Low Temperature Growth of Carbon Nanostructures

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Unis

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Abstract

Carbon nanotubes have been the subject of extensive research over the past few years. This is due to the unique properties of carbon nanotubes brought about by its electronic, mechanical and chemical properties. Low dimensional structures that were previously in the domain of theorists can now be tested experimentally with carbon nanotubes based devices. Nanostructured materials with exciting new properties are now predicted to bring about a whole new revolution to the world and the way we live.

The main focus of this work is in the area of low temperature synthesised carbon nanotubes with the extreme limiting case of synthesis at room temperature. Whilst research groups worldwide are pursuing the holy grail of synthesising perfectly structured nanotubes, using either carbon electrode arc-discharge techniques or laser ablation or a less structured form at typically 700°C using chemical vapour deposition (CVD), this thesis explores the formation of carbon nanostructures at lower temperatures using CVD techniques. Besides the advantage of using a wider variety of supporting substrates, electrodes and its possible use in conducting polymer composites, the work will also contribute and add to the knowledge base of low temperature synthesis. This thesis is focused on the characterisation of nanotubes as this is critical in understanding the properties of nanotubes and allows for the fabrication of proof of concept devices in targeted applications. In this thesis, the synthesis of low temperature carbon nanostructures and nanotubes, and spherical carbon structures will be presented and discussed. Briefly, carbon nanostructures have been successfully synthesised at below 350°C and lower defect level carbon nanotubes have been synthesised below 400°C using a novel thermal barrier layer technique.

Methodologies for exploiting the low temperature growth process for future applications are discussed.
Acknowledgement

Firstly, I would like to thank my project supervisor Prof. Ravi Silva for giving me the opportunity to work in this exciting area of research as well as for his supervision and guidance.

Extensive input and support from all the people in the Nano-Electronics Centre are also much appreciated, particularly the research fellows who have in one way or another contributed to my studies at this university. Dr. Simon Henley, Dr. Vlad Stolojan, Dr. Patrick Poa, Dr. David Cox, Dr. Nicholas Blanchard, Dr. Yann Tison, Dr. Roy Forrest, Dr. Dagou Zeze, Dr. David Carey. In addition, I am also grateful to the postgraduate students such as Cristina Giusca, Damitha Adikaari and Sean Chan for their support and making my student life enjoyable. In addition, I have to thank Dr Ernest Mendoza and Dr. Benjamin Colombeau for their support and discussion.

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## Glossary

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
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<tr>
<td>HREM</td>
<td>High Resolution Electron Microscope</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced chemical vapour deposition</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron spectroscopy</td>
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Declaration

This thesis is submitted for the degree of Doctor of Philosophy at the University of Surrey. It describes the research carried out in the Advanced Technology Institute of the School of Electronics and Physical Sciences between February 2002 and April 2005. This work has been carried out under the supervision of Professor S. R. P. Silva, head of the Nano-Electronic Centre. Except where referenced, this work is original and has not been the result of collaboration. No part of this thesis has been or is currently being submitted for any other degree, diploma or other qualification.

G.Y. Chen
June 2005
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Chapter 1

1 Introduction

1.1 Low temperature synthesis of carbon nanotubes

Carbon nanotubes and nanostructures have often been associated with the term “Nanotechnology”. The Oxford English Dictionary describes Nanotechnology as “The branch of technology that deals with dimensions and tolerances of 0.1 to 100 nanometres, or, generally, with the manipulation of individual atoms and molecules”. Another description or interpretation according to a phrase on the Institute of Nanotechnology’s website, “Nanotechnology” is “best considered as a ‘catch-all’ description of activities at the level of atoms and molecules that have applications in the real world”[1].

The attraction of nanotechnology is that it opens up new worlds of possibility, not only in terms of material properties but also across diverse fields of study. It encompasses different fields such as electronic, mechanical, chemical and biomedical applications. The idea of manipulating atoms and molecules to build the perfect material or device has sparked an explosion of interest in the study at such small scales. Carbon nanotubes have been at the forefront of Nanotechnology due to their unique shape, size and properties. These nano-sized tubes exhibit mechanical and electrical properties that have potential in a wide range of applications e.g. composite materials, field emission devices, battery electrodes, nano-electronics, etc [2-11].

This material is now a topic of intense research as evident by the huge amount of publications specifically on or related to nanotechnology published each year. We can broadly classify carbon nanotube research into two main categories (High/Low), based on their synthesis temperature. The properties of high temperature synthesized carbon nanotubes have been investigated by numerous research groups worldwide and constitute a major part of the existing literature that has been published. The area of low temperature synthesis is, however, sorely neglected which could be due to the
fact that it is difficult to actually synthesize them with sufficient yield and quality as
the process temperature decreases. This work looks into the problems associated with
low temperature synthesis. The synthesis at low temperatures would open up wider
choices of substrates and facilitate compatibility with standard microelectronic
processes.

1.2 Project aim

Carbon nanotubes have been synthesised by the catalytic decomposition of a
carbon containing reactant gas over catalyst, which is a method also known as
Chemical Vapour Deposition (CVD). Transition metals have commonly been used as
the catalyst. CVD techniques have been gaining popularity because of two main
advantages. Firstly, it allows a lower synthesis temperature as compared to other
techniques like arc-discharge and laser vaporisation. Secondly, it allows direct
synthesis on substrates with greater control. This has huge advantages in device
fabrication. However, the growth of carbon nanotubes using CVD is still typically
carried out at temperatures above 550°C, and consequently leads to silicon or high
temperature resistant glass being used as substrates.

The aim of this project is to develop and optimise the growth of carbon
nanotubes in the temperature range of 200°C to 400°C. This would allow the use of a
wider range of substrates and enable engineers and designers greater flexibility for
the devise design and fabrication of nanotube structures. It is also important to
control the quality of the carbon nanotubes as defect levels increase as the synthesis
temperature decreases.

1.3 Outline of the Thesis

The first part of the thesis is an introduction of the carbon material and its
unique properties. Chapter 2 reviews the literature of the history, properties, synthesis
and applications of carbon nanotubes is presented.
In Chapter 3, the experimental and characterisation techniques are discussed. In particular, the synthesis equipment and techniques used in the investigation of low temperature growth is presented.

In Chapter 4, the results from the investigation of carbon nanotube growth using radio frequency plasma enhanced chemical vapour deposition (PECVD) is presented and discussed. The section concludes with the key factors gathered from the results from the different growth runs at low temperature. Also presented in this chapter is the observation of amorphous hydrocarbon spheres. Analysis of these spheres reveals unique characteristics.

Chapter 5 presents the results of low temperature growth of carbon nanostructures using the direct current PECVD, using the knowledge gained from chapter 4. The chapter begins with a comparison between high and low temperature growth. The low temperature growth is then investigated as a function of process parameters such as applied bias, hydrocarbon concentration, etc.

Chapter 6 reports on the use of titanium as a thermal barrier layer for the low temperature growth of carbon nanotubes. A simple thermodynamic simulation shows the effect of using the lower thermal conductivity of titanium to create a temperature gradient between the surface and the substrate. Growth using this novel method is presented and investigated as a function of different process parameters such as applied voltage, pressure, etc.

Finally, Chapter 7 summarises the work presented in this thesis and discusses the key factors/information gained and the conclusions. Suggestions for future work are also presented and discussed.
Chapter 2

2 Literature review

This chapter presents different forms of carbon and its nanostructures. In particular, carbon nanotubes and their synthesis, properties and potential applications will be examined. The role of plasmas in the synthesis of carbon-based materials will also be discussed.

2.1 Carbon

The element carbon has an atomic number 6, i.e. the neutral atom has six protons in the nucleus and correspondingly six electrons. The electron configuration, which is the arrangement of electrons in each orbital is described as: \( 1s^2 \ 2s^2 \ 2p^2 \).

The notation \( 1s^2 \) refers to the three quantum numbers necessary to define an orbital, the number "1" referring to the K or first shell. The letter "s" refers to the sub-shell s (angular momentum quantum number) and the superscript numeral "2" refers to the number of electrons in that sub-shell.

![Figure 2-1: Orbital of element carbon](image-url)
Thus, the element carbon has 2 electrons in the K shell (which is completely filled) and is stable. The following two terms, $2s^2$ and $2p^2$ refer to the four electrons in the L shell which have two sub-shell, $s$ and $p$.

A chemical bond is formed when an electron becomes sufficiently close to two positive nuclei to be attracted by both simultaneously (unless the attraction is offset by repulsion from other atoms within the molecule). For carbon molecules, this bonding is covalent i.e. atoms share electrons and can take the form of $sp^3$, $sp^2$ and $sp$ orbital bonds. The different bonding gives rise to different structural arrangement e.g. $sp$ bonding gives rise to a linear chain structure, $sp^2$ bonding to planar aromatic sheet structures and $sp^3$ bonding to tetrahedral diamond-like structures.

The $1s^2 \ 2s^2 \ 2p^2$ configuration does not account for the tetrahedral symmetry found in diamond or methane. For this symmetry to occur, the carbon atom must be altered to a state with four valence electrons instead of two, each in a separate orbital and with its spin uncoupled from the other electrons. This alteration occurs by the formation of hybrid atomic orbitals, whereby the electrons in the L shell of the atom at the ground state $2s$ shell is promoted to the higher orbital $2p$ level. These new orbitals are called hybrids since they combine the $2s$ and $2p$ orbitals. They are labelled $sp^3$ since they are formed from one $s$ orbital and three $p$ orbitals.

![Figure 2-2: sp³ hybridization](image-url)
Chapter 2. Literature Review

The four hybrid sp³ orbitals have identical shape but different orientation, forming a regular tetrahedral with equal angles to each other of 109°28'. By convention, a directional orbital such as the sp³ is called a sigma (σ) orbital.

![sp³ hybridization](image)

Figure 2-3: sp³ hybridization

Whereas the sp³ orbital is the key to diamond and aliphatic compounds, the sp² orbital is the basis of all graphitic structures and aromatic compounds. The sp² hybridization is formed by promoting one of the 2s electrons and combining it with the 2p electrons, to form three sp² orbitals and an unhybridized free p orbital electron. The three identical sp² orbitals are in the same plane and their orientation of maximum probability forms a 120° angle from each other. The fourth orbital i.e. delocalized non-hybridized p electron is directly perpendicular to the plane of the three sp² orbitals and becomes available to form the subsidiary pi (π) with other atoms.

The sp orbital is a merger of an s and a p orbital. A sp bond consists of two sp orbitals which form an angle 180° and therefore the sp molecule is linear. The overlap bond is a sigma (σ) bond and the other two valence electrons are free, delocalized pi (π) orbital electrons forming subsidiary pi (π) bonds, similar to the sp² hybridization.

The three common allotropes of carbon are diamond, graphite, and amorphous carbon. The density of diamond is 3.5 grams per cubic centimetre (g/cm³), graphite ranges from 1.9 to 2.3 g/cm³, and amorphous carbon ranges from
1.8 to 2.1 g/cm³. Diamond is one of the hardest known materials, while graphite is one of the softest. These differences arise from the differences in bonding between the carbon atoms. In diamond, each carbon atom bonds tetrahedrally to four other carbon atoms to form a three-dimensional lattice. The shared electron pairs are held tightly in sigma bonds between adjacent atoms. Pure diamond is an isotropic, cubic, wide bandgap semiconductor and is therefore an electrical insulator (i.e. it does not conduct electric current). It is colourless and because of its hardness, is used in industrial cutting tools.

In graphite, the atoms form planar or flat layers. Each layer is made up of rings containing six carbon atoms. The rings are linked to each other in a structure that resembles the hexagonal mesh of chicken wire. Each atom has three sigma bonds (with 120° between any two of the bonds) and belongs to three neighbouring rings. The fourth electron of each atom becomes part of an extensive pi bond system. Graphite conducts electricity because the electrons in the pi bond system can move around throughout the plane. Bonds between atoms within a layer of graphite are strong, but the forces between the layers are weak. Because the layers can slip past each other, graphite is soft and can be used as a lubricant. Diamond makers can transform graphite into diamond by applying extremely high pressure (more than 100,000 times the atmospheric pressure at sea level) and high temperature (about 3000° C or 5000° F). High temperatures break the strong bonds in graphite so that the atoms can rearrange themselves into a diamond lattice. Amorphous carbon is actually made up of tiny crystal-like bits of graphite clusters with varying amounts of other elements, which are considered impurities.

The research in different forms of carbon was further boosted when in 1985, a new form of carbon allotrope called the C60 molecule was discovered. C60 is a molecule that consists of 60 carbon atoms, arranged as 12 pentagons and 20 hexagons. The shape is the same as that of a soccer ball. The scaling of the C60 molecule to a soccer ball is similar to the relationship of the soccer ball to that of earth. This emphasises the difficulties of the top down approach. The most striking property of the C60 molecule is its high symmetry. There are 120 symmetry operations, like rotations around an axis or reflections in a plane, which map the
molecule onto itself. This makes C60 the molecule with the largest number of symmetry operations, the most symmetric molecule.

Based on a theorem of the mathematician Leonhard Euler, one can show that a spherical surface entirely built up from pentagons and hexagons must have exactly 12 pentagons. Depending on the number of hexagons, molecules of different sizes are obtained. They are called Fullerenes, after the American architect Richard Buckminster Fuller who is renowned for his geodesic domes, which are based on hexagons and pentagons. The C60 molecule was discovered by Harold Kroto, Robert Curl, and Richard Smalley in 1985 [12]. The group were attempting to understand the absorption spectra of interstellar dust, which they suspected to be related to some kind of long-chained carbon molecules. Unfortunately they could not solve that problem, but in the course of their experiments discovered the fullerene which generated so much excitement among scientists and won them the 1996 Nobel prize in chemistry.

Initially, C60 could only be produced in tiny amounts. Hence limiting experiments could be performed with the material. Things changed dramatically in 1990, when Wolfgang Krätschmer, Lowell Lamb, Konstantinos Fostiropoulos, and Donald Huffman discovered how to produce pure C60 in much larger quantities [13]. This opened up new possibilities for experimental investigations and started a period of very intense research. The discovery of C60 has stimulated a large activity in chemistry. It opened up the new branch of Fullerene-Chemistry, which studies the new families of molecules that are based on Fullerenes.

2.2 Carbon nanotube

2.2.1 Brief history

Since the 70’s, very small carbon filaments (<10nm) have been prepared through the synthesis of vapour grown carbon fibres by the decomposition of hydrocarbons at high temperatures in the presence of transition metal catalyst
particles [14-18]. However it has only been since 1991, with the observation of carbon nanotubes using High-Resolution Transmission Electron Microscope (HRTEM) by Iijima at the NEC Fundamental Research Laboratory in Tsukuba, Japan that the scientific community began to look at these small structures in detail [19].

![Figure 2-4 : The observation by TEM of multi-wall coaxial nanotubes with various inner and outer diameters, \(d_i\) and \(d_o\), and the numbers of cylindrical shells \(N\) reported by Iijima in 1991: a) \(N=5, d_o=67\AA\); b) \(N=2, d_o=55\AA\); and c) \(N=7, d_i=23\AA, d_o=65\AA\) [19]](image)

The work reported by Iijima was based on nested coaxial tubes of graphitic sheets (Figure 2-4) which are now termed multi-walled carbon nanotubes. Part of the stimulus is due to the earlier work on fullerene by Kroto, Smalley, Curl and co-workers at Sussex and Rice University [12]. Smalley and others had speculated that an elongated fullerene, much like \(C_{70}\) is to \(C_{60}\), could be formed by adding belts of carbon along the equator such that it ends up as a long tube with two \(C_{60}\) hemisphere caps. It is therefore interesting that the smallest reported diameter (4Å) for a carbon nanotube is the same as the diameter of the \(C_{20}\) molecule, which is the smallest fullerene to follow the isolated pentagon rule [20]. Significant efforts were made to find an efficient technique to produce large quantities of carbon nanotubes, particularly high quality single-wall nanotubes. In 1996, Smalley and co-workers reported on the formation of ropes of single-walled nanotubes with high yield using
an arc process [21]. The high diffraction peaks from the X-Ray studies suggested that the ropes consisted of nanotubes with a very narrow distribution of diameters. This provided a source of single-wall nanotubes of high quality in sufficient abundance for properties studies.

The nanotube was predicted to have remarkable 1D quantum effects, mechanical properties and electronic properties due to its small size and structure. The most striking of the early theoretical developments was the prediction that carbon nanotubes could be either semiconducting or metallic depending on their geometrical arrangement, i.e. diameter and the orientation of their hexagons with respect to the nanotube axis (chiral angle) [22-24]. Although predicted in 1992, it was not until 1998 that these predictions were corroborated experimentally [25,26]. Since then, much progress and understanding on the properties of carbon nanotubes had been made.

2.2.2 Basic Structure and atomic arrangements

The structure of carbon nanotubes had been explored by high resolution Transmission Electron Microscope (TEM) and Scanning Tunnelling Microscope (STM) techniques [27], yielding direct confirmation that nanotubes are seamless cylinders derived from the honeycomb lattice representing a single atomic layer of crystalline graphite, called a graphene sheet. From this perspective, one can envisage two forms of carbon nanotubes; single walled and multi walled nanotubes.

The structure of the single walled carbon nanotube can be expressed in terms of the chiral vector $C_h = n\hat{a}_1 + m\hat{a}_2$, which connects two crystallographically equivalent sites on a 2D graphene sheet. Therefore, carbon nanotubes can be characterised by the pair of integers $(n,m)$ which specifies the chiral vector. The chiral angle $\theta$ is the angle between the chiral vector $C_h$ and the 'zigzag' direction ($\theta = 0$) and the unit vectors $\hat{a}_1$ and $\hat{a}_2$, of the hexagonal honeycomb lattice of the graphene sheet. The vector $C_h$ determines the direction of rolling and therefore, the diameter can be expressed as;
\[ d = \frac{a \sqrt{m^2 + mn + n^2}}{\pi} \]  

(2.1)

where \( a = 1.42 \times \sqrt{3} \ \text{Å} \) corresponds to the lattice constant in the graphite sheet.

Figure 2-5: The chiral vector \( \text{OA} \) or \( \text{Ch} = n\hat{a}_1 + m\hat{a}_2 \) is defined on the honeycomb lattice of carbon atoms by unit vectors \( \hat{a}_1 \) and \( \hat{a}_2 \) and the chiral angle \( \theta \) with respect to the zigzag axis \( \theta = 0^\circ \). Also shown are the lattice vector \( \text{OB} = T \) of the 1D nanotube unit cell and the rotation angle \( \psi \) and the translation \( \tau \) which constitute the basic symmetry operation \( R = (\psi/ \tau) \) for the carbon nanotube. The diagram is constructed for \((n,m) = (4,2)\). [22]

It is possible to construct the nanotube by rolling up the hexagonal graphene sheets in different ways. Two of these are “non-helical” in the sense that the graphite lattices at the top and the bottom of the tubes are parallel. These arrangements are termed “armchair” and “zig-zag”. In the armchair structure, two C-C bonds on opposite sides of each hexagon are perpendicular to the tube axis, whereas in the zig-zag arrangement, these bonds are parallel to the tube axis. To determine the armchair and
zigzag structure in terms of \((n,m)\) and the chiral angle \(\theta\), it is necessary to have the following conditions:

\[
\theta = 0, \quad (n,m) = (p,0) \quad \text{where } p \text{ is integer (zigzag)}
\]
\[
\theta = \pm 30^\circ, \quad (n,m) = (2p, -p) \text{ or } (p, p) \text{ (armchair)}
\]

As can be seen later, the chiral angle determines the electrical properties of single-walled carbon nanotubes i.e. semiconducting or metallic. Thus, recently there is a worldwide effort to increase the yield of single wall carbon nanotubes while reducing the diameter and chirality distribution. This would have particular importance in electronic applications. Multi-walled carbon nanotubes can be thought of as containing several co-axial cylinders, each cylinder being a single wall carbon nanotube.

### 2.2.3 Electronic properties

It is easy to assume initially that carbon nanotubes will take on the properties of graphite which is a semi-metal or zero-gap semiconductor, since it is made up of graphene sheets. This is largely true in that the mixing of \(\pi (2p_z)\) and \(\sigma (2s \text{ and } 2p_{x,y})\) carbon orbitals can be neglected near the Fermi level \([28]\) if the fibre curvature is small. However, one can still expect unique electronic properties due to the constraints of quantum confinement in the circumferential direction with small nanotube diameter.

