ROOM AND LOW TEMPERATURE SYNTHESIS OF CARBON NANOFIBRES

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This thesis is dedicated

to my wife Olivera Spasic-Boskovic, my daughters Ana and Alexandra Boskovic,
and memory of my mother Milinka Boskovic.
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Carbon nanotubes and nanofibres have attracted attention in recent years as new materials with a number of very promising potential applications. Carbon nanotubes are potential candidates for field emitters in flat panel displays. Carbon nanofibres could also be used as a hydrogen storage material and as a filling material in polymer composites. Carbon nanotubes are already used as tips in scanning probe microscopy due to their remarkable mechanical and electrical properties, and could be soon used as nanotweezers. Use of carbon nanotubes in nanoelectronics will open further miniaturisation prospects.

Temperatures ranging from 450 to 1000 °C have been a required for catalytic growth of carbon nanotubes and nanofibres. Researchers have been trying to reduce the growth temperatures for decades. Low temperature growth conditions will allow the growth of carbon nanotubes on different substrates, such glass (below 650 °C) and as plastics (below 150 °C) over relatively large areas, which is especially suitable for flat panel display applications. Room temperature growth conditions could open up the possibility of using different organic substrates and bio-substrates for carbon nanotubes synthesis.

Carbon nanofibres have been synthesised at room temperature and low temperatures below 250 °C using radio frequency plasma enhanced chemical vapour deposition (r.f. PECVD). Previously, the growth of carbon nanofibres has been via catalytic decomposition of hydrocarbons or carbon monoxide at temperatures above 300 °C. To the best of our knowledge, this is the first evidence of the growth of carbon nanofibres at temperatures lower than 300 °C by any method. The use of a transition metal catalyst and r.f.-PECVD system is required for the growth of the carbon nanofibre when a hydrocarbon flows above the catalyst. Within the semiconductor industry r.f.-PECVD is a well established technique which lends itself for the growth of carbon nanofibres for various electronic and photonic device applications.

A new catalytic method for the growth of carbon nanofibres using radio frequency supported microwave plasma-enhanced chemical vapour deposition (PECVD) has been developed. Nickel powder used as a catalyst was placed on a
A graphite strip heater vacuum system for carbon nanofibres thermal chemical vapour deposition (CVD) has been set up, using methane or acetylene as the carbon containing source gas, and nickel powder as the catalyst. Various carbon nanofibre morphologies have been produced: "whisker-like", helical, branched, bi-directional, and "bead-like". Using this low-pressure thermal CVD synthesis method carbon nanofibres and nanotubes were synthesised at relatively low temperatures from 350 °C. Optimum deposition conditions for the produced fibres with higher graphitic structures at low temperatures have been established by series of experiments varying pressure, temperature, substrate and gas mixture. Optimum growth temperature was found to be around 500 °C.

Ropes of roughly aligned carbon nanotubes have been observed after synthesis using nickel catalysed CVD of methane at temperatures of 500 °C, or after radio frequency assisted microwave PECVD. Mixtures of remaining nickel powder and synthesized carbon nanofibres and nanotubes have been treated in 35% nitric acid for periods of 3 to 10 minutes and carbon nanotube ropes have been observed in the dried sediment by scanning electron microscope examination. Rope diameters range from 20 μm up to 80 μm, and lengths up to few millimeters have been observed. The large size of these ropes means that easy manipulation is possible for their characterisation and applications.

A growth model for the room temperature and low temperature produced carbon nanofibres is proposed.

Characterisation of produced carbon nanofibres and carbon nanoropes have been performed using scanning electron microscope, Raman spectroscopy and transmission electron microscopy with electron energy loss spectroscopy.
PUBLICATION LIST

Journal Publications


Conference Presentations


**Patent**

## GLOSSARY

<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
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<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
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<td>CNT</td>
<td>Carbon Nanotubes</td>
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<td>SWCNT</td>
<td>Single-Walled Carbon Nanotubes</td>
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<td>MWCNT</td>
<td>Multi-Walled Carbon Nanotubes</td>
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<td>CNF</td>
<td>Carbon Nanofibres</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapour Deposition</td>
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<td>r.f. PECVD</td>
<td>Radio Frequency Plasma Enhanced Chemical Vapour Deposition</td>
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<td>HFCVD</td>
<td>Hot Filament Chemical Vapour Deposition</td>
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<td>PE-HFCVD</td>
<td>Plasma Enhanced Hot Filament Chemical Vapour Deposition</td>
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<td>Fe</td>
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<td>Pt</td>
<td>Platinum</td>
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<tr>
<td>CH$_4$</td>
<td>Methane</td>
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<tr>
<td>C$_2$H$_2$</td>
<td>Acetylene</td>
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<tr>
<td>SAD</td>
<td>Selected Area Electron Diffraction</td>
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<td>CFRC</td>
<td>Carbon Fibre Reinforced Composite Materials</td>
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<td>VGCF</td>
<td>Vapour Grown Carbon Fibres</td>
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<td>EM</td>
<td>Electromagnetic</td>
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<td>r.f.</td>
<td>Radio Frequency</td>
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<td>MW</td>
<td>Microwave</td>
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<tr>
<td>HOPG</td>
<td>Highly Ordered Pyrolitic Graphite</td>
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<td>RBM</td>
<td>Radial Breathing Mode</td>
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Chapter 1

INTRODUCTION

1.1. CARBON NANOTUBES AND NANOFIBRES IN NANOTECHNOLOGY

Nanotechnology is an emerging field dealing with materials and systems possessing, at least in one dimension, scales of 1 to 100 nm (1 nm = 10^{-9} m). These materials and systems are designed through processes that exhibit fundamental control over the physical and chemical attributes of molecular-scale structures, and they can be combined to form larger structures. This is the definition given by Michail C. Roco, the National Science Foundation (NSF) programme director of the National Nanotechnology Initiative in the United States of America [1.1].

The prospect of greater control at the nanoscale level opens options in many areas. In materials science, for example, a polymer could be made more durable by mixing it with nanoparticles. Particles fused to pieces of DNA could be made into medical devices to diagnose different diseases. In nanoelectronics, tiny circuits could be built up on a molecular level, rather than being etched away using standard lithography techniques [1.2].

Interdisciplinary research is required in nanotechnology with researchers from different backgrounds: electrical engineers, physicists, chemists, and biologists. The boundaries of traditional disciplines are broken by nanotechnology, physicists need to know some chemistry, and conversely a chemist needs to know some physics. However, most importantly they all need to be willing to learn.

Nanotechnology is predicted to spark a series of industrial revolutions in the next two decades that will transform our lives to a far greater extent than silicon microelectronics did in the 20th century. Carbon nanotubes, carbon nanofibres and nanoropes could play a major role in this revolution if their remarkable electrical and mechanical properties can be exploited [1.3].
1. Introduction

A carbon nanotube (CNT) can be considered as a single sheet of graphite that has been rolled into a tube. Nanotubes have an impressive list of attributes. They can behave like metals or semiconductors, can conduct electricity better than copper, can transmit heat better than diamond, and they rank among the strongest materials known. The electronic properties of the resulting nanotube depend on the direction in which the sheet was rolled up. Some nanotubes are metals with high electrical conductivity, while others are semiconductors with relatively large band gaps. Nanotubes also have remarkable mechanical properties that can be exploited to strengthen materials or act as “tips” in scanning probe microscopes. Since they are composed entirely of carbon, nanotubes also have a low specific weight. In several decades from now we may see integrated circuits with components and wires made from nanotubes, and there may even be buildings that can snap back into shape after an earthquake.

1.2. AIM OF THE PROJECT

Carbon nanotubes (CNT) produced by carbon-arc processes have generated huge interest from the scientific community since their first identification by Iijima in 1991 [1.4]. Although, carbon nanofibres (CNF), also known as carbon filaments, were synthesised from catalytic decomposition of certain hydrocarbons, other organics or carbon monoxide over small transition metal particles such as iron, cobalt and some of their alloys since the early 1950’s [1.5,1.6].

Carbon nanotubes, nanofibres and nanoropes can be synthesized efficiently by the catalytic decomposition of a reactant gas that contains carbon, when made to flow over a transition metal catalyst, in a process known as chemical vapour deposition (CVD). This process has two main advantages. Firstly, the nanotubes are obtained at a much lower temperature, however this is at the cost of lower structural quality. Secondly, the catalyst can be grown on a substrate, which allows growth of aligned nanotubes and control of their growth. The defective nature of CVD grown multiwall carbon nanotubes (MWCNT) remains poorly understood. This may be due to the relatively low temperatures that are used, which do not allow the nanotubes to fully crystallize.
Catalytic thermal CVD [1.7] and plasma-enhanced CVD [1.8] of hydrocarbons as the carbon nanotube synthesis method have both been widely studied in recent years. These methods can produce a large amount of carbon nanotubes, but with more structural defects in comparison with those produced by the carbon-arc method. Carbon nanotubes grown by catalytic CVD method have attracted considerable interest as prospective field emitters [1.9] and hydrogen storage materials [1.10]. They are potential materials for use in electrochemical capacitors (also known as super capacitors) [1.11] and for fuel cell applications [1.12].

Temperatures ranging from 450 to 1000 °C have been needed for growth of carbon nanofibres by catalytic decomposition of hydrocarbons, where mostly the type of catalyst used has dictated the temperature. Researchers have been trying to reduce the growth temperatures for decades by using different gases and catalysts with no success at temperatures below 300 °C. The aim of this project was to develop and optimise CVD processes for carbon nanofibre synthesis at low temperatures, to be suitable for applications that require carbon nanofibres to be grown on substrates such as glass (below 650 °C) and plastics (below 150 °C). An example of these applications is the flat panel display.

1.3. OUTLINE OF THE THESIS

The possible use of carbon nanotubes and nanofibres for nanotechnology applications have been discussed in Chapter 1. The aim of the research has also been given in Chapter 1.

The literature review on carbon nanomaterials including a brief history, synthesis, characteristics and applications is given in Chapter 2.

In Chapter 3, experimental details are presented with an introduction to characterisation techniques used: scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS) and Raman spectroscopy.
1. Introduction

In Chapter 4 results are presented and briefly discussed. Further discussion of the results is given in the next chapter. Growth characteristics, morphology and structure of carbon nanofibres synthesised by low pressure thermal CVD at temperatures from 350 °C, using methane as the carbon source gas and nickel powder as a catalyst are described in section 4.2. Section 4.3 is a description of how radio-frequency plasma could produce structural changes and chemical reactions at room temperature, leading to the growth of carbon nanofibres with presentation of their growth characteristics, morphology and structure. A new catalytic method for the growth of CNF using radio frequency combined microwave plasma-enhanced chemical vapour deposition (PECVD) is described in section 4.4 with growth characteristics, morphology and structure of synthesised CNF. Remarkable characteristics of carbon nanofibres branching during the growth and forming “Y” and “H” shaped junctions are presented. In section 4.5, the ropes of roughly aligned carbon nanotubes observed after nitric acid treatment of carbon nanotubes, nanofibres and remaining nickel catalyst are described.

In Chapter 5 the advantages and disadvantages of CVD synthesis compared to arc-discharge are discussed with especial emphasis on advantages of PECVD synthesis. Growth models for carbon nanofibre at low temperature CVD and at room temperature PECVD are proposed and discussed. Structure of the synthesised material was discussed based upon the transmission electron microscopy, EELS and Raman spectroscopy studies.

In Chapter 6 the conclusions from work on carbon nanofibres low temperature thermal CVD synthesis and room and low temperature PECVD synthesis and characterisation are discussed. Radio frequency PECVD (r.f. PECVD) is seen as the most promising method for carbon nanofibre synthesis, where the growth temperature is not an obstacle any more for using glass and plastics as substrates. The chapter concludes with a proposal for the future work.

In Appendix 1 a TEM analysis of unused carbon grids was conducted in order to avoid possible misinterpretation of analysed material. This analysis has revealed that carbon nanotubes could be present as contaminants on amorphous carbon grids used for
1. Introduction

TEM analysis. Carbon nanotubes, which are most likely contaminants on used TEM grids, were compared to carbon nanofibres/nanotubes synthesised by CVD in this study.

Raman spectra fitting routine used in this thesis was described and discussed in Appendix 2.

In Appendix 3 an electromagnetic heating mechanism was presented as an addition to the discussion about carbon nanofibres growth model in r.f. PECVD and r.f. combined microwave PECVD.

References

2.1. A BRIEF HISTORY OF CARBON NANOTUBES AND NANOFIBRES

The formation of carbon nanofibres (carbon filaments) from the interaction of carbon containing gases with hot metal surfaces was first reported by Paul and Léon Schützenberger in 1890 [2.1], when they found that filaments were deposited when cyanogen was passed over porcelain at "cherry-red" temperature.

Carbon filaments were first observed when electron microscopes came into widespread use around 1950 [2.2, 2.3]. Radushkievich and Luk'yanovich reported the first electron microscopy micrograph of carbon nanofibers in 1952 in Russian [2.2]. Davis et al. in 1953 published the first English language paper with carbon nanofibre electron micrographs [2.3]. The motivation for Davis and his co-workers research work was the prevention of carbon deposition in the brickwork of blast furnaces, because carbon deposition may cause the disintegration of the bricks. They found that carbon is formed by the interaction of carbon monoxide and iron oxide in the so-called iron-spots in the brick. By exposing samples of the brick containing iron spots to the carbon monoxide at an optimum temperature of about 450 °C, they produced carbon nanofibres (exhibiting a helical form) with catalyst particles located on the growing end of the fibre.

