distinctly different from the upwards cycle. As opposed to the four regular steps of the up cycle, these downward cycles are characterised by just two larger steps of unequal width.
Figure 5.9: (a) Current-field curves for o-MWNTs deposited on CF substrates (downwards cycle only) and (b) the same data plotted in Fowler-Nordheim coordinates.

5.3.3 Local Work Function Variations

One possible explanation for the steps in the FE characteristics could be local WF variations, or patch fields along the surface of the o-MWNT. These variations could be caused by various functional groups attached to the o-MWNT ends and sidewalls such as carboxyl, alcohol, ketone, epoxide and aldehyde groups, all induced by the acid oxidisation process (Figure 5.10). Each of these groups has different electronegativities, each of which would affect the surface potential by differing amounts, by withdrawing electron density away from the graphitic bulk, resulting in an inwardly pointing surface dipole.² This would result in a different WF at the locality of the different moiety species, and therefore a range of WFs along the length of the o-MWNT. At low applied fields, only the localities with the lowest WF
would be expected to emit electrons. As the applied field increases, localities with higher WFs would emit electrons in turn, leading to stepped emission corresponding to the differences in WF between each locality of the o-MWNT. Therefore, each step in Figure 5.8 would correspond to a different functional species. However, the differences in WF would not be expected to progress in equal steps, like the emission curve. Additionally, this mechanism cannot explain the differences between the up and down cycles of the FE curves. For these reasons, local WF variations are not thought to be the dominant mechanism for the staircase characteristics.

\[
\text{Carboxyl} \\
\text{Alcohol} \\
\text{sp}^2 \\
\text{Ketone} \\
\text{Epoxide} \\
\text{Aldehyde}
\]

*Figure 5.10: Summary of the different possible moieties on the o-MWNT surface.*

5.3.4 Resonant Tunnelling

A possible source of the non-linearity in the FE characteristics of the o-MWNT ink is resonant tunnelling. The theory of resonant tunnelling is outlined in Section 1.3.6. Non-linearity can arise in the FE current due to resonance when the electronic sub-levels in quantum wells are aligned, and due to negative differential resistance when the sub-levels are unaligned.

In Figure 5.11, the theoretical predictions of FE from multilayer Si-SiO\textsubscript{2}-Si-SiO\textsubscript{2} cathodes made by Kryuchenko et al. are directly compared with the Fowler-Nordheim plot of the experimental data (from Figure 5.7(b)). The two plots display strikingly similar non-linear characteristics; however the scale of the experimental
features is very different from those in the theoretical predictions. It is suggested that the non-linearity in the experimental data may be a result of a similar resonant tunnelling effect; however the ‘shape’ or the dimensions of the quantum wells may be very different, resulting in resonances in the FE current at different field strengths. However, for resonant tunnelling to occur, it is required that quantised electronic energy sub bands exist in quantum well structures. The justification of the existence of quantum wells in the o-MWNTs samples will be outlined below.

It is suggested that the carboxylic functional group at the surface of the o-MWNT gives rise to a quantum well structure which provides localised surface states necessary for resonant tunnelling to occur. It is also possible that adsorbed water molecules contribute to this effect. For many years, FE from materials has been known to be strongly influenced by the existence of adsorbates at the emitting surface. In 1967, Duke and Alferieff pointed out that resonant tunnelling through the energy levels of atoms and molecules adsorbed on metal surfaces plays a major role in field emission. The existence of the attractive potential well of an atom close to the surface of a metal can change the shape and effective thickness of the tunnelling barrier via resonant energy levels. Therefore the tunnelling probability would dramatically increase due to the existence of this adsorbate. Figure 5.12 is an idealised potential diagram, in which the potential of an adsorbate is taken to be a square well. In this case, electrons are more likely to tunnel from metal to vacuum through the energy levels of the adsorbate, due to a reduction in the effective thickness of the triangular barrier.
Duke and Alferieff illustrated this by performing a one-dimensional exact wave matching integral to evaluate the FE transmission for a triangular barrier with various combinations of square well and delta function models, representing the adsorbate. This calculation showed that the existence of adsorbates can lead to wide (~ 1 eV) resonances in the emission probability, as well as an additional peak in the electron energy distribution. Large enhancement in the FE current and reductions in the slope of the Fowler-Nordheim plots were also predicted. The first observation of resonant tunnelling through adsorbates on metal surfaces was made by Plummer et al in 1969, as peaks in the energy distribution of electrons field emitted from zirconium adsorbed onto tungsten. This early work led to the development of atomic spectroscopy for adsorbed atoms. Furthermore, in FE microscopy the emitted current will increase if an atom or molecule is adsorbed onto the local probe area, due to resonance tunnelling enhancement. More recently, resonant tunnelling through localised surface states in chemisorbed molecules has been used to explain the lobed patterns observed in FE microscopy from CNT caps. As the temperature of the CNT emitter is increased, the lobes disappear and the emission current is dramatically reduced, due to the thermal removal of the adsorbates (for example water molecules). Resonant tunnelling through surface states is also widely observed and utilised in scanning tunnelling microscopy.