The electronic structure of a single wall nanotube can be obtained from that of two dimensional graphite. By using periodic boundary conditions in the circumferential direction denoted by the chiral vector \(C_h\), the wave vector associated with the \(C_h\) direction becomes quantized, while the wave vector associated with the nanotube axis remains continuous. Thus, the energy bands consist of a set of one dimensional energy dispersion relations which are cross sections of those of a two dimensional graphite. Therefore, as a finite piece of the 2D graphene sheet is rolled
up to form a 1D tube, the periodic boundary conditions imposed by the \( C_n \) can be used to enumerate the allowed 1D subbands – the quantized states resulting from the radical confinement – as follows:

\[
C_n \cdot k = 2\pi m
\]  

(2.2)

where \( m \) is an integer. If one of these allowed subbands passes through one of the six \( K \) points of the two dimensional graphite Brillouin zone (where the \( \pi \) and the \( \pi^* \) energy bands are degenerate by symmetry), the nanotube will have a one dimensional energy band of zero band gap i.e. metallic, and otherwise semiconducting. Dresselhaus et al. [29-31] show that metallic conduction occurs when

\[
\frac{n - m}{3} = q
\]  

(2.3)

where \( q \) is an integer. Thus to a first order, it can be expected that one third of chiral \((n,m)\) and zigzag \((n,0)\) nanotubes are metallic and two-thirds are semiconducting while armchair \((n,n)\) nanotubes are metallic. Dresselhaus et al. have also calculated the electronic density of states for metallic and semiconducting nanotubes [31]. The 1D Density of States (DOS) for the metallic and semiconducting nanotubes is shown in Figure 2-6. Also shown in the figure, is the DOS of a 2D graphene sheet (in dotted lines). It can be seen that there is a finite DOS at the Fermi level \( (E=0) \) for the metallic \((9, 0)\) nanotube and a vanishing DOS for the semiconducting \((10, 0)\) nanotube. The DOS for 2D graphene shows that graphite is a semi-metal with a slightly overlapping bandgap.
The band structure of multi wall nanotubes remains uncertain to this day. While Riichiro Saito and co-workers showed through tight-binding methods that interlayer coupling for double walled nanotube had little effect on the electronic properties of the resulting tube i.e. two metallic coaxial tubes would remain metallic and two semiconducting tubes would remain semiconducting, a group from Université Catholique de Louvain, Belgium has suggested that by changing the relative position of one tube with respect to the other, certain configurations would result in the interlayer interaction changing the resulting tube property [32,33]. Effect
Chapter 2. Literature Review

of interlayer interaction has yet to be confirmed but considering that most work report that current conduction is through the outer wall of the nanotubes, we can expect metallic behaviours from large diameter nanotubes.

The electrical properties of carbon nanotubes are also highly interesting from the viewpoint of its nanometre dimensions. Many studies have been conducted to probe its electrical conduction mechanisms. At the present time, most electrical transport measurements are performed by randomly dispersing single-walled carbon nanotubes onto a substrate, followed by contacting them via lithographically defined electrodes (or vice versa). Many different phenomena such as Coulomb blockade dominated conductance, transistor like behaviours, etc are reported [11, 34-37].

2.2.4 Synthesis

The first carbon nanotubes identified by Iijima in 1991 were synthesised by an arc-discharge technique. The next technique that came into popular use was the laser vaporisation method. These two techniques are very much similar though the laser vaporisation technique offers more control. It is however realised that knowledge gained from studies in the early 70s which was focused on the prevention of carbon filamentary deposits and the present technique of vapour grown carbon fibres could be utilised to synthesis carbon nanotubes. The field of chemical vapour deposition of carbon nanotube soon gain widespread popularity.

2.2.4.1 Arc-discharge and laser vaporisation method

The arc discharge technique was used by Iijima in 1991 to produce carbon nanotubes that he used in his TEM observations. The technique is similar to the system used in the Kratschmer-Huffman experiment which reported the high yield production of C60 [13].
Chapter 2. Literature Review

The essential difference in the production of fullerenes and carbon nanotubes is the use of gas including hydrogen with the hydrogen promoting the growth of carbon nanotubes [38]. The arc discharge method is essentially the vaporisation of opposing carbon electrodes by a plasma of helium gas ignited by passing a high current through the electrodes. The carbon atoms self-assemble into the nanotube structures and can be found in the deposited soot. This technique has the characteristic of producing high quality nanotubes due to the high energy of the arc. Both multi-walled and single-walled carbon nanotubes can be produced using this method with the only difference being that single-walled nanotubes requires metallic catalyst e.g. iron, nickel, etc in the carbon anode. The carbon nanotubes grown using this method usually have few microstructure defects such as pentagon or heptagon and therefore appear very straight. The by-product of the growth process is multi-layered graphitic and polyhedral particles, around 5-20nm in diameter. The by-products together with amorphous carbon can be removed by oxidation. The multi-walled nanotubes are typically tens of microns long and have diameters of 5-30 nm. The nanotubes usually come in ropes or tight bundles held together by van der Waals interactions. The properties, structure and yield of carbon nanotubes synthesised can be changed by changing various process parameters such as pressure, applied current,
etc. For example, the effect of helium pressure has significant effect on the yield of the carbon nanotube as shown in Figure 2-8.

![Figure 2-8](image)

**Figure 2-8:** Micrographs showing the effect of helium on yield of nanotubes in arc-evaporation experiments, from the work of Ebbesen and Ajayan [40]. Samples prepared at (a) 20 Torr, (b) 100 Torr and (c) 500 Torr.

Although the yield increases with helium pressure, a large amount of polyhedral carbon particles are always present along with the nanotubes. The laser ablation method uses intense laser pulses to ablate a carbon target which is in a tube furnace heated to 1200°C. During the laser ablation, a flow of inert gas is used to carry the nanotubes formed in the plume, downstream to a cold finger for collection. As with the arc-discharge method, nanotubes produced using this method are typically of high quality. Both techniques produce by-products like fullerenes, graphitic particles, amorphous carbon, etc and typically require an additional purification process.

### 2.2.4.2 Catalytic Chemical Vapour deposition

Chemical Vapour Deposition (CVD) is a vapour based catalytic method involving the break down of carbon containing gases e.g. acetylene, ethylene, carbon monoxide, etc. over a catalyst material which is typically a transition metal. The break down of the hydrocarbon gases is usually achieved by thermal means or using a plasma. It has been known for a long time that filamentous carbon can be formed in
this manner. Investigations in the 1950s have found that carbon filaments can be produced by breaking down hydrocarbon gases in the presence of metals. The metals found to be most effective are nickel, iron and cobalt. The motivation in the early work (from 1950s to 1970s) was focused on understanding the formation of filaments in the bid to prevent its formation. The filamentous carbon was often found in carbon deposits in industrial steam crackers that are used to produce olefins and in nuclear reactor coolants [18,41].

However, by the 1990s, there was a revival in the interest of filamentous carbon by CVD growth. This is due to a need to reliably control the growth of carbon nanotubes was achieved when Chen et al. used a biased hot filament growth technique for carbon nanofibre growth [42]. Following this, much work has been done on aligned growth, notably the work by Ren et al. [43]. As shown in Figure 2-9a, the CVD technique is the only method currently available to control the alignment, size and location of the deposit.

Figure 2-9: (a) Carbon nanotubes grown without an assisting plasma, (b) nanotubes grown using anodised alumina as template [44], (c) aligned nanotubes grown on polycrystalline Ni foil using Hot-Filament CVD [45].

In general, CVD technique can be categorised into two main types; Thermal CVD and Plasma enhanced CVD. Process temperature for thermal CVD generally lie in the range of 500 to 1000°C. In hot filament CVD, the heat source is provided by a heated filament, which also results in heating the sample to above 500°C. In all cases, growth is usually assisted by catalytic transition metals. Therefore, sometimes the term Catalytic thermal or Catalytic Plasma enhanced CVD is used.
In the catalytic growth process, the deposition of carbon usually occurs on the surface of the exposed catalyst particle and therefore the growth is usually determined by the size of the catalyst. In many synthesis processes, the diameter of the resultant carbon filament is approximately equal to that of the nanoparticle and lies in the range from 5 to 500 nm. As will be shown in the experimental results in Chapter 5, if the amount of carbon arriving on the surface is balanced with the carbon consumed in the process, the above statement is usually true. However, there are some cases whereby single-walled carbon nanotubes grew from particles much bigger than themselves. This is usually put down to surface features and grain boundaries.

The apparatus for Thermal CVD usually consists of a quartz tube inside a furnace with a controllable source gas flow. There are two common methods of introducing the catalyst into the system: supported catalyst and floating catalyst. In the supported catalyst method, the catalyst is deposited onto a substrate which is then placed inside the tube furnace. In the floating catalyst method, the catalyst particles form from a source gas and are not attached to a substrate. Catalyst gases commonly used are metalloocene types or metal containing compounds such as ferrocene that sublime at low temperatures.

The catalytic nature of the carbon filament growth process was established by Tesner and co-workers [46,47] who showed that carbon filaments had metal particles associated with them. The growth mechanism leading to the formation of carbon nanofibres has been studied by many different groups. Baker et al. used in situ electron microscopy techniques to directly observe the manner by which small metal particles generated carbon nanofibres during the decomposition of acetylene [14]. From an analysis of recorded image sequences, they measured the rates of growth of the material and determined some of the kinetic parameters involved in the process. On the basis of these experiments, a growth mechanism was proposed that was later refined to include the following steps: (i) adsorption and decomposition of the reactant hydrocarbon molecule on a surface of catalyst, (ii) dissolution and diffusion of carbon species through the metal particle, and (iii) precipitation of carbon on the opposite surface of the catalyst particle to form the nanofibres structure. The proposed growth mechanism is as illustrated in Figure 2-10.
Figure 2-10 : Model proposed by Baker and Harris for the growth of catalytic carbon filaments [18].

This form of growth model is also frequently called the tip-growth method where the precipitation occurs on the bottom surface of the catalyst particle, thus elevating the particle, which remains at the tip of the nanofibre throughout the growth. According to this mechanism, the growth of the filaments starts off with the decomposition of the hydrocarbon at the ‘front’ surface of the metal catalyst particle, producing hydrogen and carbon, which then dissolves in the metal. The dissolved carbon then diffuses through the particle, to be deposited on the trailing “cool” face. The precipitation of carbon from the saturated metal particle leads to the formation of the filament. The filament growth then proceeds until the carbon feedstock is cut off or exhausted or the catalyst particle is covered or thermal energy is removed. Using controlled atmosphere electron microscopy, Baker and co-worker were able to determine the kinetics of the process, showing that the activation energy for the filament growth was about the same as the activation energy for bulk carbon diffusion in nickel [18]. Thus, according to Baker et al., the main driving force is the
temperature and the concentration gradient with the rate limiting step being the diffusion of carbon through the catalyst particle.

The supply-limited process depends on the rates of arrival of different gas species to the catalyst surface, their adsorption rates, and their respective decomposition rates. It has been argued that diffusion of carbon through the metal catalyst particle is the rate-determining step, as supported by the close agreement between the measured activation energy for nanofibre growth and that for carbon diffusion through the respective metals used as catalysts. Initially, the driving force for the bulk diffusion of carbon through the metal particle was ascribed to a temperature gradient, which was believed to develop due to exothermic reactions of decomposition on the surface of the catalyst [14, 48]. Later, it was proposed that concentration gradients drove the carbon diffusion through the catalyst particle, and there are several hypotheses about the processes involved in the formation of such concentration gradient. Nielsen and Trimm proposed that the carbon solubility at the gas/metal interface differs from that at the metal/carbon interface, since the activity of carbon in the gas phase may be much higher than one [49]. Sacco et al. suggested that the mass flux originates from the solubility difference between carbon at the alpha-iron/Fe3C interface and that between alpha-iron and carbon itself [50]. Kock et al. proposed that the driving force for bulk carbon diffusion is the gradient of the carbon content of substoichiometric carbides, whereby the carbon content decreases in the direction of the metal/carbon interface [51]. Central to the model of Alstrup is the assumption that the carbon atoms entering the selvedge, which consists of subsurface layers that differ from the ideal structure of bulk crystal, creates a “surface carbide” that forms the source of carbon atoms diffusing through the bulk of the metal particle [52]. In other words, the driving force for growth is a concentration gradient of carbon atoms from the metal-gas surface to the metal-graphite surface.

Recently, Helveg et al. performed time-resolved, atomic-resolution in situ transmission electron microscope observation of the formation of carbon nanofibres from methane decomposition over supported nickel nanocrystals [53].
As the carbon nanofibre formed, the nickel nanoparticle was found to undergo a shape change, almost adopting a partial liquid like behaviour. The growth was found to be preceded by the surface diffusion of carbon over the nickel nanoparticle. This results in an upward movement of the nickel nanoparticle as it undergoes surface atomic restructuring and an opposite downward diffusion of carbon.

The authors proposed a detailed and coherent growth mechanism, supported by density functional theory calculations, describing carbon nanofibre formation in terms of atomic-scale surface transport and restructuring of the nickel nanostructures. Accordingly, the dissociative methane adsorption is facilitated at the step edges and C atoms adsorb preferentially at the step sites. The active site/growth centre is associated with step edges at the nickel surface, mainly because carbon binds more
strongly to such sites than to sites at close-packed facets. The process involves surface diffusion of C and Ni atoms from the step edge, and includes the breaking of the C bond to the Ni step on the free surface, incorporation under the graphene sheet, and diffusion at the graphene-Ni interface. Moreover, their observations and calculations suggest that it is not necessary to include the bulk diffusion of C through the Ni particle, however, they do not eliminate such a possibility.

However, there are also in general two types of growth that are typically observed: (1) the base growth method in which the catalyst particle is anchored to the substrate at the bottom of the carbon nanotube and (2) the tip growth method whereby the catalyst stays as the top of the nanotube structure. Baker proposes that this is dependent on the catalyst-substrate interaction [41]. If the catalyst-support interaction is strong, the growth follows a base growth method and if not, the growth follows a tip growth method. The argument appears plausible and has been generally accepted. This issue has not been seriously addressed by the nanotube growth community. However, recently Merkulov et al. shows that using the same material, base and tip growth can be achieved using different synthesis techniques [54]. This suggests that growth kinetics could also be a major factor. Merkulov et al. further propose that the alignment of the structure is influenced by the growth method whether the growth occurs by tip or base growth [54].

![Figure 2-12: SEM images showing (a) Tip growth and (b) base growth [54]](image-url)
In a plasma assisted process, the tip or base growth is thought to be due to the electrostatic force exerted by the plasma determining the alignment due to its interaction with the catalyst nanoparticle. Thus, it can be seen that the growth of carbon nanotubes and nanofibres are extremely complicated and influenced by numerous factors. It is therefore also important to investigate the influence of the plasma on the growth of these nanostructures. Further literature review of plasma assisted growth is presented in the next section.

2.2.4.2.1 Plasma Enhanced CVD (PECVD) growth

The plasma enhanced chemical vapour deposition (PECVD) technique is similar to thermal CVD, with the major difference of the assisting plasma in the former. The inclusion of the plasma however complicates the growth process. While thermal CVD utilises thermal energy to break down the reactant gases, PECVD technique uses electron impact to achieve the same objective. As mentioned, PECVD is a technique that is gaining wide popularity. Besides offering advantages such as further control on the alignment, lower activation energy over thermal processes etc, it has the benefit that the electronics industry uses similar equipment for the deposition and etching of semiconducting, metallic and dielectrics.

![Figure 2-13: Plasma from (a) acetylene and (b) Nitrogen](image-url)
The plasma is also sometimes called glow discharge (see Figure 2-13). The term is due to the plasma being luminous. The glow or plasma is produced by applying a potential difference between two electrodes, much like a fluorescent lamp. The plasma is created due to the energy adsorbed difference from the mass difference between electrons, ions and molecules. Initially, the free electrons of the gas in the system are accelerated towards the anode due to the potential difference. However, free electrons in gases are rare and the plasma maintains itself by the electrons originating from the cathode. Briefly, the electrons are accelerated due to the applied field and collide with the molecules in the gas. Given sufficient energy, the impact can dissociate the molecules, creating ions and more electrons. The ionisation process gives off the luminescence that is observed in plasmas and this is the reason plasmas using different gases have different colours.

In PECVD systems, the energy source that is used to ignite the plasma varies widely. The plasma can be ignited using Direct Current (DC), Radio Frequency (RF), and microwave source. The literature is also complicated by the fact that the system design and configurations differ widely e.g. inductively coupled plasmas (ICP), hollow cathode, electron cyclotron resonance (ECR), etc [55-59]. It is therefore often difficult to re-produce or undertake a comparison from alternative systems due to the differences in electrode size and design, chamber design, etc.

The most important benefit of using the PECVD technique is the ease in which the nanotubes can be aligned. The majority of studies suggest that this is due to the electrostatic fields in the plasma [45]. There have been reports of vertical alignment using thermal CVD but only the plasma assisted growth has shown that individual freestanding multiwalled nanotubes are possible. The alignment resulting from thermal growth is attributed to overcrowding effects. The other benefit of using the PECVD technique is its apparent capability for lower temperature synthesis. PECVD technique has been used in the semiconductor industry for lower temperature synthesis of materials. Low temperature processes are highly desirable as it facilitates the integration of carbon nanotubes with standard semiconductor integrated circuit technology. Similarly for field emission display technology, the synthesis temperature has to be lower as the soda lime glass substrate has a melting point of 500°C. In general, low temperature growth (down to room temperature) has been
reported [60-63] but there are also suggestions that actual power transfer to the substrate from the electromagnetic fields, etc can be significant [64,65].

Low temperature growth model of carbon nanofibre proposed by B.O. Boskovic [60] is based on carbon filament growth models by Baker and Harris [18]. According to Boskovic, the surface of the nickel powder particles increase in roughness and form small domains inside each metal cluster. These domains act as nucleation seeds for the carbon nanofibre growth. The size of small domains within the metal corresponds to the diameter of the carbon nanofibre. The larger Ni particle could act as a thermal barrier as discussed in the work which follows as part of this thesis. This aspect has not been discussed by any researchers in this field to date. According to Boskovic, after dissociation of CH\(_4\) or C\(_2\)H\(_2\) molecules, free radicals are formed and carbon is adsorbed on to the metal domains. As carbon atoms and species are furthered supplied, a carbon metal eutectic alloy can be formed, decreasing the melting temperature of the alloy. The formation of carbon-metal eutectic alloys promotes the diffusion of carbon in the metal alloy, initiating carbon aggregation followed by the nanofibre formation. Carbon diffused at the rear face of the nickel particle precipitate at the interface to form carbon nanofibre structures. The carbon diffusion is limited to the metal domain size within the metal particle and the diameter of the nanofibre is not larger than the domain size. As the nanotube grows further, part of the metal domain is pushed upward, forming a metal cap. The metal cap saturates the dangling bonds of the nanofibre at the edge, stabilising the edges. The nanofibre stops growing when the metal particle at the tip is completely enveloped by the carbon. According to Boskovic, small but sufficient field enhancement is developed at the surface features such as micron sized nickel catalyst particles due to the nature of the plasma sheath. The radio frequency energy creates heating within the material through interaction between the electromagnetic fields and the materials molecular and electronic structure. Heating of the material occurs by dissipation of the part of the energy of the radio frequency electromagnetic field. The thermal energy normally required for carbon nanofibre growth is replaced by the radio frequency induced heating.

Hofmann et al reported the growth of carbon nanotubes at temperature as low as 120°C using a DC driven plasma [63]. The gases investigated include ammonia,
acetylene, methane and ethylene. It was concluded that the best combination of gases was ammonia and acetylene. They showed that the crystallinity of the carbon nanotube improves with temperature. They arrive at this conclusion based on the graphitic layers around the nickel while the 120°C synthesised carbon nanotube appears to be mostly amorphous. It was shown that without the aid of the plasma, no carbon nanotube growth was possible. The carbon nanotubes synthesised at 120°C follows a tip growth mechanism and grew linearly with time and exhibits a growth rate of 0.1nm/s. They report that the activation energy required is approximately 0.23eV which is similar to the 0.3eV surface diffusion activation energy of carbon on polycrystalline nickel. The effect of the plasma is to increase the dissociation of the precursor gases as well as cause local surface heating which enables efficient adsorption and diffusion for the carbon atoms.