In the 1970s and 1980s two opposing interests have motivated researches to investigate the properties and mechanisms of nanofibre growth. These are the inhibition of carbon filament growth and optimisation of carbon filament growth. The prevention of carbon deposit accumulation is a high priority objective in many processes involving hydrocarbon conversion reactors, where the presence of such nanostructures create problems including blockage of reactors, reduction of heat transfer properties and deactivation of catalyst systems due to encapsulation of the metallic components [2.4].
2. Literature Review

The discovery of the C_{60} molecule in 1985 (also known as fullerene or buckminsterfullerene) by Sir Harry Kroto from University of Sussex, Brighton, with a team led by Richard Smalley from Rice University, Houston, had marked the beginning of a new era in carbon science [2.5]. This research was awarded with the Nobel Prize for Chemistry in 1996.

In 1991, Sumio Iijima using high-resolution transmission electron microscopy at the NEC Fundamental Research Laboratory in Tsukuba, Japan, reported the first observation of structures that consisted of several concentric tubes of carbon, nested inside each other like Russian dolls [2.6]. He called them microtubules of graphitic carbon, but from 1992 Iijima and other researchers began to refer to them as carbon nanotubes. Iijima observed multi-walled carbon nanotubes (MWCNT) in the soot produced by the electric arc discharge between graphite electrodes in a helium atmosphere. Subsequently, in 1993, Iijima and Ichihashi in NEC [2.7] and Donald Bethune and co-workers at IBM, Almaden Research Center in California [2.8] independently discovered single-wall carbon nanotubes (SWCNT). Diameters of single-wall nanotubes were just one or two nanometres, compared to multi-wall nanotube diameters, being of the order of tens of nanometres. In the following years a great deal of research effort has been invested to find efficient means to produce large quantities of nanotubes. In 1992, Thomas Ebbesen and Pulickel Ajayan, also at NEC, developed a method of producing larger quantities (a few grams) of high-quality multiwall nanotubes by vapourising carbon electrodes [2.9]. Since then other carbon nanotube synthesis methods have been developed. Carbon nanotubes have been produced by vapourising a graphite target using a laser [2.10, 2.11], electron beam [2.12], and solar energy [2.13] sources. Catalytic pyrolysis and chemical vapour deposition (CVD) of hydrocarbons [2.14] are now widely used for carbon nanotube synthesis as a simple and efficient method.

By the end of the 1990s, applications of carbon nanotubes and nanofibres have attracted extensive research interest. Carbon nanotubes have proven to be good field emitters since Rinzler and co-workers reported electron emission from a single nanotube [2.15]. In the last few years, lots of research aimed at obtaining large-area films of nanotubes or nanofibres producing a uniform field emission has been carried out [2.16-2.19]. Carbon nanotubes have now been used for scanning electron microscope tips [2.21], as conducting fillers in polymer composite materials [2.22], and in fuel cells [2.23]. It has been proven that carbon nanotubes can be used in
nanoelectronics as diodes and transistors [2.24], in supercapacitors [2.25], as electromechanical actuators [2.26], and as chemical sensors [2.27].

2.2. STRUCTURE OF CARBON NANOTUBES AND NANOFIBRES

2.2.1. Carbon nanotubes

Carbon is one of the geologically most abundant elements. Moreover, it can take a variety of forms, as has already been shown in fullerene and nanotube geometries (Fig. 2.1) as well as in graphite and diamond. A nanotube can be considered as a single sheet of graphite that has been rolled into a tube and capped on each end with half of a fullerene molecule. This is termed a single-wall carbon nanotube (SWCNT). If nanotubes are nested inside each other like Russian dolls, researchers then call them multi-walled carbon nanotubes (MWCNT). Some MWCNT grown by the chemical vapour deposition (CVD) method have a very similar structure to carbon nanofibres (filaments), which usually have catalyst particles attached to one end and graphene layers adopting a fishbone or stacked cup arrangement.

Figure 2.1. (a) C60: buckminsterfullerene, (b) the first image of multiwalled carbon nanotubes (MWCNT) published by Sumio Iijima in 1991 [2.6], and (c) drawing of a singlewalled carbon nanotube (SWCNT) capped by one half of a C60 molecule from Millie Dresselhaus work where she predicted that carbon nanotubes could have metallic or semiconducting properties [2.20].
The electronic properties of nanotubes depend on the direction in which the graphene sheet is rolled up. Some nanotubes act similar to metals, with high electrical conductivity, whilst others are semiconductors, with relatively large band gaps.

Experimental observation of the smallest possible carbon nanotube with diameter 0.8 nm, corresponding to the $C_{60}$ molecule was reported in 1992 by Ajayan and Iijima [2.28]. A single wall $C_{60}$ derivated carbon nanotube consist of a bisected $C_{60}$ molecule with the two resulting hemisphere joined together by a cylindrical tube one monolayer thick and with the same diameter as $C_{60}$. If the $C_{60}$ molecule is bisected normal to the five-fold axes, the "armchair" nanotube, shown in Fig. 2.2a, is formed, and if the $C_{60}$ molecule is bisected normal to the threefold axis, the "zigzag" nanotube in Fig. 2.2b, is formed [2.29]. In addition to armchair and zigzag nanotubes, a large number of chiral nanotubes can be formed with a screw axis along the axis of the nanotube and the variety of "hemispherical"-like caps (Fig. 2.2c). Armchair and zigzag carbon nanotubes with larger diameters have correspondingly larger caps. Structures with smaller caps, for example $C_{36}$, with a diameter of 0.5 nm [2.30], and $C_{20}$, with a diameter of 0.4 nm have been reported [2.31, 2.32].

![Figure 2.2. Drawings of the SWCNT that can be capped by one half of $C_{60}$ molecule [2.29]: (a) armchair structure, (b) zigzag structure, and (c) chiral structure.](image-url)
2.2.2. Carbon nanofibres

The first researchers who reported carbon nanofibre formation [2.33, 2.34] established that carbon nanofibres had metal particles associated with them. Catalytic "ice-cream cone" or "hearth" shaped metal particles usually can be seen at the end of the nanofibre (Fig. 2.3a). Alternatively, "diamond" shaped metal catalyst particle can sometimes be seen in the middle of the nanofibre (Fig. 2.3b).

![Figures 2.3](image-url)

**Figure 2.3.** (a) Carbon nanofibre with "ice-cream cone" shaped catalyst particle (after Dawns et al., [2.35]); (b) Bi-directional carbon nanofibre with "diamond" shaped catalyst particle (after Kim et al., [2.36]).

Controlled oxidation studies of carbon nanofibres produced from the interaction of the nickel with acetylene by Baker and co-workers [2.37] revealed carbon nanofibre duplex structures. At 600 °C the central core oxidised first, and amorphous carbon was observed to oxidise under similar conditions. At 725 °C the filament skin started to oxidise and this action coincided with the onset of uncatalysed gasification of graphite. Figure 2.4 shows the situation in the oxidation sequence where the inner core has been removed leaving an oxidation-resistant tube [2.38]. Based on these experiments, Baker and co-workers [2.37] concluded that the
filaments had a duplex structure, an outer graphitic sheet surrounding an amorphous core.

![Image of nanofibres](image)

**Figure 2.4.** Effect of heating nanofibres in oxygen at 650 °C: top row, before reaction; bottom row, after partial oxidation (after Baker et al., [2.38]).

Detailed investigation of carbon nanofibre structures by high-resolution electron microscopy has revealed that the carbon nanofibres consist of cylindrical arrangements. The central part of the carbon nanofibre is less dense (more electron-transparent) than the outer region of the tube, which shows extremely, well ordered regions on which individual graphite platelets, which are usually, aligned parallel to the side faces of the catalyst particle can be observed.

Baird, Fryer and Grant [2.39, 2.40] studied the effects of heating nickel foil to 600 °C in methane or propane and identified carbon nanofibres among other carbonaceous deposits. They have performed a detailed investigation of carbon nanofibre structures by high-resolution electron microscopy (HRTEM) and revealed 0.34 nm interlayer spacing of graphite (Fig.2.5). They showed that at the nanofibre tips, the basal plane layers were parallel to the surface of the metal catalyst.
Figure 2.5. HRTEM micrograph shows the arrangement of the graphite layers of the carbon nanofibre (after Baird et al., [2.39]).

HRTEM microscopy studies by Rodriguez, Chambers and Baker [2.41] have revealed that the nanofibres consist of a well ordered graphite platelet structure, the arrangement of which can be engineered to the desired geometry by choice of the correct catalyst system. Depending on the chemical nature of the catalyst and the conditions of the reaction, assorted nanofibre structures with various morphologies and different degrees of crystallinity can be produced. Nanofibres consist of graphite platelets that can be oriented in various directions with respect to the fibre axis (Fig. 2.6).
In addition to the whisker-like carbon nanofibre structure, several other morphologies have been found including bi-directional, helical, branched and coiled (Fig. 2.7). Tubes (hollow cored structures), bi-tubes (with the catalyst particle enclosed), solid structures, and shells were also observed.
Davis and co-workers reported coiled (helical) carbon fibres for the first time in 1953 [2.34]. Motojima and co-workers [2.43] have obtained very large coiled carbon fibres using acetylene at temperatures ranging from 400 to 550 °C at atmospheric pressure with Ni powder and single crystal Ni plates as catalyst materials (Fig. 2.8). It was apparent that they had grown via a bi-directional mode where the diamond shaped catalyst particle was contained within the body of the nanofibre.

A common feature for all these structures is that the width of the nanofibre is determined by the size of the associated catalyst particle. Bernardo, Alstrup and Rostrup-Neilsen [2.44] reported different structures, with various nanofibres attached
to the same catalyst particle, which was much larger than nanofibres in width. They named this structure, (Fig. 2.9) that is obtained by using 80 at. % Cu, Ni-Cu/SiO$_2$ catalyst, octopus carbon.

![Image](image-url)

**Figure 2.9.** "Octopus" carbon formed on a 80% at.% Cu, Ni-Cu/SiO$_2$ catalyst (after Bernardo et al., [2.44, 2.45]).

### 2.2.3. Carbon nanoropes

Richard Smalley and co-workers from Rice University, Houston, Texas, together with colleagues from University of Pennsylvania and Institute Charles Sadron, Strasbourg, France, and David Tomanek's group from Michigan State University reported synthesis of crystalline ropes of metallic SWCNT in 1996 [2.46]. They produced SWCNT that were nearly uniform in diameter and self organised into "ropes", which consist of 100 to 500 SWCNT (Fig. 2.10), by the condensation of laser-vapourised carbon-nickel-cobalt mixtures at 1200 °C. The ropes were metallic, with a single-rope resistivity of $<10^{-4}$ Ωcm at room temperature. They estimated that typically 70 to 90% of the material was SWCNT ropes, and the ends of the ropes could not be found in the TEM images due to their long length.
Researchers from Sony Corporation have modified the conventional arc-discharge method for the production of SWCNT ropes by using a bowl-shaped cathode that can direct the arc plasma in a specified direction [2.47]. They used a combination of cobalt, nickel, iron and cerium as an efficient catalyst, with sulphur as a promoter and tin as a nano-welding element. Under optimised conditions, SWCNT super bundles or ropes, were synthesised with a 70% yield. The carbon ropes had a very wide distribution of diameters with the smallest diameter being a few nanometres and the largest diameter being more than 500 μm (Fig. 2.11). Most of the carbon ropes are 1-100 μm in diameter. The length of the ropes can reach 3 cm [2.48].
Long and wide ropes of SWCNT bundles with rope diameters of 100 μm and lengths up to 3 cm, synthesised by the catalytic decomposition of hydrocarbons, were described by H. M. Cheng and co-workers in China in collaboration with Millie Dresselhous’s MIT group in USA [2.48].

The carbon ropes with diameters on the micrometer scale cannot be observed by TEM in their as-prepared state. Vigorous ultrasonic dispersion is needed to prepare the samples before observation, destroying the original structure - the alignment and interrelationships. TEM observations cannot reflect the original bundle construction exactly, but many long SWCNT in small bundles and individual tubes released from the carbon ropes could be observed.

2.3. PROPERTIES OF CARBON NANOTUBES AND NANOFIBRES

2.3.1. Electrical properties

The remarkable electrical properties of single-wall carbon nanotubes stem from the unusual electronic structure of “graphene”, the 2-D material from which they are made. Graphene is simply a single atomic layer of graphite, the material that makes up pencil lead. Graphene has a two-dimensional “honeycomb” structure, made up of sp² bonded carbon atoms. Nanotubes can be semiconductors or metals depending on the manner in which the graphene sheets are rolled up into a cylinder, i.e. the so-called helicity and chirality of the nanotube.

Before measuring the conducting properties of nanotubes it is necessary to wire up the tube by attaching metal electrodes to it. The electrodes, which can be connected to either a single tube or a “bundle” of up to several hundred tubes, are usually made using electron-beam lithography. The tubes can be attached to the electrodes in a number of different ways. One way is to make the electrodes and then drop the tubes onto them. Another is to deposit the tubes on a substrate, locate them with a scanning electron microscope or atomic force microscope, and then attach leads to the tubes using lithography. More advanced techniques are also being
developed to make device fabrication more reproducible and controllable. These include the possibility of growing the tubes between the electrodes.

In semiconducting materials, a small amount of impurity added as a dopant can make electron-excess n-type or electron-deficient p-type semiconductors. A junction between p- and n-type semiconductors works as a diode. A rectifying junction can also be formed between a semiconductor and a metal. In the case of carbon nanotubes, they can be either metallic or semiconducting, depending on the topology. Hence, experimentally observed diode properties can be explained by the presence of the junction between two topologically or electronically different nanotubes. Such junctions can be designed by introducing pentagon-heptagon pair defects into otherwise hexagonal nanotube networks [2.49].

Carbon nanotubes have shown the behaviour of p-type semiconductors. One might expect an isolated semiconducting nanotube to be an “intrinsic” semiconductor, where only excess electrons would be created by thermal fluctuations alone. However, it is now believed that the metal electrodes, as well as chemical species adsorbed on the tube, “dope” the tube p-type. In other words, they remove electrons from the tube, leaving the remaining mobile holes responsible for conduction.