These resonant tunnelling effects have traditionally been observed via fine structure in the electron energy distribution of emitted electrons, whereby energy peaks visible in the energy spectra represent resonances. Otherwise, lobed patterns
observed in FE microscopy have been explained by resonant tunnelling and scattering of electrons through these adsorbates. However, fine structure in FE current due to the existence of these localised surface states has not yet been reported, possibly due to the high field resolution necessary to resolve individual resonances.

Given the theoretical predictions of FE resonant tunnelling, and the experimental observations of resonant tunnelling effects from surface adsorbates, it is plausible that the experimental results presented here do indeed represent resonant tunnelling through the localised electronic energy levels of a chemisorbed molecule (in this case the carboxyl moiety, or adsorbed water molecules). The multiple steps observed in the current-field data represent multiple electronic energy levels confined in the carboxylic potential well. As each energy level aligns with the Fermi level of the MWNT, an increase in the FE current would be expected, as observed in the experimental data. The difference between the up and down cycles in the current-field curves (Figure 5.9) could be explained in this model by slow decharging due to trapped states in the QWs. It is suggested that these staircase-like characteristics have not been previously observed in the literature, or in other samples in this work, due to the very high field resolution necessary to resolve the individual current steps (each being around 0.047 V/μm wide). This was only achievable in these samples due to the very low fields needed to extract electrons by FE.

To check whether resonant tunnelling through adsorbates is a reasonable interpretation of the data, a simulation was performed using Mathcad® to model FE through a square potential well just outside the surface of a metallic emitter. A schematic of the potential used in the simulation is shown in Figure 5.13. The WF of the electron reservoir is taken as 4.4 eV and is assumed to comprise the inner layers of the MWNT. The WF at the surface is taken as 5.1 eV, which is the value obtained at the surface of acid functionalised MWNTs. The width of the potential barrier is 0.8 nm and it has a dielectric constant of 5, whilst the width of the quantum well is 0.72 nm. These values are designed to approximate the experimental conditions, and the dimensions have been chosen to highlight resonant tunnelling through such a structure in the calculations.
Figure 5.13: Idealised potential used to calculate the FE current through a quantum well, just outside the surface of a metal.

Figure 5.14 shows how the current varies with increasing electric field, for both experiment and the theoretical model. The experimental current has been plotted against the local field for direct comparison with the theoretical data. The local field was obtained by multiplying the applied field by the enhancement factor (in this case 6200). The theoretical current density calculation was then performed in the same electric field range, and arbitrarily multiplied by 1 m² to obtain a current, such that the experiment and theory can be compared.

It is immediately apparent that sharp resonant peaks are observed in the theoretical curves, corresponding to resonant tunnelling through quantised energy levels in the quantum well structure. Comparing experimental and theoretical curves, it is first noted that the gradients of the two graphs are approximately equal, which suggests that the theoretical model is to some extent realistic. There is a significant difference in the magnitude of the current between the two graphs, largely due to the difference in area between the two data sets (1 m² for the theoretical data, and probably less than 1 cm² for the probe FE measurements), and to some extent the difference may be because the theoretical current is calculated for a flat, idealised metallic surface, unlike the experimental sample.
The resonant peaks in the theoretical data have an approximately equal spacing of 0.14 V/nm. This compares well with the step width of 0.29 V/nm in the experimental results and shows that resonances of this order of magnitude are certainly expected for FE through surface states with dimensions at the molecular scale. The peaks in the theoretical data are sharp, narrow and very well defined; however the peaks in the experimental data are broad and much less well defined. The differences in the spacing and the shape of the resonances may be due to differences between the model and reality. The model is an approximated and idealised square well at a metallic surface. However, in reality the surface moieties will form complicated parabolic potential wells which would be expected to result in discrepancies between experiment and theory and possibly a broadening of the resonant peaks. Additionally, the true dimensions of these quantum wells can only be approximated, which may also lead to error.