Recently, Minea and co-worker reported room temperature growth using Inductively Coupled Plasma (ICP) technique driven by a 13.56MHz and 2.45GHz power source [61]. This technique is further accompanied by running an alternating nitrogen and acetylene plasma. The technique allows for short nanofibre growth with a growth rate of 2nm/min. According to Minea, the growth is only possible through the etching effect of dissociated nitrogen in the plasma. The alternating plasma provides an etching phase followed by a deposition phase. The strong etching reactivity of the nitrogen plasma eliminates the amorphous carbon phase of the glowing material allowing the formation of quite well organised carbon nanofibres containing high amount of nitrogen.

### 2.2.4.3 High pressure CO conversion (HiPCO)

This is a fairly new method by the Smalley group which uses catalytic chemical vapour deposition technique for the production of single-wall carbon nanotubes [66]. The technique uses carbon monoxide as the carbon source and iron pentacarbonyl (Fe(CO)_5) as the carbon precursor/catalyst. The catalyst particles are generated in situ by thermal decomposition of the Fe(CO)_5 at 800-1000°C. The process is operated at high pressure at around 10atm. In a continuous gas flow mode,
single wall carbon nanotubes are produced by flowing CO, mixed with a small amount of Fe(CO)5 through the heated reactor. The size and diameter of the nanotubes can be roughly selected by controlling the pressure of CO [66].

2.2.5 Nanotube applications

2.2.5.1 Vacuum Microelectronics

Excellent electron emission is one of the attractive properties of carbon nanotubes. When subject to sufficiently high electric field in vacuum, electrons near the Fermi level can overcome the energy barrier to escape to the vacuum. This results in an attractive source of electrons as compared to thermionic emission since it is a quantum effect. The electrons emitted by overcoming the surface barrier results in a smaller electron energy spread. The basic physics of electron emission is usually characterised by the Fowler-Nordheim equation.

\[ I = aV^2 \exp\left(-\frac{b\phi^{3/2}}{\beta V}\right) \]  \hspace{1cm} (2.4)

where I, V, \( \Phi \), \( \beta \) are the emission current, applied voltage, work function and field enhancement factors respectively while a and b are constants. According to this equation, the ability of the material to emit electrons under electric field is determined by the work function and the field enhancement factor.
Electron emission materials have been investigated extensively for applications such as flat panel displays, electron guns in microscopes, microwave amplifiers [68] and recently, for X-ray devices [69]. Figure 2-14 shows a 4.5 in. fully sealed Field Emission Display with red, green and blue phosphor columns manufactured by Samsung Advanced Institute of Technology [70]. The display works by using carbon nanotubes as multiple electron sources, hence eliminating the need to scan the electron beam as in the case of a conventional cathode ray tube. The emitter is made of carbon nanotubes embedded in metal electrode. Samsung has now demonstrated a full colour 38” carbon nanotube based display and hopes to start production later this year.
The use of carbon nanotubes as an electron source is also being explored for applications such as parallel electron beam lithography such as micro-cathodes as shown in Figure 2-15 [72]. In Figure 2-15, the carbon nanotubes emitters are grown in micro-cavities with a poly-silicon gate. The emission current is then controlled using the gate which modulates the electric field just above the nanotube emitter, which turns the cathodes on and off.

### 2.2.5.2 Electrochemical and Energy Storage

Carbon nanotubes have also been considered for energy production and storage. Carbon based electrodes have been used for decades in fuel cells, batteries as well as other electrochemical applications [71]. The high electrochemically accessible surface area of porous nanotube arrays, combined with high electronic conductivity and useful mechanical properties make them attractive as electrodes for devices that use electrochemical double-layer charge injection such as super capacitors [70].

The use of nanotubes as electrodes in lithium batteries is also another possibility as most electrodes currently in use are carbon-graphite based. Carbon
nanotube electrodes have been reported to have higher reversible component of storage capacity at high discharge rates [74,75] with the maximum reversible capacity of 1000mA.hr/g as compared to 372mA.hr/g for graphite and 708mA.hr/g for ball-milled graphite. The large irreversible capacity is related to the large surface area of the nanotube films (~300m²/g by Brunauer-Emmett-Teller (BET) characterization) and the formation of a solid-electrolyte interface [75]. However, the exact location of the Li ions in the intercalated nanotubes is still unknown.

Nanotubes have also been identified as a potential host materials for hydrogen storage, which would find uses in fuel cells for powering electric vehicles and laptops, etc [76-78]. Electrical energy can be produced by direct electrochemical conversion. Table 1 summarises the gravimetric hydrogen storage capacity reported by various groups taken at various temperature (T) and pressure (P). [79].

Table 1: Summary of gravimetric hydrogen storage capacity reported by various groups [79]

<table>
<thead>
<tr>
<th>Material</th>
<th>Max. wt% H₂</th>
<th>T (K)</th>
<th>P (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs (Low purity)</td>
<td>5 ~10</td>
<td>133</td>
<td>0.04</td>
</tr>
<tr>
<td>SWCNTs (High purity)</td>
<td>~4</td>
<td>300</td>
<td>0.04</td>
</tr>
<tr>
<td>Graphite nanofibres (tubular)</td>
<td>11.26</td>
<td>298</td>
<td>11.35</td>
</tr>
<tr>
<td>Graphite nanofibres (herringbone)</td>
<td>67.56</td>
<td>298</td>
<td>11.35</td>
</tr>
<tr>
<td>Graphite nanofibres (platelet)</td>
<td>53.68</td>
<td>298</td>
<td>11.35</td>
</tr>
<tr>
<td>Graphite</td>
<td>4.52</td>
<td>298</td>
<td>11.35</td>
</tr>
<tr>
<td>Graphite nanofibres</td>
<td>0.4</td>
<td>298 - 773</td>
<td>0.101</td>
</tr>
<tr>
<td>Li-Graphite nanofibres</td>
<td>20</td>
<td>473 - 673</td>
<td>0.101</td>
</tr>
<tr>
<td>Li-Graphite</td>
<td>14</td>
<td>474 - 673</td>
<td>0.101</td>
</tr>
<tr>
<td>K-Graphite nanofibres</td>
<td>14</td>
<td>&lt; 313</td>
<td>0.101</td>
</tr>
<tr>
<td>K-Graphite</td>
<td>5</td>
<td>&lt; 313</td>
<td>0.101</td>
</tr>
<tr>
<td>SWCNT (high purity)</td>
<td>8.25</td>
<td>80</td>
<td>7.18</td>
</tr>
<tr>
<td>SWCNT (~60% pure)</td>
<td>4.2</td>
<td>300</td>
<td>10.1</td>
</tr>
</tbody>
</table>

However, reports of the hydrogen storage capacity have been so controversial that many claims have been proven incorrect, while others have not been independently verified. The US Department of Energy benchmark is for a hydrogen storage capacity of 6.5 weight % at room temperature. Like the lithium intercalation, the exact location of hydrogen absorption is unknown and many models have been
developed on whether the hydrogen is absorbed on the outer wall or within the inner cores [80].

Figure 2-16: Modelling of hydrogen absorption with carbon nanotubes structure [80]

Figure 2-16 shows the modelling the possible location of hydrogen adsorption within carbon nanotubes, either within or outside the nanotube walls. Currently, metal hydrides and cryo-adsorption are the two commonly used means to store hydrogen, typically at high pressure and/or low temperature.

2.2.5.3 Nano-devices

Due to its unique electronic properties, carbon nanotube has been proposed as the next generation quantum wires as well as nano-electronics devices. Various
nanometer-scale electronic devices based on CNT have been realized recently, such as the field effect transistor, single electron transistor, metal-semiconductor diode, rectifier, intermolecular-crossed CNT-CNT diodes [81-83]. In the nanotube field effect transistor design, gating is commonly achieved by a submerged gate beneath a carbon nanotube as shown in Figure 2-17 [81]. The transistors were fabricated by lithographically applying electrodes to nanotubes that were either randomly distributed on a silicon substrate or positioned on the substrate with an atomic force microscope [81,84]. The work is driven by the potential of ultra-fast devices due to the nano-sized and possible quantum/ballistic tunnelling of the carbon nanotube.

![Figure 2-17: (a) Schematic of carbon nanotube transistor, (b) nanotube tested as a channel in experimental field effect transistor.](image)

Many device concepts such as crossed nanotubes three- and four-terminal devices [85] have been demonstrated as well as a non-volatile memory that functions like an electromechanical relay [86]. Although numerous technical hurdles still exists e.g. large contact resistance, chirality control, suitable mass production techniques, etc, many research groups e.g. IBM and Infineon are still actively pursuing this technology due to its potential payoff.

Recent activities have also focused on using nanotubes as replacements for metallic wire interconnects due to its high current carrying capacity [87] and strong covalent bonding that militates against current-induced electro-migration [88].
2.2.5.4 Advanced composite

Nanotubes can be used as fillers in various matrices such as polymers, much like their larger cousins, the carbon fibre. The advantage of nanotubes are that being molecularly perfect and smaller in size potentially allows for improvements in mechanical properties of their host material and a lower packing density of fillers. The first major commercial application is likely to be in their use in electrically conducting polymers whereby dissipative or conductive polymer composites can be obtained with low loading [89]. This is partly due to the high aspect ratio of the nanotubes which results in a lower percolation threshold. Electrically conducting polymers can find applications in dissipating electrostatic, electrostatic paints, electromagnetic shielding composites, etc. The major challenges are in the uniform dispersion of the nanotubes, improving nanotube-matrix interactions to provide effective stress transfer.

Recent work has also been conducted in the area of filling photo-active polymers such as poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PPV) with nanotubes. It is shown that there are large increases in electrical conductivity as compared to pristine polymers with little loss in photoluminescence/electro-luminescence yield [90].
Chapter 3

3 Experimental Techniques

3.1 Introduction

This section presents the experimental techniques used in this project for the synthesis and analysis of carbon nanotubes. Basic principles of each technique with the current state of the art in nanotube studies are presented. The techniques described in this section includes Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS) and Raman and IR spectroscopy.

3.2 Deposition techniques

Two types of synthesis techniques were used for the synthesis of carbon nanotubes will be discussed in this section. The first system to be discussed is the direct current plasma enhanced chemical vapour deposition technique and the second is radio frequency plasma enhanced chemical vapour deposition technique. Plasma Enhanced Chemical Vapour Deposition (PECVD) is a technique in which one or more gaseous reactors are used to form a solid, insulating or conducting layer on the surface of a substrate. This is enhanced by the use of a vapour containing electrically charged particles or plasma, at lower temperatures.

3.2.1 Radio Frequency plasma enhanced chemical vapour deposition

The radio frequency plasma enhanced chemical vapour deposition (rf PECVD) system used for carbon nanotube and nanostructure growth is an industrial standard Plasma Technology DP800 system. The schematic of the system is shown in Figure 3-1. The system is of a similar type that is widely used for the growth of amorphous silicon and diamond-like amorphous carbon films. The system uses a parallel plate electrode configuration which utilises a capacitively coupled plasma. The electrodes have diameters of 20cm and an inter-electrode separation of 2cm. The
electrodes are driven by a 13.56MHz radio frequency (rf) power supply which is equipped with a matching rf tuning circuit. The tuning circuit consist of a pair of tuneable capacitors that are matched by a computer controlled step motor. The capacitors were electrically connected in series between the rf power supply and the upper electrode (driven electrode). The lower electrode is electrically grounded. The sample is typically placed on the grounded electrode which is also water cooled.

![Diagram of the experimental setup](image)

**Figure 3-1: Schematic diagram of radio frequency plasma enhanced chemical vapour deposition system**

A combination of blower and rotary pumping is used for the system pumping. A base pressure of up to $10^{-5}$ mbar could be achieved in this system. Samples are usually placed on the lower (grounded) electrode. Gases are supplied through 3 process gas lines and vented through separate line. Gases are selected by electrically controlled valves and their flow is set by mass flow controllers. The gases are first mixed inside a manifold and fed into the reaction chamber through a small showerhead located at the centre of the upper electrode. The total gas pressure inside the chamber is measured by a baratron. The pressure is controlled and maintained automatically with an actuator controlled butterfly valve.
Chapter 3. Experimental techniques

The system is able to deliver up to 400W of rf power. The hydrocarbon gas available to this system is methane, with nitrogen and helium being typically used as the carrier or dilution gas.

3.2.2 Direct current plasma enhanced chemical vapour deposition

The system is a parallel electrode configuration which comprises a thin film heater element under the graphite electrode (cathode). The graphite cathode is monitored by an embedded thermocouple. The cathode and heater is surrounded by a boron nitride ring which helps confine the plasma around the cathode. The anode which also doubles as a gas showerhead, is supported by an adjustable stand. This allows the inter-electrode distance to be controlled for operating under different pressure regimes. The stage is equipped with an encapsulated patterned thin film based graphite heater which is controlled by a Eurotherm PID controller. The patterned heater ensures a temperature uniformity of ± 2% across the 2.5” cathode.

Figure 3-2: (a) Schematic diagram of direct current plasma enhanced chemical vapour deposition system stage assembly, (b) photo of system with plasma
The sample is placed on the cathode and the plasma is driven by a 600W Glassman DC power supply, which supplies a negative voltage to the cathode. Nitrogen, hydrogen and acetylene gas is fed through 3 mass flow controllers (two 1000scm and a 200scm rating). The system is pumped down using a rotary pump and can achieve a base pressure of $10^{-3}$ torr. Process pressure is maintained by a manual diaphragm valve with typical operating pressure being between 0.5 to 15 torr.

A typical run would start by placing the sample on the cathode electrode and evacuating the chamber with the rotary pump to base pressure. The chamber is then backfilled with the carrier or dilution gas to the desired pressure. If required, the temperature is being raised before the plasma is ignited. Acetylene is introduced only after the plasma is ignited. After the deposition is carried out, the sample is allowed to cool down in nitrogen ambient before removal.

### 3.3 Scanning Electron Microscopy (SEM) of Carbon Nanotube

Electron microscopy takes advantage of the wave nature of rapidly moving electrons. Where visible light has wavelengths from 4,000 to 7,000 Angstroms, electrons accelerated to 10 KeV have a wavelength of 0.12 Angstroms. This offers much higher resolution than optical microscopes. The scanning electron microscope generates a beam of electrons in a vacuum. The e-beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils. The primary imaging method is by collecting secondary electrons that are released by the sample. The secondary electrons are detected by a scintillation display that produces flashes of light from the electrons. The light flashes are then detected and amplified by a photomultiplier tube.

By correlating the sample scan position with the resulting signal, an image (displayed by a cathode ray tube) can be formed that is strikingly similar to what would be seen through an optical microscope. The illumination and shadowing shows a relatively natural looking surface topography. As can be seen from the Figure 3-3,
the use of a SEM allows much higher resolution than optical microscopes and thus, is extremely useful for analytical studies of carbon nanotubes. Scanning electron microscopes are also often coupled with X-ray analysers. The energetic electron beam-sample interactions generate X-rays that are characteristic of the elements present in the sample. Many other imaging modes are available that provide specialized information.

![Figure 3-3: SEM image of arc-discharge synthesised nanotube bundle on silicon.](image)

The different properties of the secondary and backscattered electrons are taken advantage of in the SEM. Backscatter imaging uses high energy electrons that emerge nearly 180 degrees from the illuminating beam direction. The backscatter electron yield is a function of the average atomic number of each point on the sample, and thus can give compositional information. Since the energy of the secondary
electrons (SE) is low, they are attracted with a positively charged grid on the SE-detector. The secondary electrons show the topographic information and the morphology of the sample. The energy of the backscattered electrons is high enough to create electron-hole pairs in a semiconductor detector. They give information of the chemical composition of the target material. Therefore backscattered electron intensity is, to a first approximation, a function of the chemical composition: the brighter an area, the greater the mean atomic number of that area relative to adjacent areas. In this study, the Hitachi S4000 cold field emission SEM with a spatial resolution of 1.5nm is used.

3.4 Transmission Electron Microscopy (TEM) of carbon nanotube

A TEM works pretty much in the same way as a SEM in terms of beam generation and focusing. However instead of collecting the secondary electrons, the microscope collects the elastically scattered electrons. In another words, a TEM collects information on transmitted electrons. When electrons have sufficiently high accelerating energy, they can pass through thin samples. Some of the electrons will be elastically scattered depending on the makeup of the sample. When TEM shine a beam of electrons through the specimen, whatever part is transmitted is projected onto a phosphor screen. This yields information on the morphology such as the size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters. It also yields crystallographic information such as the arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometres in diameter.

The use of High Resolution Electron Microscopy (HREM) has undoubtedly been one of the most useful techniques in the study of carbon nanotubes. While the rest of the techniques can give great surface details (e.g. Scanning Tunnelling Microscope) or accurate crystallographic measurements (e.g. X-ray diffraction), only HREM can probe the internal structure. Together with the HREM, electron diffraction is also widely used in the study of high quality nanotubes.
Due to the lower synthesis temperature used in this work, HREM can be used to study the degree of defect of the nanotubes. Here in Surrey, a Philips CM200 TEM with a line resolution of 0.14nm, X-ray analysis, imaging and selected area diffraction and parallel EELS capabilities is available for the study of nanotubes.

3.5 Electron energy loss spectroscopy (EELS)

Electron energy loss spectroscopy (EELS) is a technique for light element analysis and can provide useful information on oxidation states and bonding [95]. For graphite and related carbon specimens, information can be obtained from two energy ranges. In the range 280 – 300eV, energy loss is associated with the excitation of an electron from the 1s carbon core to the Fermi level. The nature of the 1s core level spectra can enable estimates to be made of the relative amounts of $sp^2$ and $sp^3$ bonding by referencing to an equivalent ratio of graphite which is assumed to have 100% $sp^2$ bonding. In the region 0 – 40eV, energy loss is due to the excitation of plasmons, arising from the $\pi$ electrons and the $\pi$ and $\sigma$ states of the carbon L shell.
It was found that the EELS spectra from multi-walled nanotubes of different diameter showed that the bulk plasmon loss peak ($\sigma + \pi$) shifted to a lower energy with decreasing diameter [96,97]. This was taken to indicate that the $\pi$ electrons became delocalised as the tubes become smaller, due to the curvature-induced strain, thereby contributing less to the collective excitations. In the range of 260 – 320eV, in which the K shell excitations occur, the spectra were broadly similar to those of graphite.

Assuming that the shift in plasmon loss peak is due to the curvature induced strain, we can only expect to see similar results if we are able to synthesize nanotubes with very small diameters (~2 – 20nm in diameter).

### 3.6 Raman and IR spectroscopy

Raman spectroscopy comprises the family of spectral measurements made on molecular media based on inelastic scattering of monochromatic radiation. During this process, energy is exchanged between the photon and the molecule such that the
scattered photon is of higher or lower energy than the incident photon. The difference in energy is made up by a change in the rotational and vibrational energy of the molecule and gives information on its energy levels. Raman and optical analysis of carbon based materials have been widely used to determine its bonding properties. The phonon modes for carbon nanotubes can be obtained using similar methods to those employed in calculating the electronic properties. Dresselhaus, Jishi and co-workers have done extensive studies of symmetry assignments and spectroscopic activities of the vibrational modes for nanotubes [30, 98-101].