Charles Lieber and colleagues from Harvard University carried out one of first conductivity measurements of individual nanotubes [2.50] in 1995. To measure the electrical properties of individual carbon nanotubes (Fig. 2.12) they deposited a drop of a nanotube suspension on a flat insulating surface and covered it with a uniform layer of gold. A pattern of open slots was produced in the gold layer by conventional lithography procedures to expose the nanotube for measurement. Atomic force microscopy (AFM) studies showed that after this procedure, many of the single nanotubes have one end covered by the gold pattern and the other end extended into an open slot. With a conduction cantilever in the AFM it is now possible to establish electric contacts and measure the axial conduction through a single nanotube to the gold contacts while simultaneously recording the nanotube structure. Depositing a layer of NbN onto commercial Si$_3$N$_4$ cantilevers made the tips conducting. The nanotubes used in this study were prepared catalytically and samples consisted primarily of MWCNT with diameters between 7 and 20 nm. Measurements were made nanotubes with diameters of 8.5 nm and 13.9 nm, and their resistance was 0.41 MΩ/µm and 0.06 MΩ/µm respectively.
In order to avoid possible ambiguities due to poor sample contacts, Thomas Ebbesen and colleagues from NEC [2.51], in collaboration with Micron Europe, have developed a four-probe measurement method on single nanotubes by lithographic deposition of tungsten leads across the nanotubes (Fig. 2.13). They found that each MWCNT has unique conductivity properties and that differences between the electrical properties of different nanotubes were far greater than expected. Both metallic and semiconducting behaviour was observed on arc grown nanotubes. Ebbesen and colleagues suggested that tubes are essentially metallic. By analogy with carbon fibres and filaments [2.52], the variations in resistivities and their temperature dependence are possible due to the interplay of changes in carrier concentration and mobility in the metallic tubes.

**Figure 2.12.** Schematic diagram of the measurement of the electrical properties of an individual carbon nanotube used by Lieber and co-workers [2.50].

**Figure 2.13.** Focused ion beam image of four tungsten wires, each 80 nm wide, connected to an individual nanotube for four-probe measurement, from the work of Ebbesen and co-workers [2.51].
Resistance measurements were reported for eight different nanotubes and the results differed widely. The highest resistance was $10^8 \, \Omega/\mu m$ with a 0.8 $\Omega cm$ resistivity for the 10 nm diameter nanotube, and lowest was $2 \times 10^2 \, \Omega/\mu m$ and $4 \times 10^{-3} \, \Omega cm$ resistivity for the 18.2 nm diameter nanotube. Most of the nanotubes had a resistance of around $10^4 \, \Omega/\mu m$ and a resistivity of around $10^{-4} \, \Omega cm$. They also investigated also the temperature dependence of the conductivity of various nanotubes and the results were widely different. Finally they examined the effect of applying a magnetic field perpendicular to the axis of the tubes, but this effect was found to be negligible.

An individual SWCNT conductivity study was carried out in a collaboration between Smalley's group and Cess Dekker's group from Delft University of Technology in 1996 [2.53]. Because of the structural symmetry and stiffness of SWCNT, their molecular wave functions may extend over the entire tube. These researchers have found that electrical transport measurements on individual SWCNT confirm theoretical predictions and that they appear to behave as coherent quantum wires. Electrical conduction seems to occur through well separated, discrete electron states that are quantum-mechanically coherent over long distances, that is at least 140 nm from contact to contact. Figure 2.14 shows an AFM image of an individual tube connected to two electrodes and a corresponding circuit diagram. The two-point resistance at room temperature of single tube was generally found to be around 1 M$\Omega$.

The first measurement of the electrical properties of ropes of SWCNT was reported in a Science paper describing their synthesis by Smalley's group [2.54]. They measured electrical resistivity of a single rope using a four-point technique. They
calculated resistivity values for different ropes ranged from $0.34 \times 10^{-4}$ to $1 \times 10^{-4}$ $\Omega$cm. Smalley's group carried out a further study of the electronic properties of nanotube ropes in collaboration with researchers from the University of California at Berkeley [2.55]. They observed dramatic peaks in the conductance as a function of the gate voltage that modulated the number of electrons in the rope and interpreted these results as the effect of single electron charging and resonant tunneling through the quantised levels of the nanotubes composing the rope. Inter-tube conductance inside the rope was small compared to the conductance along the tube, inhibiting inter-tube transport.

### 2.3.2. Electron field emission properties

Electron field emission properties of individual carbon nanotubes were first reported by Richard Smalley's group in 1995 [2.15]. Carbon nanotubes were attached by van der Waals forces to the side of an 8 $\mu$m graphite fibre (Fig. 2.15). Field emission of electrons from individually mounted carbon nanotubes was found to be dramatically enhanced when the nanotube tips were opened by laser evaporation or oxidative etching. Emission currents of 0.1 to 1 mA were obtained at room temperature with a bias voltage of less than 80 V.

![Figure 2.15](image)

**Figure 2.15.** (a) Individual carbon nanotube attached to graphite fibre electrode and mounted in the vacuum to test field emission. (b) Higher resolution SEM and TEM image (inset) showing the end of stalk and single nanotube [2.15].

The emitting structures are concluded to be linear chains of carbon atoms pulled out from the open edges of the graphene wall layers of the nanotube by the
2. Literature Review

force of the electric field, in a process that resembles unravelling the sleeve of a sweater.

2.3.3. Mechanical properties

In a sheet of graphite each carbon atom is strongly bonded to three other atoms, which makes graphite very strong in certain directions. However, adjacent sheets are only weakly bonded by van der Waals forces. Layers of graphite can be easily peeled apart, as happens when writing with a pencil, but it is not easy to peel a carbon layer from a multiwalled nanotube. Carbon fibres have already been used to strengthen a wide range of materials, and the special properties of carbon nanotubes mean that they could be the ultimate-strength fibre. Carbon nanotubes remarkable mechanical properties are already exploited as “tips” in scanning probe microscopes. Since they are composed entirely of carbon, nanotubes also have a low specific weight. Nanotubes also offer great promise as the active elements in “nano-electromechanical” systems. Their remarkable mechanical and electronic properties make them excellent candidates for applications such as high-frequency oscillators and filters.

In 1996, Michael Treacy and Ebbesen, now at NEC Research in Princeton, and Murray Gibson from the University of Illinois in Urbana, measured the Young’s modulus of multiwalled nanotubes [2.56]. The Young’s modulus of a material is a measure of its elastic stiffness. Treacy and co-workers arranged multiwalled nanotubes vertically on a surface so that the tubes were fixed at the bottom and free to move at the top, and then used a transmission electron microscope (TEM) to measure the thermal vibrations of the free ends. The measured vibration amplitude revealed an exceptionally high Young’s modulus of $10^{12}$ N/m$^2$, about five times the value for steel. Young’s modulus is mainly determined by the carbon-carbon bonds within the individual layers. Jean-Paul Salvetat and co-workers from the Ecole Polytechnique Federale de Lausanne (EPFL) in Switzerland found that multiwalled nanotubes grown by arc discharge had a modulus of one or two orders of magnitude greater than those grown by catalytic CVD of hydrocarbons [2.57]. These results demonstrate that only highly ordered and well-graphitised nanotubes have a stiffness comparable to graphite, whereas those grown by catalytic decomposition have many more defects.
and hence a lower Young's modulus. The strong carbon-carbon bonds within each layer characterize well graphitised nanotubes, while the interactions between layers are weak. TEM images of CVD grown nanotubes indeed reveal that the carbon sheets are neither continuous nor parallel to the tube axis.

Rodney Ruoff and colleagues from Washington University together with coworkers from University of Wisconsin and Zyvex Company have developed and built a manipulation tool that can also be used as a mechanical loading device, which operates inside a SEM [2.58]. Individual MWCNT were picked up and then attached at each end of opposing tips of AFM cantilever probes (Fig. 2.16). Schematics of the tensile strength experiment principle are shown in Fig. 2.16a. When the top cantilever is driven upward, the lower cantilever is bent upward by distance $d$, while the nanotube is stretched from its initial length of $L$ to $L + \delta L$ because of the force exerted on it by the AFM tips. The force is calculated as $kd$, where $k$ is force constant of the lower cantilever. The strain of nanotube is $\delta L/L$. Values for the Young's modulus $E$ are shown in Fig. 2.16b. They are as follows: 945 GPa from a linear fit to the upswing part of the curve for nanotube 2 (O); linear fits of the first (470 GPa) and the second (300 GPa) upswing for the tube 15 (□), and 335 and 274 GPa from linear fits of the whole curve for nanotubes 18 (Δ) and 19 (▽). Nanotubes were stress-loaded in situ in the SEM and observations were recorded on video (Figure 2.17). Measurement of tensile strength for individual MWCNT have revealed a "sword-in-sheath" breaking mechanism, similar to that observed for carbon fibres [2.59]. Tensile strengths of up to 20 GPa were reported for graphite whiskers [2.60], which were stated to have a scroll-like structure rather than the "Russian doll" structure (nested cylinders) observed in MWCNT. The tensile strength of the outermost layer ranged from 11 to 63 GPa for the set of 19 MWCNT. Analysis of the stress-strain curves indicated that the Young's modulus, $E$, for this layer varied from 270 to 950 GPa.

Min-Feng Yu and Rodney Ruoff from Washington University in collaboration with co-workers from NASA have extended their method used to measure the strength of individual MWCNT [2.60, 2.62] to SWCNT ropes [2.62]. They measured the mechanical response of 15 SWCNT ropes under a tensile load and concluded that force-strain data fit well to a model that assumes the load is carried by the SWCNT on the perimeter of each rope. The average breaking strength of SWCNT in the perimeter of each rope ranged from 13 to 53 GPa, with a mean value of 30 GPa. Based on the
same model a Young's modulus ranging from 320 to 1470 GPa, with mean value of 1002 GPa was calculated.

![Figure 2.16. Tensile-loading experiment with individual MWCNT mounted between two opposing AFM tips [2.58]. (a) Schematic showing the principle of tensile-loading experiment, (b) Plot of stress versus strain curves for individual MCNT. (c) A SEM image of two AFM tips holding a MWCNT.](image)

![Figure 2.17. SEM images showing the breaking of MWCNT [2.61]. (a) A MWCNT attached between AFM tips under no tensile load. (b) The same MWCNT after being tensile loaded to break.](image)

Researchers from the University of North Carolina have shown in 1997 that multiwalled carbon nanotubes can be bent repeatedly through large angles using the AFM tip, without undergoing catastrophic failure suggesting that nanotubes are remarkably flexible and resilient [2.63]. They used the "Nanomanipulator" AFM system (Discoverer, Topometrix Inc., Santa Clara, CA) to produce and record
nanotube translations and bends by applying lateral stress at location along the tube (Fig. 2.18).

![AFM images of 20 nm diameter carbon nanotube bent by the tip from its straight shape (a-inset) [2.63]. The white scale bar in (a) is 300 nm, and it is same in (b).](image)

These fascinating mechanical properties of carbon nanotubes can be exploited in applications, which might include lightweight bullet-proof vests and earthquake-resistant buildings, while nanotube tips for scanning probe microscopes are already commercially available. There are a number of problems to overcome before starting to utilise nanotubes for reinforcement applications. The properties of nanotubes need to be optimised. Tubes must be efficiently bonded to the material they are reinforcing (the matrix), in order to maximize load transfer. New composite materials have been made from various polymers and carbon nanotubes. Some of these materials have shown improved mechanical or electrical properties when compared to polymers not containing nanotubes.

2.3.4. Magnetic properties

As a simplistic model, one might assume that the magnetic properties of a carbon nanotube would approximate to those of a rolled-up graphene sheet. Graphite's magnetic properties are determined by the presence of ring currents, i.e. electron orbits circulating above and below the hexagonal lattice planes, which include several atoms within their radius [2.64]. The magnetic susceptibility of carbon nanotubes was studied by Arthur Ramirez and colleagues from Bell Labs, in collaboration with Smalley's group [2.65]. They found a significantly enhanced susceptibility of carbon nanotubes compared to that of orientationally averaged graphite, which is a result of a
geometry determined band structure. These workers have studied magnetic susceptibility for a variety of carbons ($C_{60}$, diamond, carbon black, graphite and carbon nanotubes) over a range of temperatures from absolute zero to room temperature (Fig. 2.19).

![Figure 2.19](image_url)

**Figure 2.19.** Magnetic susceptibility of carbon materials as function of temperature: $C_{60}$, diamond, carbon black, highly oriented pyrolytic graphite (HOPG), and carbon nanotubes [2.65].

### 2.3.5. Optical properties

There has been relatively little work on the optical properties of carbon nanotubes. Walt de Heer and co-workers at the EPFL, Lausanne [2.66], conducted one of the few experimental studies of the optical properties of nanotubes. They used ellipsometry to determine the dielectric function, $\varepsilon$, for tubes aligned either parallel or perpendicular to a support film. The perpendicular nanotube films were found to be optically isotropic, while for parallel films the optical properties depended strongly on the whether the light was polarised parallel or perpendicular to the tubes. When the light was polarised along the tubes, the shape of the dielectric function was similar to that of highly ordered pyrolytic graphite (HOPG). With the light polarised perpendicular to the tube direction, the dielectric function could be interpreted as a mixture of the two dielectric functions of graphite parallel and perpendicular to the graphite sheets. The dielectric function for tubes aligned perpendicular to the substrate was similar to that of glassy carbon.
2.4. SYNTHESIS OF CARBON NANOVELVETUBES AND NANOFLZRES

The first carbon nanotubes identified by Iijima in 1991 were synthesised using a carbon arc-discharge [2.6]. Since then a number of other methods of carbon nanotube synthesis have been developed including vaporising a graphite target using a laser [2.10, 2.11], electron beam [2.12], and solar energy [2.13] sources. An electrochemical method for the synthesis of multiwalled carbon nanotubes has been developed by the University of Sussex group [2.68]. Mamairo Endo and colleagues from Shinshun University together with the University of Sussex have shown that multi-walled carbon nanotubes can be synthesised by the pyrolysis of benzene in the presence of hydrogen [2.69]. However, the production of relatively imperfect carbon nanotubes by catalytic chemical vapour deposition methods at high temperatures has been known for decades [2.3].