Despite the approximations made, the theoretical and experimental data compare well. The calculations have shown that resonant tunnelling is theoretically expected through localised surface states with molecular scale dimensions and that these resonances occur at similar fields as those observed in experimental results. This strongly supports the proposal that the nonlinear characteristics in the experimental data are due to resonant tunnelling through surface carboxylic groups and/or adsorbed water molecules.
5.4 Summary and Conclusions

In this chapter, a study of field emission from multiwall carbon nanotubes with differing surface functionality and therefore differing WF was performed. Lithium cation exchange by chemical reaction was chosen as a low cost, room temperature functionalisation procedure, resulting in a large reduction in the WF of o-MWNT from 5.1 eV to 4.5 eV for Li+MWNT. This reduction in WF had the effect of significantly improving the FE threshold field from 0.4 V/μm to 0.25 V/μm, which is the first time that an improvement in the FE characteristics of MWNT has been achieved by chemical functionalisation. This technique has potential to be applied to all acid functionalised CNT varieties as a quick, low cost industrial process and therefore could have implications for FE devices across the board. Additionally, stepped current-field curves were observed in FE from layered o-MWNTs on carbon fibre substrates. These were attributed to resonant tunnelling through localised surface states in the carboxylic functional group, and experimental results compared well with theoretical calculations.

Figure 5.13: Comparison of an experimental FE curve from o-MWNTs with the theoretical FE curve from a surface quantum well system, courtesy of Lucian Filip.
5.5 References

In this work, the use of a pure multiwall carbon nanotube ink as a cold cathode for field emission has been widely explored. Carbon nanotube inks have been deposited onto a variety of substrates by economical methods. The dependence of the Fowler-Nordheim equation upon the enhancement factor and the work function has been fully explained.

6.1 Transparent Electron Field Emitters

In Chapter 3, CNT ink was spin coated onto a variety of transparent substrates, forming thin, uniform layers of CNTs over large areas. The FE characteristics were measured before and after laser irradiation. For CNT ink on pristine glass substrates, $E_{th}$ was reduced from 23 V/μm before laser treatment to 8 V/μm after laser treatment at 343 mJ/cm$^2$, and the transmission was reduced from 89% to 85%. This improvement in FE characteristics was attributed to the structural and geometrical modification of the CNT layer by the laser pulse, resulting in an increase in the geometric field enhancement and reduced screening effects. The minor decrease in optical transmission was attributed to an increase in scattering from the sample due to laser-induced roughening. One single laser pulse was found to be the optimum for improving the FE characteristics.

For CNT ink on ITO-coated glass substrates, $E_{th}$ was reduced from 18 V/μm before laser irradiation to 6 V/μm after laser irradiation at 186 mJ/cm$^2$, and the optical transmission was reduced from 73% to 71%. This improvement in FE characteristics was attributed to a combination of the structural and geometrical modification of the CNT layer, and the modification of the underlying ITO thin film due to the incident laser pulse. The severe decrease in optical transmission at high laser energies was attributed to melting and chemical modification of the underlying ITO layer, resulting in increased scattering and absorption of light.

For CNT ink on plastic substrates, $E_{th}$ was reduced from 0.9 V/μm before laser irradiation to 0.5 V/μm after laser irradiation at 171 mJ/cm$^2$, and the optical transmission was reduced from 81% to 70%. This improvement in FE characteristics was attributed to a combination of the structural and geometrical modification of the CNT layer, and the modification of the underlying plastic substrate due to the
incident laser pulse. The decrease in optical transmission at high laser energies was attributed to physical and chemical modification of the underlying plastic substrate, resulting in increased scattering and absorption of light. The current density from a sample irradiated at 171 mJ/cm² was measured as 100 µA/cm² at 1 V/µm, after current conditioning. The site density was poor, but vastly improved after current conditioning.

There is a significant difference in the FE properties of the three different types of samples studied. Glass-substrate samples had the poorest FE properties, but the best optical transmission. ITO-substrate samples had slightly better FE characteristics, but reduced transmission. Plastic-substrate samples had by far the best FE characteristics with similar transmission properties to ITO-substrate samples. The wide difference in FE characteristics shows that the underlying substrate material and morphology have an important role to play in FE and optical transmission. CNT ink on plastic substrates certainly has potential for use as an excellent FE source, however more work needs to be undertaken to improve the transmission, emission uniformity and stability.

6.2 Electron Field Emitters on Paper

In Chapter 4, paper substrates of varying surface morphology were dip-coated into CNT ink and dried. The FE characteristics were measured with changing underlying surface morphology. \( E_{th} \) decreased with increasing surface roughness, from 12 V/µm for very smooth samples to 0.8 V/µm for samples with high roughness. The improvement in FE characteristics was attributed to increased geometric field enhancement and reduced screening effects resulting from the varying substrate morphology. Planar FE characterisation was carried out on the best sample to determine the current density, which was 27 µm/cm² at 1.2 V/µm. This result was comparable to values found in the literature, but measured at a lower applied electric field.