Table 2: Table of frequencies for graphitic carbon and nanotubes

<table>
<thead>
<tr>
<th>Mode assignment</th>
<th>Planar Graphite</th>
<th>Single wall tubules</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOPG$^{[102]}$</td>
<td>BHOPG$^{[102]}$</td>
</tr>
<tr>
<td>$E_{2g}$ (R, (\perp))</td>
<td>42$^a$</td>
<td></td>
</tr>
<tr>
<td>$B_{2g}$ (S, (\parallel))</td>
<td>127$^a$</td>
<td></td>
</tr>
<tr>
<td>$A_{2u}$ (Ir, (\parallel))</td>
<td>888$^b$</td>
<td>(-900^b)</td>
</tr>
<tr>
<td>$B_{2g}$ (S, (\parallel))</td>
<td>870$^d$</td>
<td>(-900^g)</td>
</tr>
<tr>
<td>$E_{2g}$ (R, (\perp))</td>
<td>1582$^b$</td>
<td>1586$^c$</td>
</tr>
<tr>
<td></td>
<td>1577$^b$</td>
<td>1591$^b$</td>
</tr>
<tr>
<td>$E_{1u}$ (Ir, (\perp))</td>
<td>1588$^a$</td>
<td>1592$^a$</td>
</tr>
<tr>
<td>$D$ (R, (\perp))</td>
<td>1350$^b$</td>
<td>1367$^b$</td>
</tr>
<tr>
<td></td>
<td>1365$^b$</td>
<td>1380$^b$</td>
</tr>
<tr>
<td>$E_{2g}$ (R, (\perp))</td>
<td>1620$^b$</td>
<td></td>
</tr>
<tr>
<td>2 x 1220 (R, (\perp))</td>
<td>2441$^b$</td>
<td>2450$^b$</td>
</tr>
<tr>
<td></td>
<td>2440$^b$</td>
<td>2440$^b$</td>
</tr>
<tr>
<td>2 x D (R, (\perp))</td>
<td>2722$^b$</td>
<td>2722$^b$</td>
</tr>
<tr>
<td></td>
<td>2746$^b$</td>
<td>2753$^b$</td>
</tr>
<tr>
<td>$E_{2g}$ + D (R, (\perp))</td>
<td>2950$^b$</td>
<td>2925$^b$</td>
</tr>
<tr>
<td></td>
<td>2974$^b$</td>
<td>2974$^b$</td>
</tr>
<tr>
<td>2$E_{2g}$ (R, (\perp))</td>
<td>3247$^b$</td>
<td>3180$^a$</td>
</tr>
<tr>
<td></td>
<td>3246$^b$</td>
<td>3180$^a$</td>
</tr>
</tbody>
</table>

* Activity: R = Raman-active, Ir = infrared active, S = optically silent, observed in neutron scattering
\(\parallel, \perp\) - Carbon atom displacement to C
Excitation wavelength: * 488nm, $^b$ 514nm, $^c$ Ir-absorption study, $^d$ predicted, $^e$ from neutron scattering
BHOPG - Boron doped HOPG
Table 2 shows the vibrational mode frequencies for graphitic carbon and nanotubes reported by various groups. However, vibrational modes have also been used to differentiate the diameter and chirality of the nanotubes [105,106]. It is however important to point out that the special vibrational modes in the radial breathing mode region can only be picked up experimentally for nanotubes with very small diameters as the Raman activity for the zone folded modes will be too small to be detected experimentally. Larger diameter nanotubes will have a Raman spectrum that is similar to graphite. Low temperature grown carbon nanotubes have Raman features which resemble amorphous carbon. This is due to the high level of defects and amorphous carbon coating. Typical CVD grown carbon nanotube would exhibit broad peaks at 1345 cm\(^{-1}\) and 1580 cm\(^{-1}\) as shown in Figure 3-6.

![Raman spectrum of typical CVD synthesis carbon nanotubes](image)

**Figure 3-6:** Raman spectrum of typical CVD synthesis carbon nanotubes

Raman spectroscopy is also a hugely popular characterisation technique as it requires little sample preparation and is non-destructive. In this study, a Raman
Microscopy Renishaw System 2000 was used with a scanning range of 300 to 3000 cm\(^{-1}\). Two possible excitation sources of 782nm and 514nm are available.

### 3.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS was developed in the mid 1960s by K. Siegbahn and his research group. K. Siegbahn was awarded the Nobel Prize for Physics in 1981 for his work in XPS. The phenomenon is based on the photoelectric effect outlined by Einstein in 1905 where the concept of the photon was used to describe the ejection of electrons from a surface when photons impinge upon it. For XPS, Al K-alpha (1486.6eV) or Mg K-alpha (1253.6eV) is often the photon energies of choice. Other X-ray lines can also be chosen such as Ti K-alpha (2040eV). The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from the solid. The energy of the photoelectrons leaving the sample is determined using a Hemispherical Analyser (HA). A spectrum with a series of photoelectron peaks is obtained and the binding energy of the peaks is characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of the materials surface. The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. With the aid of a table of core binding energies, the peak position usually specifies both the element and the core level origin of the electrons. The electron binding energy table gives the expected region for a particular core electron peak, but the precise binding energy depends on the chemical state of the parent atom. Hence, XPS allows identification of chemical states and a quantitative analysis of 0.5-3 nm thick surface layers. XPS can be applied to any element except hydrogen in the periodic table. While XPS is not typically used in the analysis of carbon nanotubes, it can be useful in getting information on the catalyst. In this study, XPS has been used to characterise the catalyst states after carbon nanotube growth in order to obtain information on the growth mechanism.
Chapter 4

4 Low temperature growth of carbon nanostructures from rf-PECVD

4.1 Low temperature carbon nanofibre/nanotubes

Catalytic growth of carbon nanotubes and nanofibres have been synthesised at temperature ranges from 450 to 1000°C. Researchers have been trying for decades to reduce the growth temperatures. Recently, low temperature growth of carbon nanofibres and nanotubes has been demonstrated by several researchers [60-63]. In particular, Boskovic et al. had shown room-temperature growth of carbon nanofibres [60]. The demonstration of room temperature growth however is hampered by two main factors which is low yield and patterned growth.

To obtain further understanding of low temperature growth, a series of experiments were planned and carried out in order to investigate the growth mechanism. The main objective is to improve the yield and control over the growth. In this study, the Plasma technology DP800 Plasma enhanced CVD (PECVD) system was used to carry out the deposition using methane as the carbon feedstock and argon as the carrier/dilution gas. Various nickel powder was used as the catalyst. Nickel powders with a mean particle size ranging from 20 nm to 7 μm from Goodfellows and various sources were used. Sputtered nickel thin films were also used in the experiments. When nickel powder was used, it was placed on a silicon substrate which was loaded into the growth chamber. After deposition, the samples were analysed using Hitachi S-4000 FE-SEM.

4.1.1 Results and discussion

Details of the experiments carried out are listed in Table 3. The chamber was cleaned using an oxygen plasma for 20 mins before loading the sample and the experiments were performed in the order as listed in Table 3. It can be seen that a
series of different methane concentration experiments were performed in a random order, which is to prevent any run-to-run deviation.

Table 3: Summary of experimental details

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Pressure (mTorr)</th>
<th>Time (min)</th>
<th>Power Self bias (V)</th>
<th>Methane Flow (sccm)</th>
<th>Methane %</th>
<th>Argon Flow (sccm)</th>
<th>Argon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>15</td>
<td>200</td>
<td>80</td>
<td>35</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>981</td>
<td>10</td>
<td>200</td>
<td>80</td>
<td>30</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>990</td>
<td>10</td>
<td>200</td>
<td>80</td>
<td>45</td>
<td>75</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>980</td>
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<td>200</td>
<td>60</td>
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<tr>
<td>5</td>
<td>980</td>
<td>10</td>
<td>200</td>
<td>60</td>
<td>24</td>
<td>40</td>
<td>36</td>
</tr>
<tr>
<td>6</td>
<td>980</td>
<td>10</td>
<td>200</td>
<td>85</td>
<td>36</td>
<td>60</td>
<td>24</td>
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<tr>
<td>7</td>
<td>980</td>
<td>10</td>
<td>200</td>
<td>60</td>
<td>24</td>
<td>40</td>
<td>36</td>
</tr>
</tbody>
</table>

Figure 4-1: SEM image of Nickel particles coated with carbon
Empirical observations on the SEM images shows that most nickel particles were coated with what looks like a thin carbon layer as shown in Figure 4-1. The samples were kept close to room temperature with the water-cooled electrodes. The plasma heating in the run was minimal due to the low pressure and the low power density. The electrodes are 20 cm in diameter, translating to a power density of 0.64W/cm² (most of which should be expended in the dissociation of the process gas). Polymers such as polystyrene pellets which have a glass transition temperature of around 100°C showed no noticeable physical changes under all the process conditions, further confirming there is minimal plasma heating.

The variety of nickel particles investigated included different mean particle sizes (nm to microns), different crystallographical features, etc. The carbon coating appears as a translucent layer around the nickel particles, and in some cases where the methane concentration is higher, the nickel particle appears completely coated. This observation is made as the surface protrusions on the nickel particles appear less obvious after the deposition. The SEM images however still clearly shows surface protrusions of the order of tens to hundreds nano-meters on some of the nickel particles, despite the coating. The series of experiments was planned to vary the carbon concentration in the system while keeping the rest of the process conditions constant. However due to the low process temperature of the experiment, it is observed that the carbon tends to condense on the nickel particle rather than diffusing and nucleating the growth of carbon nanotubes.

Experiments involving other variations of the process parameters e.g. power, pressure, etc were conducted and has proved to be inconclusive in increasing the nanotube yield. However some conclusions and suggestions based on empirical observations can still be made:

1) Work conducted thus far involves the variation of carbon concentration. Since the yield of the nanotubes are low regardless of the quantity of carbon ions/ radicals available, the amount of carbon ions/radical or species involved in the process is not a major factor at such low temperature. Thus, this factor can be effectively eliminated in the consideration of low temperature growth
as long as there is sufficient carbon that is broken down and to nucleate and form the nanotube. In fact, the carbon concentration should therefore be kept to a minimum to reduce the formation of amorphous carbon.

2) In all nanotube growth models presented in the literature, factors such as diffusion of carbon through or on the surface the nickel particle, concentration gradients across the particle, etc were considered and all these factors are basically thermodynamically driven or involve surface physics. Since there is no deliberate introduction of thermal energy within the setup, the only source of energy is from the plasma. While its not expected that rf-driven plasmas to generate much heat across the sample due to its long wavelength (as compared to say microwave where the heating can be significant), there exists the possibility of microscopic hot-spots (small areas where the temperature is much higher than its surrounding), probably due to e.g. geometric enhancement of electric field at various areas. It has also been demonstrated that small metal particles can be heated in high frequency fields, and magnetic particles have additional mechanisms for high frequency field heating [107,108]. The generation of these hot-spots could be one of the reasons for the low yield.

3) As stated in point 2, the main factors involved in the growth of nanotubes could be still thermodynamically driven to a certain extent. An observation that was widely made was that the nanotube diameter is closely linked with the size of the catalyst particle. However, as the experiments show the changes in surface nickel protrusions or particle size does not seem to play a major role in low temperature synthesis.

It is likely that if the catalyst particle is small, the carbon diffusion distance is shorter and therefore growth of the nanotube would be easier, provided that the strain energy in forming such small nanotubes is within the nucleation limit. The use of well dispersed nano-sized particles could also induce electric field enhancements and be selectively heated which could be translated to the hot spots discussed in point 2.
Next, it was attempted to use the break-up of nickel thin films as a route to obtaining well distributed nano-sized particles. However, attempts using various thicknesses of nickel also resulted in no nanotube yield. It appears that the nickel film has not been broken up in most cases by the plasma generated by the DP800 system. In most cases, the formation of an amorphous carbon thin film is again observed as shown in Figure 4-2. Figure 4-2 shows the different carbon coatings on the surface of nickel thin film processed at different conditions.

![Figure 4-2: Amorphous carbon thin film coating on nickel catalyst thin film](image)

One factor that was not studied in detail here is the use of the plasma in the synthesis. The plasma using the DP800 system is limited in its setup in several factors such as the amount of bias that can be placed on the sample, the use of acetylene which has lower dissociation energy than methane, etc. The plasma
however is fundamental in low temperature growth as the chemically driven kinetics could be crucial. This is investigated in more details in the following chapters.

Both nickel powder and thin films have been attempted using RF-PECVD, involving numerous process parameter variations. With the nickel powder, different nickel particle sizes and crystallographical features do not appear to aid in increasing the yield. This seems to be in contradiction to Boskovic’s proposed growth mechanism, where he suggested that sufficient field enhancement can be developed at the surface features such as micron sized nickel catalyst particles due to the nature of the plasma sheath. The localised field enhancement causes heating of the nickel catalyst at that particular site. The heating of the material occurs by dissipation of the part of the energy of the radio frequency electromagnetic field, which replaces the thermal energy normally required for carbon nanofibre growth. In the absence of other possible explanations, localised heating seems to be the only logical explanation.

It is observed that the process seems to coat most of the particles with carbon rather than nucleating and synthesising carbon nanotubes. This is attributed to the lack of thermodynamically driven diffusion. The carbon nanotubes/nanofibres that are grown by the proposed localised heating were not widely observed. The present approach of using the nickel catalyst as catalyst powder does not provide for practical deployment or growth of carbon nanotubes. For effective utilisation of carbon nanotubes in developing potential applications using low temperature growth, the nickel catalysis particles would have to be either deposited as a thin film or patterned as an array. Having a controllable array or growth would also facilitate the study of carbon nanotubes. However, this approach of preparing the catalyst would most likely result in a uniform dispersion of nickel nanoparticles, which in turn would have very little field enhancement. As can be seen in the experiments using only nickel thin film catalyst, no carbon nanotubes were synthesised. The plasma generated by the RF power supply does not seem sufficient in breaking up the nickel film. The process is in fact very similar to amorphous carbon thin film deposition. It was decided that the focus for effective low temperature growth should be in the control of the plasma, rather than the nickel catalyst.


4.2 Carbon spheres

It was also noticed that after the carbon plasma operation, many carbon by-products were produced. These by-products can usually be found at the side of the electrodes and were collected in powder form. Depending on the experimental parameters, various forms of carbon nanostructures can be synthesized [109]. The generation of particulates in plasmas used in chemical vapour deposition is ubiquitous [110-112]. For researchers involved in the deposition of silicon based films, the main aim is to suppress the particulate growth during the deposition of the silicon. Likewise in the deposition of carbon films using PECVD techniques, carbonaceous dust may also be generated. Carbon’s ability to hybridize as sp\(^1\), sp\(^2\) and sp\(^3\) bonds allows the formation of a variety of structures such as nanotubes and fullerenes.

The term ‘dusty’ plasma is often used when the particulate forms in the plasma after prolonged operation of the plasma. The ‘dust’ can sometimes be observed with the naked eye to be circulating within the plasma cloud, electrostatically levitated and carried by the gas flow. The ‘dust’ usually formed in a carbon based plasma is generally found to consist of rolled up films or fragments of amorphous carbon. These fragments result from a-C:H films deposited on the electrode surface peeling off to relieve built-up stress, and are of the order of tens of microns. However, the generation of white spherical carbon particulates of the order of 500nm to 1\(\mu\text{m}\) in diameter in a methane ‘dusty’ plasma is also observed. The formation of ‘white’ carbon has been reported to be produced by sublimation of pyrolytic graphite at low pressures [113]. ‘White’ carbon forms as a transparent birefringent crystal with interplanar spacings identical to those of carbon form noted in the graphite gneiss from the Ries (meteoritic) Crater of Germany [113]. The formation of nanometre and micrometer sized spherical carbon have also been reported previously using chemical vapour deposition or pressure carbonization [114-116], although this is the first sighting of white carbon spheres.
4.2.1 Results and discussion

The particles were dispersed on a conductive adhesive disc for SEM analysis. The SEM images of the particles show that the carbon particles are all spherical and do not contain other forms of carbon structures such as nanotubes or a-C fragments.

![SEM image of carbon spheres](image)

**Figure 4-3: SEM image and size distribution histogram for carbon spheres**

The size distribution of the particles was determined by SEM examination of 50 particles. The diameters of the particles ranged from 500 to 1050 nm (Figure 4-3) and the mean diameter was around 790 nm based on numerical analysis. The actual
yield of the white powder is low and in some instances, rolled up graphitic fragments could be found. These fragments could be from carbon films deposited on the top electrode that have fallen off due to peeling from thickness-induced stress. A possible explanation for the change in colour of the powder (towards brownish) could then be attributed to the increase in such fragments or based on increasing thickness of the fragments.

Figure 4-4: HRTEM images of (a) centre and (b) side of spherical carbon particles

HRTEM images revealed the particles to be completely amorphous-like (Figure 4-4), within or at the edge of the sphere. The particles bear a striking resemblance to the carbon nanoballs reported by X.Y. Liu et al. [117] by thermal pyrolysis of Fe(CO)₅ and pentane and other reports [114-116], both in terms of morphology and size, although the production techniques differs widely. In this case, the generation and formation of the carbon spheres is due to the energetic species e.g. ions and electrons and the chemistry in the plasma.

EELS measurements were carried out for the carbon spheres and the spectrum is shown in Figure 4-5. Both low loss and the carbon K-edge spectra were collected. These spectra were deconvoluted using Fourier logarithm ratio with the electron
beam passing through vacuum. The background was removed from the carbon K-edge as well as multiple scattering by deconvoluting the low loss spectrum.

![Carbon K-edge](image)

![Low Loss](image)

**Figure 4-5: EELS Spectra for carbon spheres**

From the low loss spectra, the $\pi$-resonance peak of 5.87 eV and $(\sigma+\pi)$ resonance plasmon energy of 22.2 eV was found by using a Lorentzian curve fit. The
π* peak at 285 eV of carbon K-edge was fitted by a Gaussian and its area was normalized to the σ* edge in the window of 284 – 310 eV. A sp<sup>2</sup> content of around 56% was found by referencing this ratio to that of graphite, which is assumed to have 100% sp<sup>2</sup> content. From the plasmon energy and estimated sp<sup>3</sup> fraction, the carbon particle exhibits the characteristics of typical hydrogenated amorphous carbon film as one would expect being derived from methane. The incorporation of hydrogen reduces the amorphous carbon plasmon energy by around 2 eV from its typical value of 24 eV.

![Carbon sphere (white)](image)

Figure 4-6: Raman spectroscopy of carbon sphere

Raman spectroscopy was then carried out using a 782nm laser source. For Raman spectroscopy analysis, particulates were deposited on to a silicon substrate. The Raman spectra (Figure 4-6) shows three main peaks of interests (1336cm<sup>-1</sup>, 1456cm<sup>-1</sup> and 1624cm<sup>-1</sup>) situated in the 1200 to 1750cm<sup>-1</sup> range. The peak at around 940cm<sup>-1</sup> is due to the second order Raman peak of the silicon substrate underneath. Typical amorphous carbon shows broad peaks at 1350cm<sup>-1</sup> and 1580cm<sup>-1</sup>, typically labelled as the D and G bands of graphite respectively. The D band is a disorder induced band while the G band is a characteristic of graphite-like carbon. The position of the 1336cm<sup>-1</sup> indicates a shift in the D line from 1350cm<sup>-1</sup> relating to the
increase in the degree of disorder in sp²-bonded clusters. More interesting are the two peaks at 1456 cm⁻¹ and 1624 cm⁻¹. The band at 1456 cm⁻¹ has been assigned to C-H bonds, which is normally accompanied by other bands near 2900 cm⁻¹. The fluorescence in the range of 2000 to 3000 cm⁻¹ however masks any information available to identify any peaks around the 2900 cm⁻¹ region. It should be noted that no literature of the 1450 cm⁻¹ line due to C-H bonds in a-C:H with visible Raman spectroscopy was found and UV Raman only shows vibrational modes around 2920 cm⁻¹. There is however reports of this peak using FTIR spectroscopy on amorphous carbon films [118]. The G mode of graphite at 1581 cm⁻¹ has E₂g symmetry and lies in the range of 1500 to 1630 cm⁻¹. At this point, it is uncertain if the peak at 1624 cm⁻¹ is due to the appearance of the D’ peak (~1620 cm⁻¹) commonly reported. This peak cannot be due to the shift of G mode towards higher wavenumbers as the peak does not comprise of two modes neither is it a result of the probe laser wavelength as there have been no reports of the G band situated above the 1600 cm⁻¹. The appearance of D’ occurs because of the relaxation of the q = 0 selection rule allowing higher-frequency phonons, and as phonons disperse upwards away from Γ point of phonon dispersion of a single graphite layer. However, with reference to the usual a-C:H films deposited using such process parameters, the G line is always present in amorphous carbon films.