2.4.1 Arc-evaporation

The arc-evaporation apparatus used by Iijima for carbon nanotube synthesis in 1991 [2.6] was very similar to that used in the Kratschmer-Huffman experiment for the mass production of C\textsubscript{60} one-year earlier [2.70]. In the original method used by Iijima graphite electrodes were held a short distance apart, rather than being kept in contact like in the Kratschmer-Huffman experiment. Under these conditions, some of the carbon that evaporated from the anode re-condensed as a hard deposit on the cathodic rod. Described by Iijima as graphitic carbon needles, carbon nanotubes were grown on the negative end of the carbon electrode, plentifully on only certain regions of the electrode. The carbon deposits on the electrode contained carbon nanotubes, ranging from 4 to 30 nm in diameter and up to 1 µm in length, and also polyhedral particles with a spherical shell structure, which were 5-20 nm in diameter.

A variety of different arc-evaporation reactors are now being used for nanotube synthesis. A typical chamber would be a glass-dome chamber or stainless steel vacuum chamber with a viewing point connected to a vacuum line with a diffusion pump, and helium supply. A continuous flow of helium at a given pressure
is usually preferred over a static atmosphere of the gas. The electrodes are two high purity graphitic rods. Typically, the anode is a long rod approximately 6 mm in diameter and the cathode is much shorter rod 9 mm in diameter [2.71]. Efficient water-cooling of the cathode is essential for producing good quality nanotubes, and the anode is also frequently cooled. The position of the anode should be adjustable from outside the chamber, so that a constant gap can be maintained during arc-evaporation. A voltage-stabilized DC power supply is normally used, and discharge is typically carried out at a voltage of 20 V. The current applied depends on the diameter of the rods, their separation, the gas pressure and various other factors, but is usually in the range 50-100 A.

When the pressure is stabilised, the voltage is turned on. At the start of the experiment the electrodes should not be touching, so no current will initially flow. The movable anode is now gradually moved closer to the cathode until a discharge occurs. When a stable arc is achieved, the gap between rods is maintained at approximately 1 mm or less. The rod is normally consumed at a rate of a few millimeters per minute. When the rod is consumed, the power is turned off and the chamber left to cool before venting to air pressure.

In order to further enhance cooling and to maintain optimum arcing conditions, Richard Smalley's group in collaboration with co-workers from University of Minnesota [2.72], have constructed the apparatus shown in Figure 2.22. The (top) anode and (bottom) copper cathode mounts were coaxial and equipped with computer-controlled stepper motors for rotation and translation about the vertical axis. The region around the arc was completely enclosed in water-cooled copper surfaces. Graphite electrodes as large as 19 mm in diameter were used to produce high quality nanotubes. When short lengths (<2.5 cm) of graphite rod were attached to the water-cooled cathode mount, conduction down the length of this graphite electrode was sufficient to prevent formation of the gray-white core. The best prediction of nanotube material coincided with a remarkably stable operating condition of the arc where the cathode-anode gap was 1 to 2 mm. The plasma of the arc appeared to the eye to be uniformly and extend over the entire electrode surface, with very little fluctuations. With 12.5 mm diameter electrodes, stable operation could be attained in the range of 17 to 20 V and 110 to 130 A, and with 19 mm electrodes stable voltage conditions were 17 to 20 V but 250 to 300 A. In both cases, around 90% of the carbon that evaporated from the anode deposited directly onto the cathode. The cathode being
covered by tens of thousands of parallel columns, each of which is composed of millions of parallel nanotubes, causes steady behaviour of the arc. Each of these nanotubes acts as an intense field emitter into the plasma of the arc.

Figure 2.22. Schematic illustration of arc-evaporation apparatus for the production carbon nanotubes: a- graphite anode, b- deposit, c-graphite cathode [2.72].

Subsequent modifications to the procedure by Ebbesen and Ajayan [2.9] have enabled greatly improved yields to be obtained by arc-evaporation. They reported the synthesis of graphitic nanotubes in gram quantities, demonstrating that purity and yield depend on the helium pressure in the chamber. A striking increase in the number of tubes was observed as the pressure was increased. At 20 Torr, hardly any nanotubes were found. Only amorphous sheet-like and glassy graphitic material was formed. At 100 Torr, a few nanotubes were observed in the sample. At 500 Torr the entire sample consists of carbon nanotubes and nanoparticles (cage structures). At pressures above 500 Torr the quality of the sample did not changed significantly, but a fall in the total yield was observed. Therefore at 500 Torr the total yield of nanotubes as a proportion of starting graphitic material was optimal. Under these conditions approximately 75% of the consumed graphite rod was converted to a deposit of cylindrical shape and similar diameter. The rate at which the rod deposits were formed depended on the gas pressure being a few millimetres per minute under optimal conditions. Ebbesen and Ajayan described two distinct regions in the cross-
section: an inner black core containing nanotubes and an outer grey metallic hard shell with no nanotubes. The core material containing the nanotubes is macroscopically fibrous, with fibres parallel to the direction of the current. The fact that nanotubes were found only in the core of the sample and not on the colder edge indicates that the temperature and cooling rate are critical for their formation. If the plasma is stable, a more homogeneous sample is produced.

The macroscopic structure of the deposit is particularly dependent upon the efficiency of cooling. Poor cooling results in a layered deposit, where nanotubes are found in small pockets, where they tend to orient randomly. Efficient cooling of the electrodes produces a more cylindrical and homogeneous material. A deposit of this kind has a hard outer shell, consisting of fused material, and a softer fibrous core, which contains discrete nanotubes and nanoparticles. These can be extracted by cutting open the outer shell. Examination of the fibrous core material by scanning electron microscopy has shown that it contains aligned microfibrils made up of nanotube bundles and individual nanotubes. The ratio of nanotubes to nanoparticles in the best samples is of the order of 2:1.

2.4.2. Catalytically produced nanotubes and nanofibres

Carbon filaments or whiskers, nanofibres or nanotubes can be produced by the interaction of a wide range of hydrocarbons and other carbon-containing gases with a metal catalyst, the most effective of which are iron, cobalt and nickel. The presence of hydrogen was found to enhance filament growth.

Catalytic formation of filamentous carbon by decomposition of carbon-containing gas on a hot surface has been known for over a century. Paul and Leon Schutzenberger in 1890 observed this phenomenon when cyanogen was passed over porcelain at a cherry-red temperature [2.1]. Davis and co-workers reported one of the first electron microscopy images of carbon filaments, obtained from reaction of carbon monoxide with Fe$_3$O$_4$ at 450 °C, in 1953 [2.3]. A letter in Nature in 1992 claimed that these carbon filaments could have been the carbon nanotubes [2.73]. However, fine tubes of carbon produced by catalytic methods have much less perfect
structure than the fullerene related tubes produced by arc discharge. The tubes are not closed with fullerene-like caps and usually have a metal particle attached to one end.

Intensive research into the catalytic formation of carbon filaments began in the 1970's. The work of Terry Baker and his colleagues [2.74], and other researchers in the 1970's and 1980's proceeded in two opposing directions: to inhibit carbon filament growth and to optimise growth. Research into inhibiting carbon filament growth was motivated by the fact that the presence of such filaments could constitute a serious problem in certain chemical processes, as well as in the operation of gas-cooled nuclear reactors. As a result of the huge interest in carbon nanotubes in the 1990's, catalytic carbon nanotube synthesis methods have been under intense research activity to produce large quantities of this material. Jose-Yacaman and co-workers have concluded that catalytic methods can produce carbon nanotubes with very similar characteristics to that of the carbon-arc method [2.75].

Carbon fibres and filaments have been made successfully for over ten years using a method known as chemical vapour deposition (CVD), a technique that is widely used to deposit thin films on substrates. In the CVD of carbon materials, a hydrocarbon gas is passed over a heated catalyst. The actions of the catalyst cause the hydrocarbon to decompose into hydrogen and carbon atoms, which provide the “feedstock” for carbon-fibre growth. CVD has been actively used to produce carbon nanotubes. Multiwalled nanotubes grown this way tend to have a large number of structural defects.

The CVD process of carbon nanotube and nanofibre synthesis has two main advantages. Firstly, the nanotubes are obtained at much lower temperatures, however this is at the cost of lower quality. Secondly, the catalyst can be grown on a substrate, which allows growth of aligned nanotubes and control of their growth. Nanotubes can be grown on surfaces with a degree of control that is unmatched by arc-discharge or laser-ablation techniques. The nanotubes can grow so that they are aligned with each other and are perpendicular to the surface of the substrate. This “self-orientation” is due strong Van der Waals interactions between the tubes, which cause the nanotubes to bundle together and form rigid structures.

The catalytic chemical vapour deposition method is now regarded in both the scientific and business community as the best method for cheap production of large quantities of carbon nanotubes. Carbon nanotubes produced by this method have more structural defects comparing to nanotubes produced by arc-discharge [2.6, 2.9, 2.76]
or laser vaporisation [2.10, 2.11]. However, a perfect carbon nanotube structure is not important for many applications.

The key parameters involved in growing nanotubes using CVD are the types of hydrocarbons and catalysts used, and the temperature at which the reaction take place. Most of the CVD methods used to grow multiwalled carbon nanotubes use ethylene or acetylene gas as the carbon feedstock, and iron, nickel or cobalt nanoparticles as the catalyst. The growth temperature is typically in the range of 500 to 700 °C. At these temperatures the carbon atoms dissolve in the metal nanoparticles, which eventually become saturated. The carbon then precipitates to form solid carbon tubes, the diameters of which are determined by the size of metal particles in the catalyst. Formation of carbon nanotubes and nanofibres in catalytic CVD is presented in more details in Section 2.5.

In 1998 Hongjie Dai group at Stanford University succeeded in producing single-wall nanotubes with perfect structures for the first time using CVD. Their approach used methane gas as the carbon source and temperatures in the range of 900-1000°C. Such high temperatures are needed to form single-walled nanotubes that have small diameters and high strain energies, and to produce virtually defect-free tubes.

Thermal CVD method of carbon nanotube production using a flow tube furnace [2.14, 2.69], is the most common production method, and is used by the majority of researchers at universities and companies. A hydrocarbon gas (methane, acetylene etc.) is used as the carbon source and a transition metal (nickel, iron etc.) as a catalyst inside the tube. This is well known method was recently improved to use metalocene (preferably ferrocene) benzene-based aerosols by a team at the University of Sussex [2.77]. The basic design of this system is shown at Fig. 2.23. Many research groups have now used this design.

Carbon nanotube production using a thermal CVD process or the catalytic pyrolysis of hydrocarbons is very similar to the method used for carbon nanofibre production developed and studied in the 70’s in 80’s by Terry Baker and others [2.78]. Catalytically produced carbon nanotubes using CVD process are similar to the CARBON FIBRILS™ patented by Hyperion Catalysis International [2.79].
Carbon nanotubes and nanofibres can be synthesised using plasma enhanced CVD (PECVD) where the hydrocarbon gas is in an ionised state over the transition metal catalyst (nickel, iron, cobalt, etc.). The PECVD method can use different energy sources for creation of the plasma state. Hot filament PECVD uses thermal energy for plasma creation and has been used very successfully for carbon nanotube production by Ren and co-workers [2.16]. Microwave PECVD, widely used for the preparation of diamond and diamond-like films, has also been successfully used in the production of carbon nanotubes and nanofibres [2.80-2.85]. Another method well established for diamond and diamond-like carbon film production is radio frequency PECVD. A radio frequency PECVD carbon nanofibres production method, which allows carbon nanofibre synthesis at any temperature, has been developed by Bojan Boskovic and co-workers at University of Surrey and described in this thesis [2.86].

### 2.4.2. Aligned carbon nanotubes and nanofibres

Chen and co-workers [2.87] have used plasma-assisted hot filament chemical vapour deposition (HFCVD) with a gas mixture of nitrogen and acetylene to obtain aligned nanofibres, at 20 Torr pressure and 700-800 °C temperature. The produced aligned nanofibres were of 50-100 nm in diameter and 6-10 μm length, with a density of $10^9$-$10^{10}$ cm$^{-2}$. Polished polycrystalline Ni wafers were used as substrates. A Ni particle is found on the tip of each fibre. The nanofibres have graphitic skin and
hollow tube structure. These fibres cover more than 70% of the area of the substrate surface. They observed bundles of nanofibres such as those shown in Figure 2.25.