A sample was subsequently subject to laser irradiation at varying fluence and the FE characteristics recorded. The morphology of the CNT layer was significantly affected by the incident laser pulse, resulting in prominent CNT surface features, attributed to structural defects induced by the incident laser. \( E_{th} \) was reduced from 4.8 V/µm before laser treatment to 2.1 V/µm after laser treatment at 111 mJ/cm².
This improvement in FE characteristics was attributed to the prominent CNT surface features adding to the geometric field enhancement of the sample.

Paper coated with CNT ink was incorporated into three-terminal devices via a simple lamination technique. The total thickness of the device was 230 μm and it operated with an optimum gate voltage of 60 V and an anode voltage of 400 V. The current density was calculated as 51 mA/cm².

This work demonstrates that cold cathodes can be fabricated by relatively simple ink-based methods, and that the FE properties can be improved simply by tailoring the underlying morphology to maximise geometric enhancement. Such cathodes can be fabricated on large scales, by routine, room temperature, low cost printing techniques. It has been shown that these paper cathodes are suitable for incorporation into three-terminal devices.

6.3 Chemical Derivatisation of Carbon Nanotube Inks

In Chapter 5, lithium cation exchange was performed on the carboxylic functionalised CNT ink, as a means to reduce the work function. Carbon fibre fabric substrates were dip-coated in CNT ink and Li-functionalised CNT ink, and subjected to FE characterisation. Eth decreased from 0.42 V/μm for the normal CNT ink to 0.25 V/μm for Li-functionalised CNT ink. The improvement was attributed purely to the decrease in work function.

Additionally, staircase-like steps in the FE current-field curves were observed in the carboxylic functionalised CNT inks. These characteristics were attributed to resonant tunnelling in the structure, arising from localised surface states in the surface carboxyl moiety.

Chemical tailoring of the work function of CNTs resulting in improved FE characteristics has as-yet been unreported and provides a facile route to the improvement of a wide variety of field emission devices. Equally, resonant tunnelling has not yet been reported in FE from CNTs and this could provide an insight into the physics of FE, especially from carbon nanotubes.
6.4 Future Work

The work presented here has opened up avenues for further research in several directions, such as transparent electronics, printing of CNT ink onto paper and plastic substrates, fabricating lithography-free three-terminal devices, chemical modification of FE cathode materials to reduce the work function and the exploration of resonant tunnelling in field emission from CNTs. Some of these areas are discussed below in detail.

Spin coating CNT ink onto plastic substrates needs more attention, especially investigating the use of alternative polymers, and incorporation into three-terminal devices. It may also be possible to fabricate a fully transparent field emission device by using transparent polymer spacers, thin CNT films as cold cathodes and ITO as a gate and anode.

The extension of using paper substrates for CNT cold cathodes by utilisation of inkjet printing technology could be used to fabricate patterned substrates and therefore make more complex, multi-pixel three-terminal devices. The laminate-based three-terminal devices could be optimised by using thinner laminate layers, using laser drilling for well-defined holes and by changing the cathode material. This could lead to a lithography free, scalable, lightweight, and low cost field emission displays.

A plethora of chemical reactions can be performed on CNTs, and a detailed study of how this affects the work function and field emission properties should be conducted, especially by using other cation exchange reactions with potassium and caesium. The in situ application of this technique to aligned CNTs on silicon substrates would be very interesting indeed.

The observance of resonant tunnelling in FE from CNTs certainly warrants further investigation at higher field resolutions, and with different surface functional groups. By tailoring the surface dipoles of surface groups, it may be possible to influence the resonant tunnelling characteristics. Low temperature FE characterisation of the samples may also shed more light on the phenomenon. Computer simulations derived for quantum wires rather than two-dimensional structures may provide insight into the resonant tunnelling mechanism in this case.
6.5 Closing Remarks

Pure CNT ink shows great promise as an electron field emission source. The ink can be deposited uniformly over large areas by spin-coating, or patterned at the micron-scale using inkjet printing. The ink can be transparent and can be deposited onto roughened substrates to maximise the enhancement factor. Post-deposition laser treatment can be applied to improve the electron emission properties. Their work function can be tailored by using wet chemistry techniques.

It has been one of the objectives of this work to investigate field emission from CNT ink without resorting to complex lithography steps, or high temperature evaporation techniques. This has been realised, and a three-terminal device was fabricated via an extremely simple method. It is believed that CNT ink has the potential to be used in a field emission display fabricated by efficient, low energy processes and may even contribute to the reduction of the carbon footprint of our society.