IR spectra (Figure 4-7) show major peaks between the ranges of 1300 to 1850 cm⁻¹. Most of the features can be easily assigned: 1376 cm⁻¹ (CH₃ symmetric bending mode), 1454 cm⁻¹ (CH₃ asymmetric bending and CH₂ scissor mode) and 1711 cm⁻¹ (carbonyl C=O mode). The CH stretching modes in the region of 2850 - 3000 cm⁻¹ are also evident. All these are consistent with a simple hydrocarbon. However, there are other features to complicate the interpretation. Given the prominence of the 1711 cm⁻¹ (carbonyl C=O) band and the very broad OH/H₂O band centred at 3300 cm⁻¹, there are suggestions for highly oxidising conditions being present in the sample reactor. The bands at 1560 cm⁻¹ and 1668 cm⁻¹ are consistent with carboxylate moieties.
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In summary, the IR spectra shows that the carbon spheres are rich in hydrogen and oxygen. It is not clear if the oxygen is introduced during the synthesis or after. Oxygen is known to be able to permeate through amorphous carbon.

4.2.2 Discussion

The observation of white carbon as a transparent birefringent crystal has been reported before [113] though in this case however, the formation dynamics probably follow a similar path to those observed in the silane based process. The process used by Whitaker et. al. utilised low pressure and high temperature, while in our instances, the pressure was higher and the plasma gas temperature is unlikely to reach 2550K [113]. Initial clues as to the formation of particulates can be taken with references to the literatures studying similar formation in rf discharge PECVD a-Si:H deposition. It is likely that the formation, growth and trapping of the carbon particles are related to the discharge power, gas flow and pressure. The discharge power affects the growth and formation of these particles while the trapping is due to the gas-drag force exerted by the gas flow and pressure. The actual formation, of course, could be more complicated than the a-Si:H counterpart due to carbon’s ability to hybridize, and the
formation of different radicals formed in the process. Similar to the a-Si:H process, the particulates were observed to levitate and circulate along the sides of the electrodes due to electrostatic forces in the plasma which further strengthen the hypothesis that the trapping of the particulates are related to the gas flow and pressure.

Particularly interesting is that the particulates have an amorphous structure as revealed by TEM while adopting a spherical shape. The preliminary analysis seems to lead to the conclusion of a polymeric a-C:H or an aliphatic based material. Taking the IR spectrum of the C-H stretching modes around 2900 cm$^{-1}$, the integrated weight of the curve after background subtraction gives the number of hydrogen atoms per unit area N, according to the formula [119]:

$$N = A \int \frac{\alpha(\omega)}{\omega} d\omega$$  \hspace{1cm} (4.1)$$

where A is a normalisation factor and $\alpha(\omega)$ is the frequency dependant absorption coefficient. The hydrogen content calculated from the IR spectra amounts to 36±2%. However this can only be taken as an indicator as it only takes into account of the carbon bonded hydrogen. In most cases, hydrogenated amorphous carbon has hydrogen fractions between 30 - 50% [120].

However, Raman spectroscopy reveals unusual vibrational modes (1450 cm$^{-1}$) that to our knowledge have not been reported before for a-C:H films synthesised using similar conditions. As stated, the ability of carbon to hybridize can result in the formation of different forms of carbon structures thus giving a wide variety of properties. There has been no observation of such particulate formation at other process conditions such as reduced power or methane concentration and pressure. It is noted empirically that the deposit collected using other process parameters tend to contain mostly graphitic fragments of the order of tens of microns.
4.3 Summary

In this chapter, the attempts on low temperature growth of carbon nanotubes using rf-driven PECVD system are reported. The yield is low despite numerous process variation investigations. For the nickel powder, the nickel particle size and crystallographical features do not seem to have an effect in increasing the yield. In nearly all cases, the catalyst was found to be coated in amorphous carbon. The carbon coating can be attributed to the lack of thermodynamically driven diffusion. For the nickel thin film catalyst, no carbon nanotubes or nanofibres were observed. Similar to the nickel powder catalyst, amorphous carbon thin film is found to be across the nickel thin film catalyst. The plasma generated by the RF power supply does not seem to sufficient in breaking up the nickel film. The proposed localised heating by Boskovic [60] was not controllable and it was decided that the study for effective low temperature growth should be focused on the plasma rather than the nickel catalyst. Nickel catalyst deployed in arrays or as a thin film would allow for better controllability and aid in the study of low temperature synthesis. Due to system constraints, a home built dc-driven PECVD system for the synthesis of carbon nanostructures is used to offer greater process flexibility. This is discussed in the next chapter.

The observation of white particulate formation is also reported during the operation of the plasma. The particulates are determined to polymeric amorphous hydrogenated carbon. The formation of these particulates at such low temperatures signifies that the carbon material is capable of different structural formation.
Chapter 5

5 Low temperature growth of carbon nanostructures from DC PECVD

5.1 Low temperature growth of carbon nanostructures

From the last chapter, it was envisaged that in addition to balancing the carbon arrival on the nucleating surface, the nickel catalyst would be standardised in the study of low temperature growth. This chapter reports the work done on investigating the effect on low temperature growth using DC-PECVD. The DC-PECVD system allows for more flexibility in the investigating process changes as it is equipped with a heater and allows for a higher process pressure. The electric field in the plasma can also be independently controlled, unlike the DP800 system which is controlled by the input power and the process pressure. The nickel catalyst used in this section is standardised as sputtered thin film so as to eliminate catalyst deviation.

The DC-PBCVD system is a custom built system which uses acetylene as its carbon source. The rationale for choosing acetylene is that it has lower dissociation energy when compared to methane. Most reports of lower synthesis temperature of around 500°C use acetylene as the carbon source. In this work, we investigate the synthesis as a function of temperature, hydrocarbon concentration, applied voltage and time. A modified variation of the widely accepted growth mechanism by Baker et al. is proposed to account for the observed results [121].

5.1.1 SEM analysis

Figure 5-1 shows the SEM images of the sample surface where growth was attempted at different temperatures using 10 nm of nickel thin films on silicon (100) substrates. The experiment was first carried out in the temperature range of 300 to
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700°C. The nickel catalyzed substrates were processed with a plasma bias of 450V, 5% hydrocarbon concentration at 10 Torr and for a growth time of 10 mins.

![Figure 5-1: Carbon nanostructures grown at 450V, 10torr, 5% hydrocarbon concentration at (a) 700°C, (b) 600°C, (c) 500°C, (d) 400°C and (e) 300°C for 10 mins.]

At 700°C, the nanotube growth was rapid and can reach a few microns in length within 10 mins. Different morphology and growth rates can be observed when the nanostructures are grown at 700, 600 and 500°C. The SEM examination revealed
that nanostructures cannot be grown at temperatures below 500°C. This is in agreement with the work reported in the public domain in general. At 700°C, typical nanotube structures were observed with a clear indication of the nickel catalyst being present at the tip. At 600°C, an obvious improvement in diameter uniformity and much reduced diameter is observed. At 500°C, the nanotubes were observed to appear as nucleating out of larger nickel base-islands. The most significant observation as the temperature drops, the growth rate reduces significantly. For the sample processed at 400°C and 300°C, the observation of only amorphous carbon was noted. Looking at Figure 5-1c and d, it is noted that the combined energy associated with the plasma generated with a bias of 450V and the applied thermal energy to the system are sufficient to break up the nickel film into particle-like features. This suggests that with this process, no pre-treatment of the nickel film to form particles or islands for catalyst action seems necessary. However, below 500°C the observation seems to suggest that there is either insufficient energy in the system for the nucleation of the nanofibres or the condensation of gaseous carbon is dominant over nanofibre growth at lower temperatures. It's pointed out that at 300°C, the process tends to deposit amorphous carbon even though the hydrocarbon concentration is only 5%.

In order to understand the formation of the nickel particles due to the heat treatment, a series of nickel film with different thickness is heat treated and the deposition is carried out. Figure 5-2a shows the nickel thin film after annealing at 700°C for 30 min. The initial nickel thickness was 4.5 nm, prepared by thermal evaporation of a Ni wire. The formation of nanosized islands is due to the heat applied to the sample which causes the thin film to sinter due to surface tension. Figure 5-2b shows the size distribution of the sample fitted to a log normal function giving a mean particle size of 125 nm and a standard deviation of 62 nm. It can be observed that using this technique the islands formed are generally irregular and the standard deviation is large. The average island size is about 16 times the original film thickness.
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Figure 5-2: (a) SEM image of the thermally annealed Ni film with an initial thickness of 4.5 nm. (b) Distribution of the Ni islands with a mean size of 125 nm and standard deviation of 62 nm according to the analysis of the above SEM micrograph.

SEM images of samples with different island sizes of 34, 69, 140, and 180 nm are shown in Figure 5-3a to 3d, respectively. These correspond to the initial Ni film thicknesses of 2.5, 3, 4.5, and 6.7 nm, respectively. The nanofibres grown from these substrates are shown in Figure 5-3e to 3h. These nanofibres were synthesized at 700 °C with a 5% hydrocarbon concentration and cathodes biased at -450 V. The process pressure was kept at 3.6 Torr for the 10 min duration of the growth.
Figure 5-3: (a)–(d) Show SEM images of films with different island sizes of 34, 69, 140, and 180 nm, respectively and the corresponding nanofibres grown from these substrates in (e)–(h). The nanofibres were synthesised at 700°C, 3.6 Torr, 5% hydrocarbon concentration and 450V.
The variation of the initial Ni film thickness to the island size is shown in Figure 5-4a. This is in agreement with the work of Nerushev et al. [122] and Chhowalla et al. [123] where the island size increases with thicker Ni films. Also in agreement with Ref. [123], the shape of these Ni islands is irregular. The dimensions of these islands are important as they act as the catalyst for nanotube synthesis and control the CNF diameter.

The variation of the CNF diameter with the Ni island size is shown in Figure 5-4b. It is interesting to note the CNF diameter is proportional to the island size multiplied by a factor of 0.8, which indicates that during the growth process, the Ni islands have been deformed or contracted. This reshaping of the Ni nanoparticle is due to the nucleation and growth of graphene layers around it.

![Graph showing the relationship between Ni film thickness and particle size](image1)

![Graph showing the relationship between mean CNF diameter and mean particle size](image2)

**Figure 5-4:** (a) Variation of the particle size as a function of the initial Ni thickness. (b) Variation of the mean CNF diameter as a function of the mean particle size.
To investigate the effect of applied voltage, the carbon nanotubes are synthesised at 700°C, 5 Torr, 5% hydrocarbon concentration and 5 mins of growth time. The synthesised nanotubes with different applied bias are shown in Figure 5-5.

![SEM images of carbon nanotubes](image)

**Figure 5-5: Growth of carbon nanotube at 700°C, 5 Torr, 5% hydrocarbon, 5mins as a function of applied voltage (a) 350V, (b) 400V, (c) 450V and (d) 500V**

At 350V of applied bias, which is the lowest voltage necessary to strike the plasma, the SEM image suggests that there is initial nucleation of nanotubes. Most of the nickel catalyst appears to be covered with carbon, forming dome-like structures. At 400V, the growth is evident and the synthesised nanotubes appear to be thick and stubby. The growth at 450V appears to be similar to its counterparts at 400V with the exception that the length is longer and there is considerable undergrowth. The undergrowth appears as small filamentary growth surrounding the larger nanotubes. As the voltage is increased to above 450V, clear improvement in the alignment of the nanotubes can be observed. Likewise, there are also nucleation and growth of smaller nanotubes among the larger nanotubes. In all growth, the nickel catalyst can be
clearly observed from the stark contrast between the solid nickel and carbon, suggesting a tip growth mechanism. The effect of increasing applied bias appears to be the improvements in alignment and the enhancement of the growth rates, possibly due to the increased chemical active species and ions. It should be noted that carbon nanotubes can be synthesised at 700°C even without the plasma.

Figure 5-6: Carbon nanofibres grown using (a) thermal CVD and (b) PECVD techniques, at 700°C at a pressure of 10 Torr and 5% hydrocarbon concentration for 20 mins.

Figure 5-6a and 6b show the difference between a thermal CVD and a PECVD-grown carbon nanofibres. Both samples were grown at 700 °C for 20 min with a 5% hydrocarbon concentration at 10 Torr process pressure. The sample in Figure 5-6b is synthesized with PECVD at a cathode bias of 450 V. It can be seen that if no plasma is present, the carbon nanofibres are curly and nonaligned. However, in Figure 5-6b the tubes are more uniformly grown and vertically aligned to the substrate.

Further runs were then carried out at lower hydrocarbon concentration but with no intentional heating of the substrate. In all variations without intentional heating, the maximum temperature registered was less than 200°C with the lowest being 130°C. This heating is a macroscopic value generated by the plasma alone due to the collision of the gas atoms and ions. Since the thermocouple is embedded in the graphite electrode which is exposed to the plasma, the temperature monitored is presumed to be reasonably close to the substrate temperature if thermo-equilibrium or sufficient time is achieved.
Figure 5-7 shows the growth attempted with a variation of hydrocarbon contents at process parameters of 400V, 5.85 Torr and a growth time of 20 mins. At hydrocarbon concentrations above 3%, only large amounts of amorphous carbon similar to Figure 5-1d were observed. At 3% and 2% hydrocarbon concentration, it was clearly noted that thin film formation is still dominant. This is hardly surprising as amorphous carbon thin films can be deposited under similar conditions. However, at 1% concentration, the nucleation of vertically aligned nanostructures is clearly evident. The aligned nanostructures have a wide base with a gradual diminishing tip size, i.e. conical shape. Similar conical shape structures have been reported to be synthesised by the PECVD technique [56, 124,125]. These nanostructures however differ from the high temperature grown counterparts as the nickel catalyst cannot be seen at the tip and spacing between them are much further apart.

Figure 5-7: Experimental runs carried out at 400V, 5.85 Torr, 20mins as a function of hydrocarbon concentration of (a) 1%, (b) 2% and (c) 3%. The temperature is constant around 170°C.
When only a pure nitrogen plasma was used, no form of growth was evident. It was also observed that a pure nitrogen plasma does not seem to break up the nickel film into nanoparticles, suggesting that the addition of hydrocarbon feedstock is crucial to the initial formation. In most growth experiments, the catalyst thin film is typically broken up by thermal annealing [123].

Next, the effects of bias voltage on the low temperature growth of the nanostructures was investigated. The synthesised structures are as shown in Figure 5-8. The voltage was varied from 350V to 425V, with 350V being the lowest voltage necessary to strike and maintain a plasma. The hydrocarbon concentration was kept at 1%. At 350V bias, no nucleation was observed. At all other biases, the formation of similar structures could be observed.

Figure 5-8: Experimental runs carried out at 5.86 Torr, 1% hydrocarbon concentration, 20mins as a function of bias voltage of (a) 350V, (b) 375V, (c) 400V and (d) 425V. The temperature is between 130°C to 190°C.
Empirical observations from Figure 5-8b and 8c seem to suggest that the growth rate increases with increased bias but at higher voltages, shorter length fibres could be attributed to increased bombardment/etching from the nitrogen ions. This can be compared to similar experimental observations involving plasma or thermal systems [123,126,127]. The plasma generated at different bias creates different types and densities of species due to the degree of ionization in the plasma. It is also observed that although the shorter structures appear alongside the larger structures, they appear whenever the structures grew [Figure 5-8b-d]. The spacing between the structures is also further apart than would be expected from high temperature growth. As the voltage is increased, the base width is increased from an average of 100 nm to nearly 400 nm.

![Figure 5-9](image_url)

**Figure 5-9:** Plot of average nanofibre length and base width against applied voltage

Figure 5-9 shows the plot of the average base width and length against the applied voltages over a sampling size of 50 of the largest (observed) nanostructures from the SEM. As the growth time is increased, a concomitant increase in the nanostructure length is observed. Figure 5-10 shows a sample grown for 30 mins.
Figure 5-10: Carbon nanofibres synthesized at 375V, 5.85 torr, 1% hydrocarbon concentration and a growth time of 30mins. Temperature is 135°C.

Figure 5-11: Plot of nanofibre length against deposition time. Maximum temperature is 137°C.
As expected, the nanostructure length can be seen to be increasing with time (Figure 5-11). From the gradient of the length-time plot, it can be seen that there is a gradual increase in growth rate. The temperature variation between the different growth time is less than 5°C. The length distribution is also observed to increase with time as shown by the increase in the error bar. The general observation is an expected increase in length as well as increased yield. Figure 5-12 shows the growth rate comparison between high and low temperature growth at different applied bias. The high temperature growth is carried out at 700°C as in Figure 5-5 and the low temperature growth is carried out below 200°C as in Figure 5-8.

![Figure 5-12: Growth rate comparison between high (700°C) and low temperature (<200°C) at different applied bias.](image)

Figure 5-12 shows that the trend in the growth rates due to the applied bias is similar for the two temperature regimes. For the high temperature growth regime, the growth rate first increases with increasing bias before slowing down after 450V. For the low temperature growth regime, the growth rate also increase initially with applied bias before slowing down after 400V. The growth window however appears to be smaller for the low temperature regime, suggesting that it is sensitive to the
plasma changes. This is hardly surprising as the lack of a uniform temperature gradient

5.1.2 HREM analysis

HREM analysis allows the internal morphology of the structures to be investigated. This is important in understanding the formation of the structures. Elemental mapping of the structures was also carried out using EELS to capture energy filtered images. This allows mapping of the individual elements on the HREM images. The sample preparation involves scratching the sample with a tweezer and ultrasonically dispersed in a solution of methanol. The solution was then filtered through a holey carbon grid. Figure 5-13 shows the internal morphology of the nanofibres. To get a detailed image of the entire structure, images of the parts of the structure were taken at high magnification before being put together.

![HRTEM image of internal structure of carbon nanofibre.](image)
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The bright field HRTEM image shows the conical structure to consist of many dark particles with an elongated wedge shaped structure constituting the tip. The particles at the bottom appear to be stretched outwards towards the direction of the sides of the structure. In order to visualise the internal morphology of the structure more clearly, the dark field image is also captured as shown in Figure 5-14.

![Figure 5-14: Dark field image of carbon nanostructure](image)

The dark particles are shown clearly in sharp contrast to the rest of the structure. The wedge shaped structure is also shown to have moiré fringes which
strongly suggest that it's highly crystalline. It can also be noted that most of the particles are less than 100nm in size and are situated at the base of the structure. The elemental component was determined by energy filtered TEM using EELS.

The elemental mapping was carried out for nickel, carbon and oxygen as shown in Figure 5-15.

![Figure 5-15: (a) HRTEM image of the edge of the structure. (b) Nickel map (c) Carbon map and (d) Oxygen map](image)

The energy filtered image clearly shows that the darker particles are made up of nickel. From the HREM images, the nanofibres can be described as consisting of
an internal nanowire-like nickel core with nanoparticles located at the base of the structure. The internal nickel core can be described as an elongated version of the wedge shaped catalyst particle found at the tip of nanofibres synthesised in the CVD process [128]. In the analysis of the elemental composition of the structures, besides nickel and carbon, oxygen was found in most of the structures. More energy filtered images are also shown in Figure 5-16.

Figure 5-16: (a) HRTEM image of the tip of nanostructure. (b) Nickel elemental map (c) Carbon elemental map (d) Oxygen elemental map.
The oxygen was found to be around the nickel structure. The nickel itself does not appear to be contaminated with oxygen. The carbon surrounds the nickel core protecting it from oxygen. It is not clear whether the oxygen was introduced during or after the synthesis. Defective or amorphous carbons are known to be able to allow oxygen to permeate through it [129-130].

The nickel thin film itself was also investigated for the incorporation of oxygen. The HRTEM and energy filtered images are as shown in Figure 5-17.

Figure 5-17: Energy filtered image of the nickel thin film showing (a) Cross sectional HRTEM image of nickel thin film, (b) Nickel map, (c) Carbon map and (d) Oxygen map.
The elemental mapping was carried out on the cross-sectional nickel thin film. The sample was first bonded to another silicon wafer with epoxy and polished down to a few hundred nanometres. The sample was then ion milled to reveal the cross-section. The 10nm nickel film is polycrystalline and forms a continuous thin film. From the energy filtered elemental mapping, it is found that the oxygen has permeated throughout the nickel film.