![SEM micrograph of bundle like nanofibres](image)

**Figure 2.25.** SEM micrograph of bundle like nanofibres (after Chen et al., [2.87]).

Ren, Huang and co-workers in 1998 [2.88, 2.89] reported successful growth of large-scale well-aligned carbon nanofibres on nickel foils and nickel-coated glass at temperatures below 666 °C. Acetylene gas was used as the carbon source and mixed with ammonia (ratio from 1:2 to 1:10) in a plasma enhanced hot filament chemical vapour deposition (PE-HFCVD) system. Carbon nanofibre films were grown at pressures of 1-20 Torr maintained by flowing acetylene and ammonia gases with total flow rate of 120-200 sccm. They concluded that plasma intensity, acetylene to ammonia gas ratio, and their flow rates affect the diameter and uniformity of the carbon nanofibres. A spherical ball of Ni was found to cap each nanofibre. Aligned carbon nanofibres grown on polycrystalline Ni foil are shown at Figure 2.26.
The same research team reported [2.90] patterned growth of freestanding carbon nanofibres on submicron nickel dots on silicon. A thin film nickel grid was fabricated on a silicon wafer by standard microlithographic techniques, and PE-HFCVD was performed using an acetylene and ammonia mixture. Growth was performed at a pressure of 1-10 Torr at temperature below 660 °C for 5 min. Figure 2.27 shows representative selective growth of carbon structures on an array of Ni dot patterns.
2.5. GROWTH MECHANISM OF CATALYTIC CARBON NANOTUBES AND CARBON NANOFIBRES

Carbon nanofibres can be grown from catalytic decomposition of certain hydrocarbons or carbon monoxide over small transition metal particles such as iron, nickel and some of their alloys [2.91-2.99]. The typical catalytically grown carbon nanofibre structure shown in Fig. 2.3 has been produced from methane decomposition over the nickel particles at 550 °C.

First experiments on carbon filament growth in the 1950s were with carbon monoxide [2.91, 2.92]. In the 1970s researcher started to use methane [2.94, 2.100] and other hydrocarbons [2.95, 2.97, 2.98]. Nickel was and still is the most popular catalyst, followed by iron and then cobalt.

Many researchers have speculated about possible explanations of carbon nanofibre growth: Roston et al. [2.93], Baker et al. [2.95], Boehm [2.96], Oberlin et al. [2.98], Rostrup-Neilsen and Trimm [2.99] and Yang and Chen [2.101]. However, no complete mechanism has yet been proposed which can explain the various, and often conflicting data. One of the first attempts to explain the carbon nanofibre growth mechanism was made by Ruston and his co-workers in 1969 [2.93]. They concluded that carbonisation of the bulk of the metal takes place by interstitial diffusion of carbon atoms.

Baker and co-workers in 1972 developed the most influential model for carbon nanofibre growth as a result of direct growth observations using controlled atmosphere microscopy assuming that diffusion flow was primarily driven by the temperature gradient [2.95]. They observed initial flocculent deposits around nickel particles just before the start of carbon nanofibre growth (Fig. 2.28a). Decomposition of acetylene on the exposed surface of the nickel particle produced a considerable amount of heat. Since acetylene is unlikely to decompose rapidly on the protected regions of the particle a temperature gradient will be set up within the particle. Carbon from decomposed acetylene is taken into solution, diffuses down the thermal gradient to be deposited predominantly in the protected regions to produce the situation shown in Fig. 2.28b.
The precipitation of carbon at the rear of the particle builds up a deposit of carbon, which forces the particle away from the support. The initial mode of growth is responsible for distortion of the particle as shown in Fig. 2.28b. For such distortion to occur the metal must be assumed to have properties of a liquid. In that event, the ultimate detachment of the particle from the support will be so rapid that deposition of carbon in this region will probably not have taken place, which accounts for the initial appearance of a hollow channel. This could explain the initiation period.

The difference in character between the skin and bulk material of the nanofibre is quite definite and suggests that different processes produce these two phases. It is possible that the bulk material arises from carbon transported through the particle and the skin develops because of carbon transport around peripheral surfaces, as shown in Fig. 2.28c. Carbon deposited at the rear of the particle loses contact with the metal in a shorter time after its formation than that constituting skin. It would thus be expected that the bulk material of the filament would show less structural order than the skin and as a consequence a higher reactivity towards oxygen. Deposition of carbon at the rear face of the particle is an endothermic reaction (+40.5 kJ/mol). Baker and co-workers calculated that for a linear filament a growth rate of 90nm/s, and assuming filament a density of 2.2 g/cm³, radiation loss energy balance gives a heat input of 900 K. To support the postulate that diffusion of carbon through the liquid
particle determines the growth rate, they calculated an activation energy of 145.0 kJ/mol which can be compared to the activation energy of the diffusion of carbon in nickel containing 0.5% carbon which is in the range of 138 to 145.5 kJ/mol.

If excess carbon on the surface does not move away to form the nanofibre skin rapidly enough, then the fraction of free particle surface available for adsorption and decomposition of acetylene slowly decreases. Since this results in a decrease in heat input to the particle, which allows cooling and a subsequent decrease in the rate of diffusion of carbon through the particle, a consequent slowing of the growth rate is observed. Ultimately, the situation shown in Fig. 2.28d is reached, where the particle is completely encapsulated by surface carbon and nanofibre growth ceases. The particle is said to have lost its activity. It was observed that when the nanofibres were combusted in oxygen so that all the carbon was removed, nanofibre growth proceeded when acetylene was reintroduced, and the growth rate curves were similar in form and magnitude.

Although, many researchers have accepted the mechanism suggested by Baker and co-workers, it has not received universal acceptance. A slightly more divergent variation occurs in the case of nanofibres, which do not grow from a free particle, but from a particle that remains attached to the support surface. Baker and Waite [2.103] proposed a simple modification to the above mechanism for the nanofibres produced from the Fe-Pt/C2H2 system and this is depicted schematically in Figure 2.29.

Figure 2.29. Stages in the growth of nanofibres from Pt-Fe/C2H2 (after Baker and Waite, [2.103]).
Observations indicate separation of Fe and Pt before carbon nanofibre growth (Fig. 2.29a). Some of the carbon produced from the hydrocarbon decomposition will be taken into solution by Pt and will diffuse down the temperature gradient created in this metal by the acetylene decomposition. Carbon will tend to move towards the cooler Fe surfaces (Fig. 2.29b). The upper surface of the Fe core is cooled when the carbon endothermally precipitate to form the inner segment of the filament (Fig. 2.29c). If carbon at the particle surface is not removed to form the nanofibre skin fast enough, then the Pt surface will rapidly become blocked. The source of the temperature gradient in the Pt will be removed, and passage of the carbon through the particle will cease (Fig. 2.29d). It was found that deactivated catalyst particles could sometimes be regenerated by reaction in H\textsubscript{2}, followed by re-introduction of acetylene.

Baird, Fryer and Grant in 1974 [2.97] agreed that the Baker and Harris model [2.95], accounted well for the growth of long non-graphitic filaments, but did not account for the structural features of the hollow filaments formed in slower reactions or for platelet graphite formation.

Oberlin, Endo and Koyama in 1976 [2.98] proposed a two-step growth process. The first step is responsible for the formation of the inner core containing long, straight and parallel carbon layers cylindrically rolled around a hollow tube. The secondary process is the thickening of the fibre by a pyrolytic deposit. Small “liquid-like” iron droplets deposited on the furnace wall create nucleation sites for the hydrocarbon to diffuse, and as result the first carbon shell is formed. New metal hydrocarbon species dissociate on its edges and carbon layers develop by lateral growth following the external surface of the catalyst (Fig. 2.30a and 2.30b). Such lateral growth exerts a force strong enough to lift up the catalyst particle above the surface of the substrate (Fig. 2.30c). Layers always progress laterally in the same manner and result in a nanofibre growth. The hollow channel in the centre is due to the fact that no carbon supply can reach the back of the droplet, the surface of which is protected from downward surface migration by the lateral carbon layers. When carbon layers at the tip cover the whole droplet, the diffusion stops and growth ends.
Rostup-Nielsen and Trimm in 1977 [2.99] introduced a concentration driven mechanism for diffusion of carbon through the metal instead of a temperature driven process such as proposed in Baker's model [2.95]. They concluded that transportation of nickel at the surface of the growing carbon could not be completely explained in terms of temperature driven dissolution-precipitation and that is an unlikely result of carbonaceous specie migration. The most probable explanation, according to them, would seem to involve diffusion of carbon through the nickel under a concentration gradient, where precipitation occurs at a dislocation.

Sacco, Thacker, Chang and Chiang in 1984 [2.104] agreed with Baker's model of the carbon diffusion through the reduced metal for carbon nanofibre growth and proposed an initiation mechanism. They concluded from examination of iron foils in an electron microscope that the surface breaks up into nodular morphology, and these nodules are comprised of carbon nanofibres. The proposed initiation mechanism assumes that Fe₃C acts to increase overall surface area through surface break-up and also acts as a catalyst for carbon deposition and subsequent nanofibre growth.

Tibbetts, Devor and Rodda [2.105] agreed with the model of concentration driven carbon diffusion proposed by Rostrup-Nielson and Trimm [2.99]. They looked for a model that could explain growth of carbon fibres as rapid as millimetres per minute. They showed that the high thermal conductivity of the iron makes the temperature gradient too small to account for the observed flux of carbon atoms.

Yang and Chan proposed [2.101] the following mechanism for carbon nanofibre growth. Carbon is first formed and dissolved in metal, followed by graphite/metal segregation and metal reconstruction/faceting. This is the incubation period. The ensuing step is a steady-state filament growth period involving
decomposition of hydrocarbon on the gas/metal interfaces and graphite precipitation on the graphite/metal interfaces. This step continues until the gas/metal interfaces are encapsulated by carbon. The basis for the concentration-driven mechanism for steady-state nanofibre growth as suggested in the literature [2.99] is inadequate. A temperature-driven mechanism without exothermal surface reaction is proposed. The two driving forces are not mutually exclusive and may both contribute to the filament growth.

Transition metals, such as iron, nickel and cobalt are well known to be active catalyst, but the exact mechanism of their action is still uncertain. Reactions with hydrocarbons are favoured by the presence of hydrogen, and oxides can also help. For experiments with iron catalysts, some authors claim that the active catalyst could be an iron carbide Fe₇C₃ [2.93], FeC [2.106] or Fe₃C [2.96]. In this case, in order to explain the hollow tube, it is necessary to assume that the carbon layers may only nucleate on a specific face of the carbide crystal.

The interaction between the metal catalyst particle and supporting medium is a further factor that influences the nanofibre growth characteristics. The influence of the two different types of metal-support interactions on the nanofibre growth is schematically presented on Figure 2.31. A weak interaction results in "whisker-like" growth or "tip growth" model, and a strong interaction resulting in growth by the extrusion mode or "base growth" model. In strong interactions the catalyst particle remains attached to the support. Strong interaction example is when ruthenium particles were supported on either graphite or silica in a reaction with acetylene. In contrast, when metal is supported on titanium under the same conditions weak metal/support interaction occurs [2.107].

\[ \text{Support} \]
\[ \text{Support} \]

(a) (b)

**Figure 2.31.** Influence of the metal-support interaction on the mode of carbon nanofibre growth: (a) Weak metal-support interaction – "tip growth"; (b) Strong metal-support interaction- "base growth", (from [2.108]).
2.6. APPLICATIONS OF CARBON NANOTUBES AND NANOFLATRES

2.6.1. Nanoelectronics

The age of semiconductor technology started in 1947, just half a century ago, when the first semiconductor device, a germanium-based transistor, was invented at the Bell Telephone Laboratories [2.109]. Since then, the miniaturization of devices has been continuous, and computers have become faster and smaller. Meanwhile, silicon has become the most popular device material, owing to its geological abundance and suitable physical properties. Nowadays, the size of a typical device is halved every 18 months. But how far into the future can this continue? The present path should end when we go from the present 0.18 μm to the nanometer (~10 nm) size where materials are known to behave quite differently because of quantum effects.

At the present pace of miniaturisation, we will reach this end within a decade [2.109]. In order to overcome this technological limit, several types of devices are being investigated that make use of quantum effects rather than trying to overcome them. For this reason, the nanometre-scale carbon materials, namely the fullerenes and nanotubes, have attracted great interest not only in the scientific fields, but also in the fields of semiconductor technology. Solid C60 is semiconducting [2.110], whereas nanotubes can be semiconducting or metallic, depending on their network topology [2.111], and several device structures have been theoretically proposed [2.112].

Collins et al. reported an experimentally functioning carbon nanodevice based on nanotubes [2.113]. In general, there are two kinds of elemental device structures, two-terminal and three terminal devices. The transistor is a three-terminal device with variety of structures, materials, and basic functional mechanisms. A typical two-terminal device is the diode, having also a variety of structures and applications, such as switching, rectification, and solar cells. The “nanotube nanodevice” reported by Collins and co-workers is kind of nanodiode.

Semiconducting nanotubes can work as transistors. The tube can be made to conduct (turned “on”) by applying a negative bias to the gate, and turned “off” with
positive bias. A negative bias induces holes on the tube and allows it to conduct. Positive biases, on the other hand, deplete the holes and decrease the conductance. The resistance of the “off” state can be more than a million times greater than the “on” state. This behaviour is analogous to that of a p-type metal-oxide-silicon field effect transistor (MOSFET), except that the nanotube replaces silicon as the material that hosts the charge carriers. It has been shown that a field effect transistor (FET) can be made from individual semiconducting single walled nanotubes by Cees Dekker and colleagues at the Delf University of Technology in the Netherlands [2.114], and later by Phaedon Avouris and co-workers at IBM at Yorktown Heights [2.115] (Fig. 2.32).

![Diagram](image.png)

**Figure 2.32.** Schematic cross section of the field emission transistor (FET) devices. A single nanotube which bridges the gap between the gold electrodes could be either multi-walled carbon nanotube (MWNT) or single-walled carbon nanotube (SWNT). The silicon substrate is used as back gate [2.115].

These tiny MOSFET-like devices will probably be just the first in a host of new semiconducting device structures based on carbon nanotubes. Other devices, such as nanotube p-n junction diodes and bipolar transistors, have been discussed theoretically and are likely to be realised soon.