5.1.3 Discussion

High temperature growth was carried out between 300°C to 700°C, within the pressure range of 3.6 to 10 torr. The results and observation from the high temperature growth would allow for both characterisation of the new system, and high temperature growth regime. In the first variation (see Figure 5-1), a temperature variation series was carried out between 300°C to 700°C, with all other process parameters such as applied voltage, pressure and hydrocarbon concentration kept constant. The SEM analysis clearly shows that as the temperature is reduced, the deposition gradually changes from carbon nanotube synthesis to amorphous carbon deposition. This is consistent with the findings reported in the last chapter. The relationship of the nickel catalyst particles with the carbon nanotube growth was found to be consistent with the literature findings. The carbon nanotube diameter was found to collate closely with the nickel catalyst island size. The carbon nanotube diameter, which was consistently smaller than the nickel island size by a factor of 0.8, shows that the nickel particle is changing its shape during the growth (as the nanotube diameter is the same as the nickel particle found at the tip). This provides clear evidence that the control of the carbon nanotube diameter can be achieved through control over the nickel island sizes.

The applied bias variation shows that the plasma plays an important role in the synthesis of the carbon nanotubes. At the lowest applied bias of 350V (see Figure 5-5), no carbon nanotubes are synthesised. This suggests that in plasma based process, sufficient energy still has to be provided even during the high temperature growth regime. The high temperature growth results provide support for the issues raised in the discussion in the last chapter, where the carbon concentration in the
system has to be kept to a minimum and the standardisation of nickel catalyst as a thin film effectively eliminates uncontrollable variables such as nickel surface features and growth control due to the catalyst.

Low temperature synthesis is then investigated as a function of plasma variation without the use of the heater. The growth of carbon nanofibres at low temperatures (< 500°C) is particularly dependent on the process parameters. The above results points to two main factors which are critical to the growth of nanofibre like structures at low temperatures. Firstly, the rate or quantity of carbon arriving at the catalyst plays a crucial role. The much lower substrate temperature does not allow rapid diffusion and interaction of carbon in/with the nickel catalyst. Therefore, if a typical hydrocarbon concentration of above 5% is used, this rapidly leads to thin film formation which does not allow the nanostructure to nucleate and form. This is also shown in the high temperature growth where no nanotubes were synthesised at 300°C with 5% hydrocarbon concentration. It could be possible that higher hydrocarbon concentrations can be used if gases which have a higher carbon etch rate such as ammonia are used. Secondly, the amount of applied voltage to the plasma determines the morphology of the structure. In other words, the applied voltage determines the type and density of plasma species generated and the amount of energy consumed in the system. However, given the small amount of hydrocarbon used, the reasonable conclusion lies in the generation of increased amounts of nitrogen ions taking part in the bombardment/etching of the surface. The bombardment of the ions however would be unlikely to induce any sputtering as the process pressure is much too high to allow the ions to accumulate sufficient energy. In comparison to physical sputtering, the typical process pressure would be in the range of milli-torr. Process pressure is one of the most crucial plasma parameters, and increasing pressure generally has the opposite effect to that of increasing applied power. An increase in pressure at constant power level leads to a decrease in the average amount of energy for each species in the gas phase. Consequently, the rates of chemical reactions in the bulk of the plasma are reduced and the plasma becomes dimmer. At pressures above one torr, most of the energy is dissipated in the gas atoms colliding among themselves. At higher pressures, this translates to less ion energy and more gas heating.
The two factors identified are similar to the observations from the high temperature growth. Having established these two initial factors necessary in the growth, further information can be acquired from the HRTEM images of the synthesised structures. With analogy to the growth mechanism proposed by Baker et al. [121], the nucleation and growth of the nanofibre at temperatures below 200°C can be hypothesised.

![Figure 5-18: Proposed formation of carbon nanostructure.](image)

Firstly, the nickel film is broken up to form nanoparticles. Due to absence of additional heating, diffusion is limited by the energy provided by the plasma. The localised heating of the plasma and the diffusion of the carbon along the grain boundaries helps to break up the nickel film. This is critical as a nitrogen plasma at the same conditions did not break up the film into nanoparticles. The thin film is broken into nanoparticles due to surface tension and compressive stress within the film.

Next, the nucleation of the carbon nanostructure proceeds after the nanoparticle formation. The activation energy for plasma assisted growth of CNT
reported by Chhowalla et al. [123] is found to be 0.53eV, which is much lower than that of 1.5eV for thermal growth reported by Baker et al. [121]. Hofmann found that the activation energy from a plasma only process was only 0.23eV which corresponds closely to carbon surface diffusion activation energy of 0.3eV [63]. The lower activation energy means that the nucleation and growth of CNTs can be achieved at much lower temperatures through the use of plasma assisted dissociation. The diffusion however is likely to be surface based rather than through the bulk of the nickel particle since the activation energy of carbon surface diffusion is much lower than that of bulk diffusion. The shape of the elongated wedge shaped nickel core suggests that the nickel catalyst adopts liquid like behaviour during the growth. One observation is that the nickel core is much larger in volume than those typically found at the tip for high temperature growth. A possible reason is that the melting point of nanoparticles is dependent on their size [131,132]. The nickel core in this case could be due to the nickel droplets combining during the growth to form such a large structure (as suggested by the presence of numerous nickel nanoparticles at the base). The eventual formation of the elongated wedge shape could be due to the large temperature gradient between the tip and the substrate as the nanofibre grows, since there is no heating provided to the substrate. The diffusion of carbon towards the wedge then lifts the nickel core as the growth proceeds. The observation of moiré fringes in the nickel core suggest that if the nickel particles are fused together as suggested, then there must have been significant re-arrangement of the nickel structure. Moire fringes appear due to interference patterns generated between two regular sets of crystalline regions such as crystal planes. This meant that the nickel core consist of regular phases along the whole length of the core which is an interesting observation.

This leads to the factor of whether plasma heating/chemistry alone is sufficient in the nucleation and growth of the nanofibres. In the HRTEM analysis, other nanostructures have been observed.
An example is the onion like structure at the tip of the nickel particle shown in Figure 5-19. The HRTEM image also clearly shows that the immediate carbon around the nickel is in the form of graphene layers. The line profile slice of the graphene layers around the nickel is as shown in Figure 5-20. The intensity line profile is taken from the graphene layers around the nickel tip (shown in Figure 5-19) and shows the number of graphitic layers.
The number of graphene layers around the nickel particle at the particular region is estimated to be between 8-10 graphene layers as shown by the peaks in the intensity line plot. The separation between the graphene layers is approximately 0.34nm which is the inter-atomic separation between graphite planes. A layer of amorphous carbon coating is observed around the graphene layer region. Besides onion-like structures, nanotubes/nanofibres are also observed.

Figure 5-21: (a) TEM image of carbon nanotube growing out of the sidewall of the cone-like nanostructure. (b) Energy filtered TEM carbon map of nanotube.

The nanotubes/nanofibres are occasionally found to be growing from the sidewall of the larger cone-like structure. This is shown in the TEM images in Figure 5-21. The observation of graphene formation around the nickel catalyst and the formation of carbon nanotube and nano-onions are particularly significant. This further supports the hypothesis that despite the lower process synthesis temperature, the combination of plasma chemistry/heating and catalytic effect is sufficient in the formation of nanostructures. The low temperature synthesis of carbon nanotubes can therefore be achieve with careful tailoring of the plasma.
5.2 Summary

A DC-PECVD system which allow for greater flexibility in investigating process changes has been constructed. The key difference is that this system is equipped with a heater, allows for a higher process pressure and independent control over the electric field in the plasma. The use of acetylene which has lower dissociation energy is also available in this system. The growth has been investigated as a function of temperature and applied bias. This allows for a reference to study the changes in the growth as a result of decreasing temperature and plasma changes. The high temperature growth is characterised and was found to produce similar results as reported in literature.

Growth was then carried out without the use of the heater. It was found that the amount of hydrocarbon content in the system is critical to the growth of carbon nanostructures with cone-like features. When the usual hydrocarbon concentration for high temperature growth is used, the deposits take the form of a thin film coating. It was found that only by decreasing the hydrocarbon concentration that nucleation and growth of the cone-like nanostructures were possible. This findings are consistent to the conclusions arrived by Minea [61]. Minea uses an alternating nitrogen and acetylene plasma which he terms Layer-by-Layer technique. Minea suggests that the carbon atoms poorly migrate at room temperature on the catalyst surface. Therefore, the etching of weak bonds at the nanoparticle surface is fundamental to slow down the growth. Their process would allow the carbon and nitrogen atoms to spend enough time before forming a covalent bond in an energetically favourable site. Minea also emphasised that the use of acetylene and nitrogen in a 1:1 ratio did not lead to any carbon nanofibre formation. This supports the hypothesis that lower hydrocarbon is key to the growth at low temperature as alternating the different plasmas (acetylene and nitrogen) results in a lower carbon arrival rate at the given cycle. This would be similar to reducing the hydrocarbon concentration to allow for more time for the carbon covalent bonding to occur.

The TEM analysis reveals that most of the cone-like structures to consist of a nickel wedge shaped core with numerous nickel nanoparticles at the base. The carbon nanostructures also appeared to contain oxygen which could have been introduced
through permeation through the amorphous carbon layer or in the initial oxidised nickel film. Carbon nanostructures such as nano-onions and small carbon filaments are also found to be synthesised. Based on the data obtained, a growth mechanism based on Baker et al’s model is proposed [121].
Chapter 6

6 Deployment of titanium layer for low temperature growth of carbon nanotubes

6.1 Introduction

Previous sections have shown that combinational plasma heating/chemistry and catalytic effects are sufficient for the nucleation and growth of cone-like nanostructures. The observation of graphitic layers around the nickel catalyst is significant as it suggests that by increasing the energy in the system, synthesis of carbon nanotubes is possible.

There are numerous techniques to increase the energy in the system. One can examine the energy in any particular system as taking either of the two forms; physical and kinetic. In carbon nanotube growth, high temperature processes are predominantly thermodynamically driven. In low temperature growth processes, the understanding of the growth mechanism is still not well established. From the literature, it appears that the driving force for nanotube growth after initial nucleation is still through physical energy such as heating. This leads to most conclusions that heating is necessary for the nanotube growth (65, 133).

While plasma driven process and its induced chemistry are more complicated than a thermally driven process, it does offer the advantage of additional control. The concept of top-down heating using a plasma to create the growth kinetics we believed can be as important or even more so than conventional external heating in low temperature growth. The top down heating approach means that the substrate can be kept at a lower temperature with suitable cooling schemes, while offering independent control at the growth surface.

In this chapter, the parallel plate Direct Current-PECVD system is used in the growth using acetylene as the carbon feedstock and nitrogen/hydrogen as the
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carrier/dilution gas. The samples used are 30 nm nickel films deposited on 500 nm of
titanium with silicon (100) substrate and were not pre-treated in any form before the
carbon nanotube deposition. The main aim is to investigate the approach of using
plasma heating to achieve carbon nanotube growth.

6.2 Results

6.2.1 Titanium as a thermal barrier

Among the metals, titanium has relatively low thermal conductivity (value
0.219 W/(cm.K) @ 25°C) which means that it can be utilised as an thermal barrier
which is conductive. The need of a conductive thermal barrier is necessary to prevent
excessive charge accumulation in a direct current plasma. In this section, a simple
thermodynamic simulation is used to model the temperature distribution across the
proposed structure of nickel/titanium on silicon. The objective of the simulation is to
determine if the titanium layer can be used to contain the significant plasma heating
at the surface whilst allowing the substrate to be cooled to a much lower temperature,
as a consequence of its lower thermal conductivity. This approach of keeping the
substrate cool is only possible if the heating is initiated at the surface via plasma
heating, Infra-Red heating, etc. Conventional thermal growth using resistive heaters
are typically configured with the heaters located under the sample, thereby restricting
any possible configuration or scheme of keeping the substrate temperature low. This
approach will potentially allow for the growth of high quality carbon nanotubes while
keeping the substrate temperature low.

The simulation uses COMSOL FEMLAB's heat transfer module to model
conduction across the multi-layered structure. When there exist a temperature
gradient within a body, heat energy will flow from the region of high temperature to
the region of low temperature. This phenomenon is known as conduction heat
transfer and is described by the Fourier's Law,

\[ q = -k \nabla T \]  \hspace{1cm} (6.1)

where
- \( q \) is the heat flux
- \( k \) is the thermal conductivity
- \( T \) is the temperature

The minus sign ensures that heat flows down the temperature gradient. The equation describes the flow of heat flux across the structure based on temperature difference. Besides thermal conductivity, heat transfer is also determined by the material’s density and heat capacity. However, for a steady state model, temperature does not change with time and the terms in the heat equation containing \( p \) (density) and \( C \) (heat capacity) vanishes.

The structure modelled together with the mesh defined is shown in Figure 6-1.

![Figure 6-1: Modelled multi-layered structure showing the defined mesh layout](image)

The structure is modelled as a 10nm nickel layer, followed by a titanium layer where the thickness is varied from 50 to 300nm. The substrate is a 1000nm silicon layer. The mesh is defined to be heavily concentrated on the first two layers. The surface is kept at 550°C, while the base of the substrate is cooled to 27°C, thereby creating a
temperature gradient of over 500°C from surface to base. The boundary on each side is taken as a perfect thermal insulator.

Figure 6-2: Temperature distribution across the structure with 300nm titanium layer at steady state.

Figure 6-2 shows the temperature distribution across the structure with a 300nm titanium layer. The simulation shows that the substrate can be kept below 200°C, despite the large temperature difference. It can be seen that approximately 350°C is kept within the nickel and titanium layer.

To demonstrate the effect of different titanium layer thickness, the titanium layer is varied from 50 to 300nm. Since the simulation is based on the thermal conductivity of the material, it can be expected that reducing the titanium layer thickness will result in a smaller temperature difference being kept within the nickel and titanium layers.
Figure 6-3: Temperature distribution across the multi-layered structure as a function of titanium layer thickness.

It shows that at steady state, increasingly large amounts of heating can be contained near the surface using increasing titanium layer thicknesses (Figure 6-3). The simple thermodynamic simulation shows that the temperature difference across the titanium layer increases as a function of the titanium layer thickness. This is based on the increased thickness of the titanium layer and the lower thermal conductivity of titanium as compared to silicon.

The simulation shows that having a layer with low thermal conductivity will allow for most of the temperature drop to be concentrated on the top layers. The factors to be considered in applying this approach in practice are the heating from the edges of the sample, thermal stress in multilayered structures and the usage of other substrate material. However, the simulation highlights the possibility of this approach of top-down heating in the synthesis of carbon nanotubes while keeping the substrate temperature low. The following sections will show that despite not keeping the substrate at constant temperature, the growth of carbon nanotubes is possible at low
process temperatures. Although the temperature at each end is not kept at a constant level, the titanium layer is still effective in holding significant heat at the surface.

The deposited films used in the samples are analysed using SEM. Figure 6-4 shows the SEM observations of the Ni catalyst film after being sputtered onto 500nm Ti layer. The surface morphology appears to follow a bimodal nucleation mode, forming a larger polycrystalline grain structure and a smaller particle distribution.

![SEM image of 30nm Ni film on 500nm polycrystalline Ti](image)

Figure 6-4: SEM image of 30nm Ni film on 500nm polycrystalline Ti

The larger grain size is between 65 to 120nm while the smaller particles are 15 to 25nm. The large grain size is typical of thicker films where the stress is relieved by grain size growth. While it is unclear as to the actual formation of this bimodal growth, one possibility is that the smaller particles are due to the nickel film and the larger polycrystalline grains as the Ti layer. It does help to see the surface morphology of the sample to help establish any relationship between the initial catalyst sample and the growth.
6.2.2 Hydrocarbon concentration

The effect of varying the concentration of hydrocarbon on the growth of carbon nanotubes is shown in Figure 6-5. Based on the observations and knowledge gained in the last chapters, the importance of balancing the amount of carbon arriving at the surface and the carbon consumed by the process is investigated here.

Figure 6-5: SEM images of the carbon nanotubes grown at different concentrations of hydrocarbon; (a) 1%, (b) 2%, (c) 3%, (d) 6% and (e) higher magnification of carbon nanotubes grown in (a)
Chapter 6. Deployment of titanium for low temperature growth of carbon nanotubes

Carbon nanotubes were synthesized with the plasma ignited at 500V bias and 10 torr. The growth is carried out for 45 mins. Nanotube growth has been observed for all hydrocarbon concentrations and the amount of amorphous carbon increases as the hydrocarbon concentration increased. For all hydrocarbon variation runs, the substrate temperature was below 380°C (see Figure 6-6). At 1% concentration, the synthesised nanotubes appear as tightly packed vertically aligned bundles. From Figure 6-5a, it is observed that the nanotubes grow in bundles with sizes remarkably close to the larger polycrystalline grains shown in Figure 6-4. The sizes of the nanotubes are between 4.5 to 15nm which is similar to the nano-particle sizes. In Figure 6-5a, the nanotubes support each other, forming the bundles. The forming of the bundles vertically upwards is due to the plasma electric field. There are currently no reports of isolated freestanding nanotubes in the literature with diameter sizes of that order which might help explain why the carbon nanotubes bundle together for support.

When the concentration is increased, the growth appears to be increasingly consisting of fibrous amorphous carbon. As the concentration is increased, it was observed that the nanotube yield decreases. Upon reaching 6%, the film begins to resemble a thin film of amorphous carbon. The results are similar to the previous chapter where balance of hydrocarbon is critical. However as the plasma heating in this instance is more significant (where the previous chapter recorded temperatures only up to 200°C), carbon nanotube growth was observed in all runs. At the lowest concentration where the nanotubes are in abundance, the nanotube diameters are typically much smaller than nanotubes found to grown from nickel films thickness greater than 10nm [123]. This is unusual since the diameters of the nanotubes typically depend on the thickness of the catalyst films i.e. nanotube diameter either similar or larger than the film thickness [123]. This frequently observed trend is due to the nanotube nucleating from the catalyst nanoparticles that forms from the breaking down of the thin film catalyst. Chhowalla et al. reports that the average catalyst island diameter varies in proportion to the catalyst film thickness and is much larger than the film thickness [123]. The carbon nanotube is then grown with the diameter approximately equal to the island size.
The plasma heating is only slightly influenced by the type of gases used. The mean temperature reached in all runs was 361°C, with the experiment using the lowest hydrocarbon concentration reaching 371°C (Figure 6-6). The temperature typically stabilised within 15 mins indicating that thermodynamic equilibrium had been reached. Since the cathode electrode surface area is higher than the sample surface, it can be assumed that the measured temperature is fairly close to the sample substrate temperature. However, it is important to note that without the titanium layer (or thinner titanium layers), no carbon nanotube growth was observed in similar runs. This suggests that the titanium layer is crucial in the carbon nanotube growth. The effect of a buffer layer is known to affect the growth of carbon nanotubes [123], but it can be ruled out in this analysis since similarly deposited titanium layers up to 200nm have been found not been able to sustain similar growth. This shows that the heat flux flow is retarded in the titanium and nickel layer. This means that the sample surface temperature could be higher than the measured substrate temperature. In typical CVD processes, without any deliberate modifications/setup, nanotube growth would not be observed typically at these temperatures.
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The first structure that was analysed by TEM is the amorphous carbon cone-like structure that was synthesised using a 500V applied voltage (the bottom electrode substrate holder is biased with a -500V with respect to the earthed top electrode). The process is carried out at 10 torr, 3% hydrocarbon content and for 45 mins. The cone-like structures have been shown previously in Figure 6-5c. A typical TEM image of the structure is shown in Figure 6-7. The TEM analysis reveals that the structure consists of numerous particles and amorphous carbon. The nanoparticles are revealed clearly as dark solid particles structures under bright field conditions. There are also numerous nanotube-like structures nucleating from the main nickel core.

More information of the structures can be determined from energy filtered TEM images. The EELS spectrum is collected and the background from multiple scattering removed. From the EELS adsorption edges, it was revealed that that the structures contained carbon, nitrogen, oxygen, nickel and titanium. Part of the spectrum (showing the adsorption edges for carbon, nitrogen, titanium and oxygen) is shown in Figure 6-8.

Figure 6-7: TEM image of cone-like structure, corresponding to the sample in Figure 6-5c.
Figure 6-8: EELS spectrum of cone-like structures, corresponding to the sample in Figure 6-5c.