### 2.6.2. Field emission displays

The development of field emission displays, equally bright but thinner and more power-efficient, has long been seen as a potential multibillion-dollar technology that would replace bulky, inefficient cathode ray tube televisions and computer monitors. The hope is that field emission displays with nanotubes may clear the way for an alternative to cathode-ray tubes and liquid-crystal panels.
The field emission properties of films formed from multiwall carbon nanotubes were discovered in 1995 by Walt de Heer in collaboration with Daniel Ugarate at the Ecole Polytechnique Federale de Lausanne, Switzerland [2.116, 2.117], and field emission displays with carbon nanotubes was proposed.

It is surprisingly easy to make a high-current field emitter from nanotubes by mixing them into a composite paste with plastics, smearing them onto an electrode, and applying a voltage. Invariably some of the nanotubes in the layer will point toward the opposite electrode and will emit electrons. That is exactly what Walt de Heer and his colleagues did to make the first flat panel display experiment (Fig. 2.33). They first created an electron conducting polymer film with tens of thousands nanotubes sticking up from it, and then connected a ground electrode to that film. On top of the film, they then layered a screen-like grid, using a thin insulating sheet of mica. The whole was covered with 3 mm diameter and 50% transmitting 200 mesh electron microscopy copper grid. The copper grid and polymer containing nanotube film were connected to opposite poles of a 200 V battery, copper to positive and polymer to negative. Applying a voltage to the carbon nanotube film produced an electron beam that passed through the grid and was detected at the anode.

Some companies have announced that they are developing products that use carbon nanotubes as field emitters. ISE Electronics in Ise, Japan, have used nanotube composite films to make prototype vacuum-tube lamps in six colours that are twice as bright as conventional light bulbs, and longer-lived. They run for well over 10000 hours without failure. An electric field extracts electrons from the film and subsequently accelerates them towards a phosphorescent screen, which light up
brightly [2.118]. The lamp does not require a heated filament and it is very energy efficient. These lamps can be switched on and off very rapidly. The colour of the lamp can be easily adjusted by changing the phosphor. Jongmin Kim and co-workers at Samsung have demonstrated a functioning 9-inch colour display in December 1999 [2.119, 2.120]. They spread nanotubes in a thin film over control electronics and then put phosphor-coated glass on top to make a prototype flat panel display [2.121]. The flat panel video display is a very challenging project because it requires very densely packed arrays of field emitting elements that can be switched at video rates. A standard video image is refreshed about 100 times per second [2.119].

2.6.3. Fuel cells

In early 1997 Dillon and co-workers have shown that hydrogen gas can condense to a high density inside narrow, single-wall carbon nanotubes (SWCNT) [2.23]. The very high hydrogen uptake in carbon nanotubes suggested that they might be effective as a hydrogen-storage material for fuel cells in electric vehicles. The fuel cell relies on the conversion of molecular hydrogen to water using a catalyst. The reaction energy is released as electronic energy, which means that the fuel cell is essentially a chemical battery [2.119]. Hydrogen, however, is a flammable gas, which makes it difficult to store. High-pressure storage tanks are not considered to be viable due to safety concerns.

A team from Northeastern University in Boston led by Terry Baker and Nelly Rodriguez in 1998 attracted a lot of attention by claiming 67 weight % of hydrogen could be stored in carbon nanofibres with a herring-bone structure at 120 atmospheres and room temperature [2.122]. Many researchers view this data as a highly controversial, but this team is continuing to work on hydrogen storage in carbon nanofibres [2.123] and carbon nanofibre fuel cell applications [2.124]. A number of groups at universities and companies have investigated hydrogen storage and release properties of carbon nanotubes for fuel cell applications [2.125, 2.126].
2.6.4. Composite materials

Composite materials containing carbon fibres are already widely used in applications ranging from aerospace to sports equipment. In such materials the matrix can be plastic, epoxy, metal or carbon. The incorporation of carbon fibres into a matrix not only increases strength and elasticity to the material but also greatly enhances toughness, that is its ability to resist cracking. Carbon nanotubes mixed with polymers have improved mechanical or electrical properties of these composite materials. To make such composites it is essential that a strong bond can be formed between the nanotubes and the host material. Ajayan and colleagues embedded purified nanotubes into an epoxy resin [2.127]. They were interested in obtaining cross-sectioned images of nanotubes and attempted to achieve this by embedding purified nanotubes into an epoxy resin and then cutting the hardened composite into thin slices with a diamond knife. However, no nanotube cross sections were observed following this treatment, instead the nanotubes were found to have become aligned in the direction of the knife movement (Fig. 2.34). This work has shown that alignment of carbon nanotubes can be achieved during processing of the composite.

![Figure 2.34. A TEM image showing alignment of carbon nanotubes in a polymer matrix after cutting with microtome. Defects on nanotubes are marked by arrows. [2.127].](image)

Electrical conductivity of composite material containing carbon nanotubes in a luminescent polymer PmPV was increased up to eight orders of magnitude compared to the conductivity of PmPV polymer, with no degradation of optical properties.
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[2.22]. It was shown that this composite could be used as the emissive layer in an organic light-emitting diode, which promises future applications in optoelectronics.

There is much interest in producing plastic materials that conduct electricity to some degree. This property is useful for protecting electronic components from destructive electrostatic voltage during storage and shipping. Such investigations have produced a weakly conducting organic polymer mixed with carbon nanotubes to form a wholly organic conductor. Research on carbon nanotubes as conductive fillers in polymer composites for electrical applications is being carried out in several laboratories, but little has appeared in the open literature [2.128].

2.6.5. Tips for scanning probe microscopy

The length and rigidity of nanotubes suggest that they could be ideal for scanning probe microscopy. The elongated shape and small diameter of carbon nanotubes enable them to probe better than currently used microfabricated pyramids of silicon or silicon nitride. Hongjie Dai and co-workers in Smalley's group were the first to show that carbon nanotubes might constitute well-defined tips for scanning probe microscopy [2.21] (Fig. 2.35). The nanotubes were bonded to the side of the tip of a conventional silicon cantilever using a soft acrylic adhesive 1-10 nm thick. This permits the nanotube to bend away from its connection whenever the tip is inadvertently "crashed" into a hard surface, and then to snap back to its original straight position when the tip is withdrawn.

![Figure 2.35. A single nanotube attached to the pyramidal tip of a silicon cantilever for scanning force microscopy (SFM) [2.21].](image)
Charles Lieber and co-workers from Harvard University have developed a technique for growing individual carbon nanotube probe tips by the CVD technique from ends of silicon AFM tips [2.129]. Firstly they flattened a conventional silicon tip at its apex by contact AFM imaging and anodizing in hydrogen fluoride to create nanopores of 50-100 nm diameter along the tip axis. An iron catalyst is electrodeposited into the pores from FeSO₄ solution, and nanotubes are grown by CVD with ethylene and hydrogen at 750 °C after a reaction lasting 10 min. The oriented pore structure was chosen for the catalyst support in order to control the direction of growth and enable the reproducible production of nanotube tips for imaging. CVD grown nanotubes are usually too long to be used as tips, and are shortened by an in situ AFM technique [2.129].

There is also the possibility of functionalising the nanotubes in order to use these tips for “chemical force microscopy”. There are potential problems with using nanotubes for atomic resolution imaging due to relatively large thermal vibrations observed at room temperature [2.130]. Tips for Scanning Tunneling Microscope and Atomic Force Microscope (STM/AFM) with attached carbon nanotube made by Piezomax Technology Inc are on market with at a price $1000 for 4 tips [2.131].

2.6.6. Actuators

The direct conversion of electrical energy to mechanical energy through a material response is critically important for robotics, prosthetic devices, optical fibre switches, optical displays, and microscopic pumps. Ray Baughman from AlliedSignal, in the USA and teams of researchers from the USA, Australia, Italy, and Germany have shown that electromechanical actuators based on sheets of single-walled carbon nanotubes can generate higher stresses than natural muscle [2.132]. Like natural muscle, the nanotube sheet actuators are arrays of nanofibre actuators [2.133]. The nanotube sheets ("nanotube paper") composed of mats of nanotubes assembled as electrolyte-filled electrodes of supercapacitors will expand and contract in an electrochemical cell. The commercially obtained single-wall carbon nanotubes were purified in nitric acid. Cycles of washing and centrifugation were then carried out, followed by cross-flow filtration. The nanotube sheets were formed by vacuum filtration of a nanotube suspension on a poly (tetrafluorethylene) filter, and dried
nanotube sheets were peeled from the filter. These free-standing sheets (composed of highly entangled nanotube bundles) were used as they were obtained, without any effort to optimise the mechanical properties, surface area, or electrical conductivity, all of which are important for actuator applications. Demonstration of a carbon nanotube actuator was surprisingly simple to perform. An actuator consisting of cut strips of nanotube paper (3 mm by 20 mm and 25 to 50 μm thick) that were adhesively applied to opposite sides of a 10% larger piece of Scotch Double Stick Tape. An insulating plastic clamp at the upper end of the three-layer strip supported the device vertically in 1 M NaCl electrolyte and held two platinum foil electrical leads in contact with nanotube paper sheets (Figure 2.36). When a DC potential of a few volts was applied to these leads, a deflection of up to about a centimetre was observed for the cantilever tip, which reversed on reversing the potential. When a square wave potential was applied, oscillation was visually observed up to least 15 Hz as the actuator pushed the electrolyte back and forth. Similar operation was observed for a type of actuator made from nanotube paper that had been annealed at 1100 °C for 1 hour in flowing argon.

![Figure 2.36](image_url)

**Figure 2.36.** (a) Schematic of contralever-based actuator operated in aquatic NaCl, which consist of two strips of SWCNT (shaded) with an intermediate layer of double-sided Scotch tape (white), and (b) apparatus used for characterising actuator [2.132].

The apparatus used for characterising an actuator, consisting of strips of SWCNT symmetrically laminated (with an intermediate layer of double-sided Scotch tape) on opposite sides of a strip of PVC is shown in Fig. 2.36b. Differential changes
in the lengths of the nanotube strips bend the actuator causing a displacement of the mirror, which is measured by the optical sensor.

Low voltage operation of these actuators is major a advantage for medical applications. This actuator was demonstrated to operate in an environment electrochemically like blood and seawater. Using high-temperature electrolytes (molten or solid state) it may be possible to make nanotube actuators that function at high temperatures, which might be important for such applications such as airflow control in jet engines.

2.6.7. Nanotweezers

Nanotweezers developed by Lieber and Kim from Harvard University are electromechanical systems based on carbon nanotubes for manipulation of nanostructures [2.134, 2.135]. Electrically conducting and mechanically robust carbon nanotubes were attached to independent electrodes fabricated on pulled glass micropipettes (Fig. 2.37). Voltages applied to the electrodes closed and opened the free ends of the nanotubes. Removal of the applied voltage relaxes the tweezers but does not open them because of van der Waals interactions between the carbon nanotubes. Application of the appropriate bias voltage reopens the tweezers. The mechanical properties of nanotweezers were demonstrated by grabbing and manipulating submicron clusters and nanowires.

Figure 2.37. Nanotube nanotweezers: (a) SEM image of nanotweezers after mounting two MWCNT bundles on each electrode. Scale bar 2 \( \mu \text{m} \) [2.134]. (b) Sketch showing nanotweezers grabbing a nanoparticle and move it to a desired location [2.135].
The ability of the nanotweezers to grasp and physically extract a nanoscale component from a complex mixture and then make an electrical measurement across it could make them a valuable analytical tool for studying the electrical properties of nanoscale devices. Manipulation of biological structures on surfaces or even within cells is another possible application of nanotweezers.

### 2.6.8. Chemical sensors

The electrical properties of single-walled carbon nanotubes were shown to be extremely sensitive to the chemical environment. Alex Zettl and co-workers at University of California have shown that exposure to air or oxygen dramatically influences the nanotubes electrical resistance, as determined by transport measurement and scanning tunnelling spectroscopy [2.136]. These electronic parameters can be reversibly “tuned” by surprisingly small concentrations of adsorbed gases, and an apparent semiconducting nanotube can be converted into an apparent metal through such exposure. Hongjie Dai and colleagues at Stanford University found that exposure to NO₂ or NH₃ molecules increase or decrease dramatically electrical resistance of semiconducting single-wall carbon nanotubes [2.137]. This serves as the basis for nanotube molecular sensors. The nanotube sensor exhibits a faster response and a substantially higher sensitivity than that existing solid-state sensor at room temperature.

### References


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[2.131] Piezomax Technologies Inc web site: www.piezomax.com


Chapter 3

EXPERIMENTAL DETAILS

3.1. INTRODUCTION

The carbon nanofibres (CNF) have been produced by chemical vapour deposition using three different methods using three different apparatus. Thermal chemical vapour deposition (CVD) was used and plasma enhanced chemical vapour deposition (PECVD). PECVD of CNF was conducted in two different apparatus, one using radio frequency PECVD and the other a radio frequency assisted microwave PECVD system. Radio frequency electromagnetic spectrum lies between a few kHz to about 1 GHz, with wavelength from many kilometres to about 0.3 m, and microwave frequencies lie between 1 GHz to 300 GHz, with corresponding wavelengths from roughly 30 cm to 0.1 mm.

In the thermal CVD system, CNF were produced from the interaction of nickel powder with methane and methane/nitrogen mixtures at temperatures ranging from 350 to 750 °C over a period of one to three hours at pressures between $10^{-3}$ to 2 mbar. The thermal chemical vapour deposition system was custom made with a graphite strip heater and designed to operate at low pressures.

The radio frequency PECVD system used for carbon nanofibre growth was an industrial standard Plasma Technology DP800, widely used for thin film growth in the semiconductor industry. It was operated at a radio frequency of 13.56 MHz and 200W power with a 1000 mTorr process pressure. Methane gas was used for plasma glow discharge and nickel powder was used as a catalyst for CNF growth.

The radio frequency assisted microwave PECVD system was custom designed for reactive ion etching and PECVD. Carbon nanofibre and nanotube growth in radio frequency assisted microwave PECVD was performed with 100 W radio wave (13.56 MHz) power and microwave (2.45 GHz) power ranging from 250 to 850 W with methane gas as the carbon source and nickel powder as the catalyst.
The characterisations of the nanofibres were conducted using conventional scanning electron microscopy (SEM) on the Hitachi S 3200 N and the S 4000, and transmission electron microscopy (TEM) on the Philips CM 200, operating in high-resolution mode for bright field imaging equipped with a Gatan Imaging Filter GIF2000. Raman analysis was performed using a Renishaw RM 1000 Raman Microscope.

3.2. LOW PRESSURE THERMAL CHEMICAL VAPOUR DEPOSITION

The low pressure thermal chemical vapour deposition system used in this study is shown schematically in Figure 3.1. This system consisted of a heated graphite strip placed in the water-cooled vacuum chamber with a gas inlet. The system is pumped using a combination of a diffusion and rotary pump.

![Figure 3.1. Low pressure thermal CVD carbon nanofibre deposition system.](image)

As input gases we have used methane or methane nitrogen mixtures. The methane (CP-Grade, 99% purity), and nitrogen (99.99% purity) gases used in these
3. Experimental

Experiments were obtained from BOC Gases Ltd. The catalyst used for carbon nanofibre deposition was a nickel powder (99% purity) with particle diameter 4 to 7 μm, obtained from Goodfellow Cambridge Ltd. For support material graphite or silicon wafer plates (10×10×3 mm³) and commercial carbon fibres T650/35, with diameter of 7 μm were used and these were obtained from Goodfellow Cambridge Ltd.

Heating of the graphite strip is driven by a Graphite Strip RTA Power Unit and controlled by a Temperature Controller. The Graphite Strip Power Unit is a transformer providing a 10 V power-supply to the graphite strip which has water-cooled feedthroughs. The Temperature Control Unit is a RC K-type thermocouple connected to the temperature controller. The temperature controller is custom made and has the possibility of being at two levels, low and high (Figure 3.2). When connected to a mains supply, the system is at the LOW temperature level. When the Start button is pressed, the system switches to the HIGH temperature level for a period of "Time Delay" (from 1 s to 2500 s) that is set on the temperature controller. At the LOW level the graphite strip heater can operate in the temperature range from 250 °C to 850 °C. The temperature calibration line for different LOW level temperature adjustments on the temperature controller is shown in Figure 3.3. At the HIGH level, the graphite strip can be heated to 1020 °C.

Figure 3.2. Temperature controller diagram.
The Gas Control Unit controlled the inlet of gas or gases mixtures. It is possible to have mixtures of two desired gases and one gas inlet line. Nitrogen was used in a mixture with methane for carbon nanofibre and nanotube growth, and also for purging the chamber to atmospheric pressure. Gas cylinders were placed in the gas cabinet with a gas leak detector control-alarm system. Nitrogen cylinders were not placed in gas cabinets.

Approximately 50 mg of nickel powder catalyst was dispersed in a uniform thin layer on graphite, silicon or glass plate substrate, and placed on the top of graphite strip heater. Reactant gas (methane) or gases (methane and nitrogen mixtures) were introduced into the vacuum chamber prior to switching on the graphite strip heater. The graphite strip heater was switched on when the reactant gas or gases were flowing at a steady rate. The temperature in the vacuum chamber was maintained at a constant value between 350 °C and 750 °C. Temperature was maintained constant during the experiment. Reactor temperatures were accurate to ±1°C. The base pressure of the deposition chamber was $4 \times 10^{-6}$ mbar. The reactor pressure for carbon nanofibre growth was set between $10^{-3}$ mbar and 2 mbar. For pressures lower than $10^{-1}$ mbar, both rotary and diffusion pumps were used, and for higher pressures only mechanical rotary pumping was needed. Typically, experiments were run for 1 hour, but not shorter than 30min and not longer than 3 hours. Samples were allowed to cool-down in flowing reactant gas before nitrogen was introduced to

![Figure 3.3. Temperature calibration for LOW level adjustments.](image-url)
3. Experimental

bring the pressure up to that of air. The sample was cooled from its reaction
temperature to ambient in approximately ten minutes. Nanofibres were reproducibly
grown in the above conditions.

3.3. RADIO FREQUENCY PLASMA ENHANCED
CHEMICAL VAPOUR DEPOSITION

The radio frequency plasma enhanced chemical vapour deposition (r.f.
PECVD) system used for carbon nanofibre and nanotube growth was an industrially
standard Plasma Technology DP800 system, shown schematically in Figure 3.4. The
system is of the same type that is widely used for the growth of amorphous silicon and
diamond-like amorphous carbon films. This system consisted of two circular parallel
plate electrodes with diameters of 20 cm, and a distance between them of 2 cm. The
electrodes were placed in a vacuum chamber built on top of the console. The 13.56
MHz radio frequency (r.f.) power supply unit was incorporated in the control console,
together with the control unit for the capacitatively-matching r.f. tuning circuit. The
tuning circuit consisted of a pair of tunable capacitors that were operated by a step
motor. The capacitors were electrically connected in series between the r.f. power
supply and the upper electrode (driven electrode). The lower electrode was
electrically connected to the ground. A combination of diffusion and rotary pumping
was used for system pumping. The pumping port on the reaction chamber was located
underneath the lower electrode, as shown in Figure 3.4. Base pressure of up to \(10^{-5}\)
mbar could be achieved using this pumping system. Samples were placed on the
bottom, grounded electrode. Gases were supplied through 3 process gas lines, and
vented through separate line. Gases were selected by means of electrically controlled
valves, and their flow was set by the mass-flow controllers, and monitored by flow
meters. The gases were then mixed inside a manifold, and fed into the reaction
chamber through a small showerhead located at the center of the upper electrode. The
total gas pressure inside the reaction chamber was measured by a baratron while the
plasma was on, and the pressure was maintained by an automatically controlled
butterfly valve located between the gate valve and the reaction chamber. Steady gas
flow was introduced through the showerhead holes in the top powered electrode before striking the plasma. The plasma was ignited between electrodes.

The radio frequency PECVD system was operated at 200W forwarded power at 1000 mTorr process pressure. In all experiments the reflected power was below 10 W. A methane gas (BOC Gases Ltd., 99.999% purity) with flow rate of 30 sccm was used to strike the plasma. The plasma was stable, and its brightness was homogeneous through its volume, when viewed through the viewing window shown with dotted lines in Fig. 3.4. The top and bottom plasma sheaths were clearly visible. The dark space between the top plasma sheath and the upper electrode (r.f. driven) was between 0.5 and 1 cm, and the plasma sheath and the lower earthed electrode were only few millimetres apart. The differences in plasma sheath-electrode separation are result of the different d.c. self-bias which is much greater for driven (upper) electrode than for earthed (bottom) electrode. The catalyst used for carbon nanofibre deposition was nickel powder obtained from Goodfellow Cambridge Ltd (99% purity) with an average particle diameter from 4 to 7 μm. Approximately 50 mg of the nickel powder catalyst was dispersed as an uniform thin layer on the top of a graphite, silicon wafer, glass or plastic foil substrate. Experiments were performed at temperatures 30 °C, 100 °C and 250 °C, and were run for 15 and 30 min durations.

![Figure 3.4. Schematic diagram of radio-frequency plasma-enhanced chemical vapour deposition system used for carbon nanofibres synthesis.](image-url)
Carbon nanofibres were produced in all experiments using methane gas as carbon feedstock. Methane was used in some experiments in a mixture with hydrogen, with the methane flow rate kept constant at 30 sccm and the hydrogen flow rate maintained at 50 sccm. In this experiment, before introducing methane nickel powder was treated in hydrogen plasma for 20 min at r.f. power of 200W, temperature 250 °C, and a process pressure of 1000 mTorr.

3.4. RADIO FREQUENCY ASSISTED MICROWAVE PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

Carbon nanofibres growth in radio frequency supported microwave PECVD (Fig. 3.5) was performed with 100 W radio wave (frequency 13.56 MHz) power and microwave frequency of 2.45 GHz, with power ranging from 250 to 850 W. The microwave and radio frequency plasma input power was kept constant during a deposition. In order to achieve room temperature growth conditions the substrate was placed on a water-cooled sample holder and heated directly by plasma without any other heating source. As the final plasma coupling source to the substrates is the r.f. power supply, with the microwave plasma being a remote plasma, it is unlikely that substrate temperature increases above 50 °C during the experiment. The substrate holder temperature was measured using a RC K-type thermocouple and found to be approximately 24 °C, when an applied r.f. power was 200 W the substrate temperature rose to approximately 30 °C.

The radio frequency assisted microwave plasma enhanced chemical vapour deposition system was constructed by JLS working with designs supplied by Prof Silva. The stainless steel chamber is evacuated to a pressure of approximately 10^-7 mTorr (as measured by a Penning gauge) using rotary and turbo vacuum pumps. Gases are supplied through 4 process gas lines, each incorporating valves and mass flow controllers, and a vent gas line. Process pressures are measured with a baratron gauge. A magnetron generator fed by a 1200 W power supply produced the 2.46 GHz microwaves. The 13.56 MHz radio frequency radiations were produced by a 300 W r.f. power supply using the water-cooled substrate table as the powered electrode. The
microwave's generator grid electrode serves as the powered (r.f. driven) electrode for the purposes of using the chamber for generating plasma using the r.f power source. Both the microwave and radio frequency units are manually tuned, both supplies have their supplied and reflected power monitored, and the radio frequency self-bias produced at the substrate table is measured. Reflected power was kept below 5% of forwarded power during experiments. Self-bias voltage ($V_{sb}$) was approximately -260 V in all experiments.

**Figure 3.5.** Radio frequency assisted microwave PECVD used for carbon nanofibres growth.

Nickel powder (99% purity), with average particle diameter from 4 to 7 μm (Goodfellow Cambridge Ltd.), was used as a catalyst in the CNT and CNF growth process. As a carbon source gas a methane gas (99.999% purity, BOC Gases Ltd.) was used at a flow rate of 70 sccm. Approximately 50 mg of nickel powder catalyst was dispersed in an uniform thin layer on the top of a graphite or silicon plate substrate. Methane gas was introduced into the chamber prior to switching on the radio frequency and microwave power supplies. Experiments were run for 15 minutes at a process pressure of 12 mTorr.
3.5. PURIFICATION AND CARBON NANOROPES

After chemical vapour deposition the resulting material is a mixture of as-prepared nanofibres and remaining nickel powder particles. In order to remove the remaining nickel particles a nitric acid treatment was applied. As-prepared carbon nanofibres were treated in 35% nitric acid for periods ranging from 3 min to 2 hours. Acid treatment was stopped by dilution with distilled water. The resulting solution containing nickel salt and carbon nanofibres was filtered through filtration paper. After filtration, carbon deposits were washed from the filtration paper with methanol or iso-propanol (IPA). Alcohol from this suspension was left to evaporate overnight and carbon deposits containing nanoropes were collected from the dry sediment. Dry sediments and as-prepared samples were examined by SEM using a Hitachi S3200N and Hitachi S4000 microscope and by TEM using Philips CM 200.

3.6. CHARACTERISATION

Characterisation of carbon nanomaterials is of great importance in understanding formation and properties of these materials. Better understanding of formation and properties will lead to large-scale synthesis of these materials with further development of their applications. The main techniques used for carbon nanofibres characterisation were electron microscopy techniques using a scanning electron microscope (SEM) and a transmission electron microscope (TEM) together with electron energy loss spectroscopy (EELS) and Raman spectroscopy.

The characterisation of the nanofibres was performed using a conventional SEM Hitachi S-3200N, and Hitachi S-4000, and TEM Philips CM200 equipped GIF2001 for EELS analysis. Raman spectra were taken using Renishaw RM 1000 Raman Microscope.
3.6.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) provides images of surface morphology of conducting specimens. Images showing surface topography were formed using secondary electrons from the specimen that are ejected by the beam of electrons from filament. An insulating sample needs to be coated with a conducting material in order to avoid electron charging effects which reduce the quality of the image that can be obtained. In this study most of the carbon nanofibres and remaining nickel catalyst samples were not coated, but gold coating was used for these samples that were coated. When coated, secondary electrons for imaging are evolved from the gold coating. Most of the SEM images were taken using Hitachi S-3200N microscope at accelerating voltage of 15 kV. The Hitachi S-3200 is equipped with tungsten filament with an emission current ranging from $10^{-12}$ to $10^{-7}$ A, and has an accelerating voltage ranging from 0.3 kV to 30 kV. The secondary electron image resolution in the HIGH VACUUM mode is around 3.5 nm. Magnification ranging from 20x to 300,000x could be achieved in 63 steps. For this study, specimen surfaces were imaged using secondary electron operating mode. Field emission gun (FEG) Hitachi S4000 SEM was also used.

3.6.2. Energy Dispersive X-ray (EDX) Spectroscopy

Energy dispersive x-ray (EDX) spectroscopy is a standard procedure for identifying and quantifying the elemental composition of samples. Within an electron microscope, when the beam of electrons impact the sample, the electrons surrounding each nucleus of sample material is excited by the electron from the beam. X-rays are generated as a result of de-excitation. The energy range of the x-rays produced lies between zero and the energy of the incoming electron from the beam. The detected x-rays provide qualitative and quantitative elemental analysis including elements distribution within sample (x-ray imaging). However, the accuracy is only sufficient to yield rough elemental stoichiometries (10-20%) when compared to EELS.