Using the EELS data, energy filtered TEM images for the structure can be captured to determine the location of the elements. Figure 6-9 shows the collected area and the energy windows corresponding to nickel, titanium and nitrogen. Oxygen
and calcium is found to be in small quantities throughout the collected area. Calcium (shown in Figure 6-8 at 350eV) is determined to be a result of contaminants from the sample preparation.

Figure 6-9: Energy filtered image for cone-like structure for (b) nickel, (c) titanium and (d) nitrogen for sample deposited shown in Figure 6-5c.

The interesting aspect revealed by the energy filtered TEM images is large amount of titanium within the structure. Although the nickel location is not very clear from the energy filtered images, the titanium and nitrogen mapping helps to highlight the location of the nickel as shown in Figure 6-9d. It appears that nitrogen is
incorporated predominately in the core of the structure. It is difficult to determine if the nitrogen is incorporated or trapped in the carbon network and Raman spectroscopy does not reveal any suggestion of C-N or C=N bonds.

Figure 6-10: Carbon nanotube formation for cone-like structures shown in Figure 6-5c.
Higher magnification images around the core are shown in Figure 6-10. Carbon nanotube structures are found to be nucleating and growing from the nickel nanoparticles. Figure 6-10 shows that the carbon nanotube consisting of 5 to 6 graphitic layers is growing through a base growth mechanism. Most of the carbon nanotubes are short and stubby. It can also be observed that most nanotubes are covered with a thin layer of amorphous carbon.

The other structure analysed with the TEM are those that consist predominately of carbon nanotubes or nanofibres. These structures are synthesised at low hydrocarbon concentration and high applied voltages. The structures appear in the SEM as shown in Figure 6-5a.

Figure 6-11: TEM image of predominately carbon nanotube/nanofibre growth as shown in Figure 6-5a
Figure 6-11 shows the TEM image of a mass of filamentary growth. The filamentary carbons are predominately below 50nm in diameter and appear to follow a base growth method, similar to previously observed structures. This is deduced from the concentration of nanoparticles and the lack of catalyst nanoparticles at the tip. The hollow core of the filamentary structures can be clearly observed.

Figure 6-12: TEM image of carbon nanotube structure from Figure 6-5a.
Figure 6-12 shows the higher magnification TEM image of the carbon nanotubes and can be seen to be multi-walled nanotubes which have numerous defects. Like previously observed growth in Figure 6-5c, the nanotubes are coated with a layer of amorphous carbon.

Figure 6-13: TEM image of carbon nanofibres found in sample shown in Figure 6-5a.
Figure 6-13 shows the TEM images of the carbon nanofibres found in the growth. As can be seen, the graphitic planes are not aligned to the filament axis. The carbon nanofibres have graphitic planes that appear to 'extend' in a cone-like manner.

Carbon nanofibres differ from carbon nanotubes in that the internal structure of carbon nanofibres varies and can comprise of different arrangements of modified graphene sheets. The main distinguishing characteristic of the nanofibres from the nanotubes is the stacking of graphene sheets of varying shapes and angles. As seen from Figure 6-13, the graphene sheets are not perpendicular to the axis of the filament. Both carbon nanotubes and nanofibres are observed in the sample shown in Figure 6-5a.

Observations of possibly fullerene-like structures and very small diameter filamentary growth have also been observed in high bias plasma deposition which is shown in Figure 6-15.
The fullerene-like structures appear as single graphene planes that form elongated spheres. Giant fullerenes would have sizes up to several nm. The fullerene-like structures are observed to be attached to the sides of the filamentary growth. In some observations, it is not known if filaments of fullerene-like structures or amorphous carbon (approximately 2-4nm in diameters) are formed (see Figure 6-15).
Figure 6-16: Raman spectrum of sample synthesised at 550V

Figure 6-16 shows the Raman spectrum of sample synthesised at 550V. Between the wavenumber of 1000 to 1750cm⁻¹, the spectrum can be fitted with 2 peaks. These correspond to the $D$ and $G$ peak commonly found with amorphous carbon. The $G$ and $D$ peaks are due to $sp^2$ sites only. The $G$ peak is due to the bond stretching of all pairs of $sp^2$ atoms in both rings and chains. The $D$ peak is due to the breathing modes of rings. The broad $D$ and $G$ band suggest that there is a fair amount of disorder and defective carbon in the sample. The 1323cm⁻¹ peak is lower than the 1350cm⁻¹ position due to the longer excitation wavelength.

The main region of interest however is below 750cm⁻¹, where there are three main peaks of interest; 213, 559 and 644cm⁻¹. However, analysis of these three peaks is complicated by the observation of fullerene like material and filamentary growth of similar size to single-wall carbon nanotube by TEM and the verification of oxygen near the location of titanium by energy filtered TEM. TiO₂ is also known to have Raman signatures in the region depending on the oxidation state.
6.2.3 Effect of applied bias

Figure 6-17 shows the effect of changing the applied bias on the synthesis. The plasma was ignited at 10 torr with a 3% hydrocarbon concentration for 45mins. Variation of the applied bias has a significant effect on the growth as it affects the plasma chemistry, ion energies, etc. In general, increasing applied bias has the effect of increased ion energy and dissociation. As will be seen later, the increased ion energy results in a higher measured substrate temperature due to more energetic ion and molecule collisions.

![SEM images of the effect of different applied bias](image)

Figure 6-17: SEM images of the effect of different applied bias; (a) 450V, (b) 475V, (c) 500V and (d) 550V. Process is carried out at 10torr, 3% hydrocarbon concentration for 45mins.

It can be seen that at the lowest voltage, the plasma was only sufficient in forming small carbon nanostructures. As the voltage increases, the structures changes from pillars of the sizes of around 100nm to nanotube bundles. The pillar-like
structures synthesised at 475V resembles carbon nanotubes but it was observed that most to the structures are not electron transparent. The internal morphology of these structures will be investigated in more details in the later sections. At 500V, although nanotubes were observed, the structures consist of predominantly amorphous carbon. At the highest voltage of 550V, the nanotubes were observed to be formed in a similar manner as in Figure 6-5a.

Figure 6-18: SEM image of (a) carbon nanotube grown at 550V taken at 30° angle and (b) magnified image of insert box in (a)
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The sample grown at 550V was cleaved and it can be seen that the nanotubes are intertwined together, forming cone like bundles (Figure 6-18). The bundles extend vertically upwards and reach a few microns in height. There appears to be good adhesion between the nanotube and the titanium layer which is clearly visible.

The observation of abundant carbon nanotubes formed at 550V suggests two points. One, the growth of the carbon nanotubes is possible due to the changes in plasma chemistry and dissociation as a result of increased bias. Two, the carbon nanotube growth is a result of increased plasma heating. In the applied bias variation runs, the measured substrate temperature was between 350 to 417°C. Figure 6-19 shows the substrate temperature monitored as a function of the plasma bias.

![Temperature vs Applied Bias](image)

Figure 6-19: Substrate temperature against applied plasma bias

The substrate temperature increases from 350°C to nearly 420°C with increasing applied plasma voltage. This is as expected as more energy is applied to
the system. It can be noted that the substrate temperature is still relatively lower than those expected and reported for typical synthesis in the literature.

In relation to the two points raised earlier on the higher yield of carbon nanotubes at 550V, it can be seen that the measured temperature difference at 500V and 550V is nearly 70°C. Therefore, increased plasma heating have to be taken into account as to the higher yield of carbon nanotubes. However, the changes in plasma chemistry and dissociation due to the increased bias are more difficult to verify. On one hand, increased plasma heating can result in increased carbon diffusion and nanotube formation while on the other, the changes in plasma dissociation can generate etching effect as reported by M. Chhowalla [123]. However, in this instance, the deposition or etching rate is not easily determined as the synthesised structures at 500V and 550V are significantly different.

In order to gather more information to understand the composition and state of the carbon nanotube and nanofibre bundle structures synthesised at 550V, XPS measurements were carried out.

![XPS spectrum for carbon (sample in Figure 6-17d)](image)

*Figure 6-20: XPS spectrum for carbon (sample in Figure 6-17d)*
Detailed measurements of the spectrum are carried out for Carbon, Nickel, Titanium and Oxygen. The XPS spectrum for the carbon adsorption edge is shown in Figure 6-20. The carbon XPS spectrum can be deconvoluted to three main peaks centred at 284.7, 285.6 and 288.7eV. The first peak at 284.7eV can be attributed to either graphite or to C-H bonding [134, 135]. The second peak at 285.6eV can be assigned to aliphatic non functionalized sp² carbon [136, 137] while the small carboxylic peak at 288.7eV is also detected [134]. It should be noted that the peak at 285.6eV is also very close to the peak reported for C-N bonding at 285.7eV [138]. The 288.7eV peak is much smaller in comparison with the graphite and can be attributed to surface adsorption of oxygen.

![Figure 6-21: XPS Spectrum for Nickel (sample in Figure 6-17d)](image)

The nickel XPS spectrum is shown in Figure 6-21 and can be deconvoluted to two main components. The component at 853.4eV can be attributed to metallic nickel [139], while the component at lower binding energy of 856.4eV is due to Ni(OH)$_2$.
There is also a small satellite peak at 854.1 eV which can be attributed to NiO. Although there is evidence for oxygen reactions with nickel, the XPS peaks are small in comparison to metallic nickel, suggesting that most of the nickel remains in the metallic state.

There are two peaks which can be deconvoluted into four components in the XPS spectrum of the Ti. (Figure 6-22) The first component at 456 eV can be attributed to Ti$_2$O$_3$ and the second component at 458 eV can be assigned to TiO$_2$ [141]. The second peak consists of two components at 461.5 and 463.8 eV. The first component can be assigned to TiN and the second to either TiO$_2$ or TiN [142-144]. From the XPS data, most of the Ti can be assumed to be oxidised. Titanium carbide has peaks below 455 eV and therefore can be presumed have no or little interaction with carbon. XPS spectrum on nitrogen is inconclusive and has a single peak at
398.6eV. The peak is usually attributed to ammonia. There is no evidence of TiN or C-N bonding.

The oxygen XPS spectrum is shown in Figure 6-23. The main peak is situated at 532eV can be attributed to hydroxy (O-H) functional groups. The small satellite peak at 529.9eV can be either oxygen or metal oxides and water adsorption is evidence from the peak at 535.4eV. Water adsorption is usually typical of any sample exposed to air.

![Figure 6-23: XPS spectrum of oxygen](image)

The XPS data is consistent with EELS data in the elemental analysis. From the XPS data, it can be seen that all the metals have been oxidised especially Ti. From the titanium and nickel spectrum, it can be assumed that most of the oxygen is associated with titanium. However, the oxidation level is low as energy filtered TEM has not been able to detect localisation of oxygen. There was also hydrogenation in the sample as observed from the carbon, nickel and oxygen spectrum.
6.2.4 Effect of process pressure

The influence of pressure on the synthesis is also important. This stems from the plasma characteristics. At low pressures (<10mtorr), the ions formed from the electron-atom interaction, possess large amount of energy and hence for example, low pressure plasmas are used in semiconductor processes for sputter deposition where atoms on the target is physically removed by the high energy ions. This is due to the large mean free path of the ions which results in a larger possibility of gaining sufficient amount of energy before collision. The ions driven by the electric field gains enough energy to physically remove atoms on the targeted material.

As the pressure increases, the mean free path decreases. As a result, although the number of ions may be increased, the average ion energy decreases substantially. CVD deposition is typically carried out in the pressure range of milli-Torr to tens of Torrs. The mean free path of the gas molecules in the process can be estimated by assuming that the gas is at room temperature and using the nitrogen molecule as a reference. Obviously, when at a higher temperature and taking account of the presence of larger molecules, the mean free path would decrease due to higher gas kinetics and collision area. The Ideal Gas Law is given by;

\[ \frac{N}{V} = \frac{P}{kT} \]  

(6.2)

Where

- \( N \) is number of gas molecules
- \( V \) is the volume
- \( P \) is the absolute pressure
- \( K \) is Boltzmann's constant
- \( T \) is the gas temperature (in Kelvins)

The number of gas molecules per unit volume is therefore \( 3.24 \times 10^{23} / m^3 \) at 10 Torr and room temperature. The mean free path of the nitrogen atom is:
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\[ \lambda = \frac{1}{\sqrt{2 \pi d^2} \frac{N}{\nu}} \]  \hspace{1cm} (6.3)

Where

- \( \lambda \) is the mean free path
- \( d \) is 3Å (diameter of the nitrogen molecule)

This yields a mean free path of \( 7.8 \times 10^{-6} \) m. This value (assuming room temperature and nitrogen molecule) is based on an ideal gas system and implies that the mean free path of ions in the sheath could be smaller. However, in the positive column of the plasma (which is where most of the ionisation occurs), the gas temperature increases substantially as the pressure increases due to the increased collisions between electrons, ions and atoms. Assuming a sheath thickness of 2mm, there would be much collision within the sheath itself.

As shown in Figure 6-24, the measured temperature increases from 230°C to 366°C as the pressure rises from 3 Torr to 10 Torr.

![Figure 6-24: Substrate temperature rise as a function of process pressure](image)
The temperature rise against the process pressure is approximately linear, increasing at approximately 19°C per torr. In this work, the plasma is an effective tool as it provides plasma heating from ion bombardment and the gas temperature can also be raised using the pressure. Purely from the viewpoint of heating, the plasma can be controlled via the pressure and the applied voltage.

The growth shown in Figure 6-25 was carried out by varying the pressure at 500V and with a 3% hydrocarbon concentration for 45 mins.

Figure 6-25: Influence of pressure on the synthesis of carbon nanostructures; (a) 3, (b) 5, (c) 7.5 and (d) 10 torr. Process was carried out at 500V, 3% hydrocarbon concentration for 45 mins.

At the lowest pressure where the recorded substrate temperature is 230°C, there was no observation of growth. The film appears to be roughened by the plasma treatment. Above 5 torr, some forms of structures appear to be forming in the shape
of approximately 50nm protrusions. As the pressure increases, signs of growth appear in the form of aligned structures. At high pressures, the structures appear cone like with the nanotubes/nanofibres entangled within. The structures are generally accompanied with lots of carboneous material. It should be noted that nanotubes/nanofibres were found only at 10 torr (see Figure 6-26). All lower pressures, only result in amorphous carbon deposition. Unfortunately, the system is only able to sustain stable plasma below 12 torr.

![Figure 6-26: High magnification image of structures synthesis at 500V, 3% hydrocarbon concentration, 10 torr and 45mins.](image)

The effect of increasing the pressure can be analysed in two methods. One, the increase in pressure means that the surface temperature increases (Figure 6-24) due to the increase in gas temperature. This is straightforward as if the heating reaches a high enough level, it should resemble typical thermally driven growth (ignoring plasma effect and chemistry). However, the highest temperature registered in all the runs is still lower than typical growth temperatures of 500°C. Two, the increase in
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pressure also meant that the residence time of the carbon species in the system is longer. The gas residence time is the mean time that a gas molecule stays in the chamber before being pumped away and is related to the volume of the chamber, pressure and flow rate of the gases. Taking the chamber volume of 16 litres and a flow rate of 100 standard cubic centimeter, the gas residence time difference between 3 and 10 torr would be approximately 66 seconds (with 3 torr = ~28s and 10 torr = ~94s). This effect can be seen by the actual increase of carboneous material in the deposited samples as the pressure increases. When carbon nanotubes/nanofibres were observed, the structures also incorporates large amount of amorphous and particle-like carbon. This could be an important factor as increasing pressure is an easier route to increased plasma heating when compared to increasing applied bias (compare Figure 6-19 and Figure 6-24). The increased deposition of amorphous carbon would then have to be balanced by hydrocarbon concentration or introduction of other gases such as ammonia which is known to etch amorphous carbon.

6.2.5 Effect of synthesis time

It has been observed that the nanostructures grow approximately linearly with time. However in the previous sections, it was observed that the nanostructures synthesised at low applied voltages (475V, Figure 6-17b) appears to be pillar-like. The pillar-like structures are significantly different from the smaller intertwined carbon nanotubes that were formed at higher voltages.

These structures are of interest as they appear to be the starting point of nanostructure growth. As the applied bias increases (from 475V to 550V), the structures changes from pillar-like (475V, Figure 6-17b) to particle-like (500V, Figure 6-17c) and to carbon nanotubes (550V, Figure 6-17d). These nanostructures do not appear electron transparent as normally observed with carbon nanotubes. Understanding their formation would provide an insight to the growth changes as the applied bias is increased. In this section, the pillar-like nanostructure’s growth is varied as a function of time as shown in Figure 6-27.
Figure 6-27: Growth carried out for (a) 15, (b) 30, (c) 45, (d) 60 and (e) 75 mins. (f) scratched edge of sample grown for 75 mins.

The growth series shows that the nanostructures grew longer with time as did the accumulation of amorphous carbon. Empirical observations of the samples turning black for growth time greater than 15 mins, supports the increasing amount of carbon are deposited.
Figure 6-27f shows a scratched edge of sample grown for the longest time of 75 mins. It can be observed that the growth consist predominately of the pillar-like structures and carboneous material. The image is tilted at an angle of 30° and can be seen to be longer than 1μm.

The registered temperature as a function of time shows that the temperature remains fairly constant at around 370°C, despite the increase in process time. This suggests that a thermo-equilibrium state has been reached. Contrary to the literature, where there were some questions on the actual substrate temperature due to power transfer from electromagnetic fields due to the plasma, the results seems to suggest that even at temperatures below 400°C, the growth of carbon nanotubes/nanofibres is evident [64,65].
TEM analysis is carried out to investigate the internal morphology of the synthesised structures. The sample investigated is grown at 475V, 10 torr, 3% hydrocarbon concentration for 60mins, as shown in Figure 6-27d.

The TEM image shows a large solid core with numerous nanoparticles at the base. The solid core is clearly evident from the carbon. It is reasonable to deduce that the solid core is the reason that the structures are non-electron transparent for the SEM images. It is also likely that the solid core gives rise to the tapered structures observed in the Figure 6-27b, suggesting that this solid core is formed first. The TEM image also shows the formation of filamentary growth from the base of the structure. The filamentary growth is observed to follow a base growth method as evident by the lack of catalyst nanoparticles at the tip.
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The energy filtered TEM image of the structure is collected for elemental analysis. Figure 6-30 shows the elemental mapping for nickel, titanium, carbon and oxygen.

![Energy filtered TEM image of the pillar like structures synthesised at 475V collected for (a) nickel, (b) titanium, (c) carbon and (d) oxygen](image)

The nickel mapping shows that the large solid core is nickel with the rest of the nickel appearing as the nanoparticles at the base. The base also consists of titanium as shown in Figure 6-30b. The titanium appears to be located closer to the central core of the base and as a thin coating around the nickel core. The filamentary growth
is shown to be carbon and the lack of carbon in the nickel core suggests that the formation is likely to be a surface diffusion process rather than a bulk diffusion effect. Finally, the oxygen mapping reveals that it is located primarily at the base. This is different from the structures grown at higher applied bias (Figure 6-9 and Figure 6-11) where oxygen is not found to be concentrated in any locations.

![Image](image.jpg)

**Figure 6-31: High magnification image of the base of the pillar-like structure synthesised at 475V**

The higher magnification TEM image of the base (Figure 6-31) shows that the nanoparticles are approximately 10nm in size. The base of the structure is also found to consist of amorphous and filamentary carbon. Figure 6-32 shows the high resolution TEM image of the filamentary carbon. It is found that the structure resembles carbon nanofibres. Carbon nanofibres differ from carbon nanotubes where the graphitic planes are not aligned to the nanotube axis. The carbon nanofibres here are shown to be highly defective and coated with a thin layer of amorphous carbon.
Figure 6-32: High magnification TEM image of filamentary carbon structure from samples grown at 475V, 10 torr, 3% hydrocarbon concentration and 60 mins.
The SEM analysis reveals that the solid core of nickel is formed first, followed by formation of nanoparticles in the base of the structure as the growth proceeds. TEM analysis determined that filamentary growth is predominately carbon nanofibres following a base growth mechanism. Similar to samples deposited at 500V (see Figure 6-9), titanium was found to be within the core of the structure. This meant that in low temperature growth process, the titanium is diffusing upwards towards the structure. Oxygen which is not found in samples deposited at higher voltages is located within the structures synthesised at 475V. The oxygen could be incorporated due to the higher level of defects which is a result of the lower applied bias. Evidence of higher level of defects is given by the observation of only carbon nanofibres rather than nanotubes in the sample.

6.2.6 Discussion

In this chapter, it is shown that the low temperature growth can be achieved by a combining plasma assisted growth with a titanium thermal barrier layer. The plasma assisted growth is built on the factors identified to be critical to low temperature growth in the last chapter. The work shows that nanotubes can be formed at low temperatures using the combined effects of the plasma and the titanium layer. In plasma-assisted growth, the surface heating from the plasma is often ignored or assumed to be similar to the set substrate temperature. The significance of plasma heating has been highlighted by Teo et al [65]. In this study, the temperature from plasma heating is monitored without any intentional cooling hence resulting in heating solely from the plasma. The results show that despite the lower process temperature as compared to the usual temperatures reported, synthesis or growth of nanotubes is clearly evident. However, to achieve the growth of nanotubes with lower defect levels then is typical for low temperature synthesis [60,61,63], the titanium layer is proposed to create a large temperature difference between the surface and the substrate. This ensures that despite the lower synthesis temperature, the surface temperature is at a level sufficient for the growth of the nanotubes. The steady state heat difference through the multilayer structure in the experimental work would be minimal. However, as shown in the results, the difference is sufficient for
carbon nanotube synthesis. This approach would allow for low substrate temperature when substrate cooling is available.

The series of experiments carried out in this thesis show the relationship of the plasma with the growth of carbon nanostructures. Firstly, the importance of the balance of carbon in the system is evident as observed from the data presented in section 6.2.2. The growth is carried out such that an equilibrium state is reached between etching and deposition process. In low temperature growth, the synthesis is carried out more in the etching ‘mode’ rather than deposition. The effect of increasing hydrocarbon concentration is reflected in the synthesis change from carbon nanotubes to amorphous carbon thin film formation. The lack of thermally driven diffusion means that this imbalance is especially important at lower temperatures. Since the plasma is a key factor in the synthesis at low temperatures, different process variations are carried out to study its effect. For different hydrocarbon variation, the temperature resulting from the plasma is kept at an average of 360°C. The maximum temperature recorded is taken when thermal equilibrium is reached (see Figure 6-28).

The plasma heating however is much more affected by the applied voltage and the process pressure (Figure 6-19 & Figure 6-24). The rise in temperature due to increasing voltages is easily explained by the increasing power density (since the electrode area does not change). The effect of pressure in increasing the gas temperature is due to an increasing gas atoms, electrons and ion collisions resulting in increased gas temperature. The higher pressure also means that the gas residence time is longer. The increase in bias from 450V to 550V sees the synthesis changing from surface protrusions to carbon nanotube bundles. From the TEM images shown in Figure 6-29, the pillar-like structures which are synthesised at lower voltages (475V) bare some resemblance to the structures synthesised in Chapter 5. Both are cone-like in overall shape and have wedge shaped metal cores. Both structures also have numerous nano-particles located at the base. It is perhaps not surprising as both structures are synthesised at 500V or below and uses low hydrocarbon concentrations. The only major difference is the presence of more carbon nanofibres for the titanium layer samples. At higher voltages, and low hydrocarbon concentration, the synthesised structures can be converted to mostly carbon
nanofibres. From the energy filtered TEM images, it is found that titanium is also present in the base. Although the titanium is diffusing upwards and incorporating into the structure, the formation of large amount of nanoparticles at the base provides evidence that it is following a similar route as the proposed growth mechanism in Chapter 5. Both structures have nickel cores which are significantly large in volume as compared to the typical nanoparticles expected from the plasma treatment using inert gases.

The growth appears to follow a growth mechanism expected for the vapour-liquid-solid (VLS) growth. In VLS growth, the reactants are supplied in the vapour phase and the diameters are determined by the size of the metallic seed/catalyst particles. The mechanism implies that the solid wire is formed by precipitation from a droplet of metal reacting from the vapour reactants resulting in a melting point depression due to the formation of a eutectic melt. This work differs as the growth is carried out below the eutectic point which then contradicts the theory of VLS mechanism. However, from the shape of the nickel core, it can be seen that the nickel has adopted a partial liquid like behaviour, much like the process described by Helveg et al. [53]. The understanding of the growth mechanism is therefore complicated by a few issues. Firstly, the melting point of a nano-sized material can differ from bulk based data depending on its dimensions [145]. In addition to the lack of data on the melting point dependence on the size of nickel, it is further complicated by the inclusion of carbon. The second issue is the role of the plasma in the synthesis. Although, the dissociation of the reactant gas can be said to be predominately through a plasma-assisted (electric field) process, rather than a purely catalytically driven process, it is not known how the plasma affects the diffusion of carbon through or around the catalyst. Chhowalla has reported that plasma activated growth has an activation energy of 0.56eV while bulk carbon diffusion has an activation energy of 1.5eV [123]. He suggested that the low activation energy for plasma assisted growth is significant and may indicate a supersaturation of carbon in the metal. In this work, there is no evidence of significant carbide formation or high carbon concentration within the nickel catalyst particles. It is therefore likely that the plasma promotes a surface diffusion process rather than bulk diffusion to reduced activation energies from ion bombardment on the surface.
However, these complications seem to arise as a result of the low temperature processing. The large nickel core can be found in practically all process conditions except at high applied voltages and extremely low hydrocarbon concentrations where the growth appears as bundles of carbon nanotubes. It is initially thought that the growth of carbon nanotubes can be achieved by increasing the applied voltages (thereby increasing the temperature) and thus helping to move towards the realm of high temperature growth. This has been shown in the experiment where 550V is applied and the maximum temperature reaches 420°C. The synthesis of the carbon nanotube bundles at 1% hydrocarbon with an applied voltage of 500V had a registered temperature of 370°C. However, in the applied voltage series using a 3% concentration of hydrocarbon, only the highest applied voltage of 550V has shown the growth of similar bundles. The two processes only have a temperature difference of less than 50°C. The difference between the processes condition is in the voltage and hydrocarbon concentration. This difference brings forward two important points.

Firstly, although a certain level of power must be injected into the system, the applied voltage (or power) plays the critical role of balancing the carbon process in the system. From a chemistry viewpoint, the dissociation or plasma activation for the required species is possibly insufficient at lower power. From a physical viewpoint, the low power densities result in less plasma heating. Under such conditions, the formation of carbon nanotubes is only possible when the hydrocarbon concentration in the system is low. At high power levels, the opposite applies and the carbon diffusion can be increased by considering thermal means alone. This is often observed in high temperature growth, whereby the hydrocarbon content ranges from 5% to 20%.

The second point is the role of carbon in the synthesis of different nanostructures. When there is partial decomposition or too much carbon in the system, it is observed that the cone or pillar-like structures are formed. This occurs at exactly the opposite state of the conditions discussed in the previous point where the power levels are low or the hydrocarbon concentrations are high. It is likely that these structures follow a slightly different growth mechanism as compared to typical carbon nanotube growth. The reason for this lies in the observation of nanoparticles in the structure. It is proposed in Chapter 5 that the nanoparticles fused together to
form the large core while many nanoparticles are left at the base as the structure grows vertically upwards. This effect of ‘sucking’ up the nanoparticles is supported by the energy filtered TEM image showing the presence of Ti nanoparticles in Figure 6-9 and Figure 6-29. It should be highlighted that although the process is carried out with a bias towards etching (due to lower hydrocarbon concentration), these structures are not due to sputtering effects. The strongest evidence for that is the high process pressure which leads to low ion energies and the size of the nickel core. The nickel core length is over 400nm in some cases. Process carried out at the same conditions without the use of any carbon source would result in fragmentation of the thin film rather than any growth. Again, this points to the importance of the role played by the carbon diffusion. The growth mechanism from the experimental series can therefore be separated into two regimes; (1) high power or low hydrocarbon concentration, and (2) low power or high hydrocarbon concentration.

![Figure 6-33: Proposed growth mechanism for regime at high power or low hydrocarbon concentration](image)

The first regime achieved a balance in carbon diffusion. The break-up of the nickel particles is achieved by the sufficiently high power plasma or the sufficiently
low carbon which provided enough time for the nickel nanoparticles to form, rather than thin film formation. The proposed growth mechanism then follows as proposed in Figure 6-33. The carbon diffusion starts on the surface of the nickel nanoparticles, forming the initial carbon nanotube closed cap. The carbon diffusion proceeds to drive the closed cap upwards. The carbon absorption is continuously catalysed by the nickel particle which forms graphitic fringes both within and outside the nickel (as suggested by the TEM images from Figure 6-13).

The second regime where there is partial or too much hydrocarbon decomposition results in the formation of nanostructures with a large nickel core. The proposed growth mechanism is shown in Figure 6-34.

The process probably starts with the simultaneous deposition of carbon and the formation of nickel nanoparticles. The deposition of carbon assists the nickel nanoparticle formation by diffusion and results in the nickel exhibiting a partial liquid like phenomena. Partly assisted by the plasma and the nickel, the carbon starts to pull the nanoparticles upwards. The nickel nanoparticles fuse together, forming a wedge shape structure. As the growth proceeds, if the energy is sufficiently high in the system, subsequent nucleation of carbon nanotubes and nanofibres starts and grow from the nickel nanoparticles at the base.

Finally, while the SEM images provide physical observations of the growth changes and the energy filtered TEM images show the location of the elements, XPS analysis provides the information on the chemical bonding of these elements.
XPS analysis shows that the elements carbon, nitrogen, oxygen, nickel and titanium are present in the sample. This is consistent with the EELS analysis. The XPS spectrum for C1s (carbon) shows that it is predominately graphitic, with surface adsorption of oxygen. The carbon component includes bonding with hydrogen and nitrogen, both of which are used in the dilution gas. The nickel XPS Ni2p spectrum shows that the nickel is largely un-oxidised although there is evidence of low level of oxygen interaction at low applied bias. Again this in agreement with the energy filtered TEM images where oxygen can be seen to be absent in locations of the nickel particles. The oxygen interaction with nickel also comes with O-H bonding, which suggests the possibility that oxygen might have been incorporated by exposure to air in the form of water vapour. Oxygen is known to be able to permeate through thin carbon coatings. This is supported by the titanium XPS Ti2p spectrum which shows that the Ti is largely oxidised. Titanium is known to be highly reactive to oxygen and can form carbides and nitrides. It is reasonable to presume that the oxygen has permeated through the carbon coating and oxidised the titanium. The formation of titanium nitride and not its carbide counterpart is however surprising. The high abundance of carbon in the same vicinity as titanium has not resulted in any carbide formation while titanium nitride is formed.

Figure 6-35: Titanium-carbon and titanium-nitrogen phase diagram
One possible suggestion for this is the rapid formation of the nitride first before the carbon can react with titanium. However, this is also unlikely as sputtering of titanium with nitrogen has shown that it is only possible to form titanium nitride at elevated temperatures. It is not clear as to the actual reason although from the titanium phase diagrams, titanium nitride can be formed as Ti$_2$N with less than 5% nitrogen incorporation while TiC would require approximately 12% carbon as shown in the Figure 6-35.

6.2.7 Summary

The growth of carbon nanostructures at low substrate temperatures is carried out using a combination of plasma assistance and titanium thermal barrier layers. The work investigates the growth in a series of experiments involving hydrocarbon concentration, applied voltage, pressure and time. The carbon nanostructures synthesised ranges from amorphous cone-like structures to pillar-like structures to carbon nanotubes and nanofibres. The role of the plasma and carbon is highlighted and the growth regime and mechanism for carbon nanotubes and nanofibres is hypothesised. Two growth regimes are proposed involving 1) carbon nanotube and nanofibre growth and 2) cone and pillar-like structures. The proposed growth regimes essentially bridges low and high temperature growth.

The XPS analysis detects the presence of carbon, nitrogen, oxygen, nickel and titanium which is consistent with the EELS data. The analysis shows that nitrogen is detected in all the samples when the carbon nanofibres/nanotube are synthesised. There is little nickel oxidation despite the carbon coating and the titanium existing predominately as an oxide. This is supported by energy filtered TEM images.
Chapter 7

7 Conclusions

The work presented in this thesis involves the study of low temperature synthesis of the carbon nanostructures. Various synthesis techniques such as radio-frequency and direct current Chemical Vapour Deposition have been investigated, resulting in a custom designed chemical vapour deposition system being built. The changes from high to low temperature growth is investigated and subsequently, successfully applied in the synthesis of carbon nanotubes at below 450°C. The study highlights the importance of the plasma and the carbon balance in the system for low temperature growth. The approach of using top-down heating and thermal barrier is proposed to allow for potentially very low substrate temperature synthesis. This will pave the way for wider substrate options and novel application development.

7.1 RF-PECVD

The low temperature growth of carbon nanotubes using rf-driven PECVD are investigated against a variety of process parameters. The yield is generally low despite changes in process variation. Different nickel particle size and crystallographical features have also been investigated and do not seem to aid in increasing the yield. The general empirical observation is that the process tends to coat most of the particles with carbon thin film rather than nucleate and synthesis carbon nanotubes. This is attributed to the lack of thermodynamically driven diffusion. Possible reasons for the limited growth could be a result of hot spots generated by the electric field distribution. These hot spots could be either due to selective heating of metallic nanoparticles or features by the electromagnetic fields generated. It was concluded that the current system is not adequately equipped to
investigate the influence of the plasma, which is a key factor for low temperature growth.

The observation of white particulate formation is also reported during the operation of the plasma. The conditions which these particulates are formed are also used in the synthesis of amorphous carbon thin films and carbon nanofibres (with nickel). The by-products of the plasma are an issue in all material processing and synthesis. The carbon spheres are investigated using a variety of techniques and are found to be a mix of hydrocarbon and carboxylate moieties. The formation of these particulates at such low temperatures signifies that the carbon material is capable of different structural formation.

7.2 DC-PECVD

A custom designed DC-PECVD deploying a parallel plate configuration is built and tested for the investigation of low temperature synthesis. The system allows for wider process investigation in aspects of pressure, gas, power and temperature. Correlation between the nickel particles size and nanotube growth is established and variation between process factors was investigated. High temperature growth is studied as a function of temperature and applied bias. The yield of the carbon nanotubes decreases rapidly as temperature drops. At 400°C, no growth was observed. The effect of the increasing bias appears to improve the yield and growth rates within the possible growth window. Characterisation of the high temperature growth shows that the system is capable of producing results similar to those reported in the literature.

Subsequent growth is carried out without any intentional heating. The main finding in this study is that the control of the amount of hydrocarbon content in the system is critical to the growth of carbon nanostructures. The lowering of the hydrocarbon content allows for repeatable growth and control of cone-like nanostructures. This is found to be consistent with the findings of Minea where an alternating nitrogen and acetylene plasma is used [61]. The alternating plasma would have a similar effect as the reducing hydrocarbon concentration approach used. The
control over the arrival rate of the carbon on the surface is the common critical factor. The TEM analysis reveals these cone-like nanostructures to consist of a nickel wedge shaped core with numerous nickel nanoparticles at the base. A modified growth mechanism is proposed based on Baker et al.'s original model [121]. The TEM analysis also showed other carbon nanostructures such as nano-onions and small carbon filaments. This shows that the plasma should be sufficient or capable of synthesising carbon nanotubes through the reduction of hydrocarbon concentration. The carbon nanostructures also appear to contain oxygen, which could have been introduced through permeation through the amorphous carbon layer or in the initial oxidised nickel film.

### 7.3 Titanium thermal barrier

The work combines the lessons learned in the previous experiments with the use of a titanium thermal barrier. The approach utilises a top down heating method to achieve growth of carbon nanotubes with lower defect levels at low substrate temperatures. Titanium is chosen as the thermal barrier as it has a lower thermal conductivity among the metals.

The concept of the titanium as a thermal layer is simulated using a simple steady state thermodynamic model of heat transfer. It is found that at steady state, increasing temperature difference between the surface and the substrate can be achieved by increasing the titanium layer thickness. This is based on cooling of the substrate base and plasma heating of the surface. The lower thermal conductivity of titanium provides the basis of this effect. The concept could therefore be extended to any material with low thermal conductivity such as SiO₂. In this case, since a DC-PECVD growth is used, the substrate has to be conductive hence the choice of using titanium. The growth of carbon nanostructures at low substrate temperatures is carried out using both plasma assistance and a titanium thermal barrier. The work investigates the growth using a series of experiments involving hydrocarbon concentration, applied voltage, pressure and time. Different carbon nanostructures are synthesised and again, the key factors identified earlier such as lower hydrocarbon
concentration are proven to be consistent. The role and importance of the plasma and carbon is highlighted and the different growth regime and mechanism for carbon nanotubes and nanofibres is hypothesised. The work also provides the avenues to which the surface heating can be control through applied bias (or in a stricter sense, power density) and pressure. TEM shows the internal morphology of the synthesised structures and is built into the discussion of the growth hypothesis.

XPS analysis provides chemical information on the synthesised samples offering more understanding to the growth mechanism and structure. Different elements were detected and the presence of carbon, nitrogen, oxygen, nickel and titanium is found to be consistent with the EELS data. The analysis shows that the carbon nanotubes possibly contain nitrogen species and similarly to the previous structures, there is evidence of oxygen incorporation. However, through XPS analysis, the oxygen is established to be likely due to atmosphere exposure. This is deduced from the fact that the titanium (which is known to be easily oxidised) analysed is found to exist as an oxide while the nickel is only slightly affected. This is supported by energy filtered TEM images.

A noteworthy point is that the room temperature growth reported by Minea uses a 500nm SiO₂ layer and alternating plasma [61]. This is similar to the approach where top-down heating, thermal barrier, suitable cooling and reduced hydrocarbon are used. The successful application would possibly allow substrate temperature below 200°C, with suitable cooling whilst still achieving good quality carbon nanotube growth. This would be invaluable to the development of carbon nanotube hybrid microelectronics, as well as open up the use of temperature sensitive substrate materials such as plastics.

7.4 Suggestion for future work

There are a number of areas that can be pursued as possible future work, including:

- Growth of carbon nanotubes on plastic substrates using RF-PECVD system for organic hybrid devices. The RF-PECVD would allow for the use of
insulating substrates such as plastic since the alternating electric field would prevent the built-up of charges. Aligned carbon nanotubes can be directly grown on plastic substrates in the fabrication of organic devices for improvement in electrical and thermal conductivity.

- Growth of carbon nanotube interconnects for hybrid silicon microelectronics. The low temperature synthesis should make it ideal for interconnect fabrication. The process can be used to study if the surface heating will affect dopant diffusion in complex structures and compatibility of low melting point materials such as aluminium. The carbon nanotubes can be investigated for electron transport mechanism and current carrying capacity.

- Optimisation for control over growth of carbon nanotubes using thermal layer approach. Further optimisation can be carried out to achieve control similar to its high temperature counterparts. Various factors such as patterned catalyst film, catalyst film thickness, thermal barrier material and thickness, etc can be investigated. An example would be to use Spin-on-Glass as a thermal barrier.

- The top-down heating approach can be further extended to IR heating. The advantages of IR heating are that it has rapid heating cycles and is compatible with standard microelectronic processes such as rapid thermal annealing. The added advantage that silicon is largely transparent to IR could prove useful in integrating carbon nanotubes into hybrid silicon based microelectronics.

- Low hydrocarbon concentration has been identified as a critical factor in low temperature growth. This is due the low carbon diffusion at low temperatures. The effect of using reactive gases such as ammonia and carbon tetra-fluoride would have a strong effect on the chemical etching of substrates from the plasma. Effectiveness of etching reactants can be investigated to see if the process can be further improved.

- Low temperature growth has shown to be able to incorporate underlying materials to be incorporated into the structure. One example of this is the titanium nanoparticles found in structures shown in chapter 6. This ‘sucking’ effect of the growth which incorporates materials into the structure can be extended to include other materials such as lithium. This could prove
interesting in investigating incorporation of different elements into the nanostructures. The formation of the long nickel core could also be investigated as filling of the core of the nanostructure with different materials.
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- Deployment of titanium thermal barrier for low temperature carbon nanotube growth
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