The limitations of EDX are that information is gathered from a relatively small volume and that the composition could not be found directly as only elemental...
information can be directly acquired. Standard samples containing known compositions of a similar alloy can be analysed and compared to give a more accurate quantitative interpretation of the spectrum. Alternatively, the counts from each element detected can be related to the amount present by making several corrections, to account for differences in atomic number (Z), absorption (A) and fluorescence (F). These corrections are known as the ZAF corrections. Both methods are time consuming and not 100% accurate. Another problem is that the light elements like carbon, oxygen and nitrogen all have peaks very close to one another. At low concentrations it becomes very difficult to define the difference between these peaks as they overlap and shadow one another.

The Hitachi 3200N SEM and Philips CM200 TEM were both equipped with Oxford Instruments energy dispersive x-ray (EDX) detector, allowing elemental detection and mapping.

3.6.3. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) examines micro and nanostructures by passing electrons through the specimen. Electrons are usually liberated from hot tungsten, LaB₆ filament (2400-2500 °C) or a field emitter and accelerated by a high voltage (100 - 400 keV). The interaction of the elastically scattered electrons with the sample is responsible for the image formed, which appears as a shadow of the specimen on a phosphorescent screen. The virtual image of the electron source is focused in the specimen plane by the condenser lenses system of the microscope. Changes in the stabilised current passing through the condenser lenses system are used to vary the intensity of the electron beam in the specimen plane. In this way it is possible to alter the brightness of the subsequent image at the fluorescent screen of the microscope. Bright field TEM imaging gives visible evidence for the specimen microstructure and nanostructure. When used in the dark field diffraction mode, information about the crystallinity of the specimen can be acquired by TEM using selected area diffraction (SAD) technique.

In order to secure the passage of the electrons, the specimen must be very thin usually less then 100 nm for 100-200 keV accelerating voltage. Small powdered
nanomaterials can be directly analysed by deposition on a TEM grid with a carbon support film. A few drops of the suspension of these materials in various alcohols on TEM grid are usually used for TEM sample preparation.

Bright field images were taken from the TEM Philips CM 200 operating in high resolution (HR-TEM) mode. Philips CM 200 TEM had a LaB$_6$ filament and was operated at 200 kV high tension voltage. In addition to bright field imaging, selected area electron diffraction patterns were obtained in the dark field TEM operating mode. Energy dispersive x-ray (EDX) microanalysis was conducted using Oxford Instruments EDX detector. Philips CM 200 TEM was equipped with Gatan Image Filter GIF2001 used for electron energy-loss spectroscopy (EELS) and energy-filtered TEM (EFTEM) analysis. Suitable TEM specimens were prepared by ultrasonic dispersion of sections of the deposit in isopropanol (~2 cm$^3$) and two drops of the suspension deposited on a thin amorphous “holey” carbon film supported on a copper grid (Àger Scientific Ltd, 300 mesh) and allowed to dry.

In order to avoid the possibility that carbon nanotube contaminants on the TEM grids could be mistaken for sample material, TEM characterisation of unused “holey” carbon films on copper grids was carried out (see Appendix 1).

### 3.6.4. Electron Energy Loss Spectroscopy (EELS)

In electron energy loss spectroscopy (EELS) the energy distribution of monoenergetic electrons after inelastic collisions with specimen is analysed [3.1]. The beam of transmitted electrons is directed into a high-resolution electron spectrometer, which separates electrons according to their kinetic energy and produces an electron energy loss spectrum showing the scattered intensity as a function of the decrease in the kinetic energy of the fast electrons. EELS is frequently used in association with TEM or scanning transmission electron microscopy (STEM), and it is a valuable technique for light element analysis providing useful information on oxidation states and bonding. In TEM or STEM, the losses arise in the bulk sample, as the beam travels through the thin specimen to the EELS detector. The energy loss in the electron energy loss spectrum can be attributed to plasmon and phonon losses. Plasmons are collective excitations of the electron “gas” in the materials and, typically, several eV in magnitude. Phonon losses are much smaller, and the energy
loss associated with phonons is too small to be detected. Phonons are quantised sound waves within the solid (i.e. vibration of the whole arrays of atoms or oscillation of the valence-electron density).

In a typical loss spectrum, the first zero-loss peak represents electrons that are transmitted without suffering any measurable energy loss, including those that are scattered elastically in the forward direction, and those, which have excited phonon modes, for that the energy loss is less than the experimental energy resolution. Inelastic scattering from outer-shell electrons is visible as a peak in the 5-50 eV region of the spectrum. Inner-shell excitations take the form of edges rather than peaks because inner-shell intensity rises more rapidly and the falls more slowly with increasing energy loss. The sharp rise is attributed to the ionisation threshold, whose energy loss corresponds to binding energies of the relevant atomic shell. Binding energies of the inner-shell are dependent on the atomic number and therefore the ionisation edges in an energy-loss spectrum indicate which elements occur within the specimen. Quantitative elemental analysis is possible by measuring an area under the appropriate ionisation edge, making allowances for the background intensity. Both the valence-electron (low-loss) peaks and the ionisation edges show a fine structure, which reflects the crystallographic or energy-band structure of the specimen.

![Figure 3.6](image)

**Figure 3.6.** Low-loss and K-ionisation regions of the EELS spectra of diamond, graphite and amorphous carbon. The plasmon peaks occur at different energies (33 eV diamond, 27 eV in graphite, 25 eV in amorphous carbon) because of the different valence-electron densities. The k-edge threshold is shifted upward by about 5 eV in diamond owing to the formation of energy gap. The broad peaks shown by dashed line are caused by electrons, which undergo both inner-shell and plasmon scattering [3.1].
For graphite related carbon specimens, information can be obtained from two energy ranges (Fig. 3.6). Between approximately 280 and 300 eV, energy loss is associated with the excitation of an electron from the 1s carbon orbital to the Fermi level. The nature of the 1s core level spectra can enable estimates to be made of the relative amounts of sp² and sp³ bonding. In the region of 0-40 eV, energy loss is due to excitation of plasmons, arising from π electrons and π and σ states of carbon the K shell. Highly ordered graphite gives a broad peak in this region, centred on about 28 eV. A comparison between typical spectra of multi-walled and single-walled carbon nanotubes and amorphous carbon is shown in Figure 3.7 [3.2].

![Figure 3.7. EELS spectra of multi-walled carbon nanotube with 30 nm diameter (MSN - multi shell nanotube) compared to spectra of single-walled carbon nanotube with 1 nm diameter (SSN- single shell nanotube) and amorphous carbon [3.2].](image)

EELS analysis were performed on VG 501 STEM with a McMullan PEELS system at the University of Cambridge and on Philips CM200 TEM equipped with Gatan Imaging Filter (GIF) GIF2001 at the University of Surrey.

### 3.6.5. Raman spectroscopy

An Indian physicist C.V. Raman discovered the Raman effect in 1928 [3.3]. He discovered that when molecules are irradiated with monochromatic light, a portion of the light is scattered, where most of this scattered radiation (about 99%) has the
original frequency (Rayleigh scattering), but a small portion (<1%) is found at other frequencies. The difference in frequency between these new frequencies (called Raman lines or bands) and the original frequency is characteristic of the molecule irradiation and numerically identical to certain vibrational and rotational frequencies of that molecule.

In Rayleigh scattering, the oscillating electric and magnetic forces constituting the incident light induce a dipole moment in molecules. Molecules then radiate, in all directions, light of the same frequency (elastic scattering) as the incident or exciting radiation. Rayleigh scattering always accompanies Raman scattering.

In Raman scattering, some of the energy of the incident light may be used for molecule excitation to a higher vibrational or rotational energy level. In this case radiation emitted (scattered) by the molecule (called a Stokes line) will be of corresponding lower energy and frequency. Alternatively, since some of the molecules encountered by radiation will already be in higher vibrational or rotational energy states, the molecule may contribute this extra energy to the scattered photon, resulting in emitted radiation (called an anti-Stokes line). The radiated energy is then higher than that of the incident radiation by an amount corresponding to the vibrational or rotational transition energy of the molecule. In practice, the anti-Stokes lines are much weaker than the Stokes lines and are generally ignored in conventional Raman spectroscopy, since they carry the same information as the Stokes lines. Since Raman scattering involves a change in energy, the collision between the molecule and the incident photon is inelastic.

When an incident photon with an energy $h\nu_o$ interacts with a molecule in any of its stable states, the energy of the molecule $E_o$ is raised by the amount $h\nu_o$. In the resulting energy state $E_o+h\nu_o$ is not stable allowed energy of the molecule, and the molecule immediately returns to the lower energy state and the corresponding amount of energy is emitted (scattered). If $E_o+h\nu_o$ is an allowed energy level, the incident light is absorbed; any radiation that is subsequently remitted when the molecule returns to a lower energy state is called fluorescent radiation.

For a particular mode of vibration to appear in the Raman spectrum, i.e. to be Raman-active, the molecules polarisability must change during the course of this vibration. If a rotation were studied, it too would have to be accompanied by a change in polarisability in order to be Raman-active. However, rotational transitions are of
little analytical importance in Raman spectra. The polarisability of a molecule is the ability of the molecule to be polarised under the action of an electric field such as the alternating field of a light wave, and it can be defined in terms of the dipole moment \( D \) produced by the electric field \( E \)

\[
D = \alpha E,
\]

where \( \alpha \) is polarisability. The polarisability is a measure of the efficiency with which a varying electric field will induce a dipole moment in a molecule.

In measuring the Raman effect, visible light is used in most of the cases as the incident radiation. Under the influence of visible light, only electrons (not nuclei) oscillate, since nuclei cannot follow such rapid oscillation. Polarisability measures the displacement of electrons by the electric field, polarisability will change, slightly whenever the atomic distance changes. Polarisability can be expected to depend also on molecular rotation, since the ease of displacing electrons will depend on the orientation of the molecule in the field.

The Raman spectra of all forms of carbon show several common features in the 800 to 2000 \( \text{cm}^{-1} \) wave number region including the so-called G and D peaks or bands, which lie at about 1580 and about 1355 \( \text{cm}^{-1} \) [3.4]. The first order Raman spectrum of diamond consists of a single peak at 1332 \( \text{cm}^{-1} \). The spectrum of large single-crystal graphite also has a single high frequency peak, the G peak at about 1580 \( \text{cm}^{-1} \). In the Raman spectrum of small graphite crystallites (basal plane dimension < 20 nm) two further peaks are observed in addition to the G peak. These two peaks are the disorder D peak at about 1355 \( \text{cm}^{-1} \), and the D' peak at about 1620 \( \text{cm}^{-1} \). Changes in the Raman spectrum can be explained by reference to the phonon density of states and the D' peak being attributed to the maximum density of states [3.5].

The Raman spectra of carbon nanotubes grown by various methods were studied by Cheol Lee and co-workers from Kunsan National Institute, Chonbuk National University and Samsung Advanced Institute of Technology in Republic of Korea [3.6]. They used Renishaw micro-Raman 2000 system with an excitation wavelength of 632.8 nm of a He-Ne laser. In the spectra of SWCNT synthesised by arc discharge the G line at 1583 \( \text{cm}^{-1} \) is clearly shown in Fig. 3.8a. In addition to the G peak, the side peak at 1544 \( \text{cm}^{-1} \) indicated the existence of SWCNT with different diameters [3.7]. Prominent low energy peaks at 191 \( \text{cm}^{-1} \) and 216 \( \text{cm}^{-1} \) are the breathing modes of nanotubes vibrating along the radial direction [3.7]. The peak at
1724 cm\(^{-1}\) results from the second order Raman scattering of the breathing mode (190 cm\(^{-1}\)) and one of the G lines, and it is also ascribed to the SWCNT. The peak at 1303 cm\(^{-1}\) originates from either defective carbon or carbonaceous particles [3.8]. The peaks ranging from 400 cm\(^{-1}\) to 1000 cm\(^{-1}\) are usually observed in SWCNT and could be related to the finite length of the carbon nanotubes [3.9]. The Raman spectrum of MWCNT synthesised by arc discharge without metal particles is presented in Fig. 3.8b. The average diameter was about 100 nm. The clear G line at 1573 cm\(^{-1}\) with a small shoulder at 1620 cm\(^{-1}\) is assigned to MWCNT. No second order peak near 1720 cm\(^{-1}\) is indication of MWCNT. Breathing modes are significantly diminished in the case of MWCNT. The Raman spectrum of carbon nanotubes grown by thermal CVD on Co-coated Si substrates (Fig. 3.8c) clearly shows the G peak at 1587 cm\(^{-1}\) and no peak around 1730 cm\(^{-1}\). The broad D peak near 1337 cm\(^{-1}\) indicates the existence of defective graphitic layers.

![Raman spectra](https://example.com/figure3.8.png)

**Figure 3.8.** Raman spectra of carbon nanotubes synthesised with various methods: (a) catalytically synthesised SWCNT with Ni-Fe mixture at 360 Torr by arc discharge of a graphite rod, (b) MWCNT synthesised by arc discharge without transition metals at 500 Torr, (c) carbon nanotubes grown on Co-coated Si substrate by thermal CVD of acetylene at 850-900 °C. (after Cheol Lee et al, [3.6]).
Raman spectra in the study described in this thesis were taken under ambient conditions using Renishaw RM 1000 Raman Microscope, equipped with a charge coupled device (CCD) multi-channel detector, at the University of Sheffield. The excitation source used was a 514.5 nm Ar\(^ +\) laser with optical power at the source of 20 mW. The scattered light was collected in a backscattered configuration.

References

Chapter 4

RESULTS

4.1. INTRODUCTION

The carbon nanofibres (CNF) were synthesised by thermal chemical vapour deposition (CVD) and plasma enhanced chemical vapour deposition (PECVD) at room and low temperatures. Methane and acetylene gases were used as carbon sources in thermal CVD, and methane was used as the carbon source in PECVD. Nickel powder was used as a catalyst in both thermal and plasma enhanced CVD. Radio frequency power and radio frequency assisted microwave power was used to generate plasma in the two PECVD systems used for CNF growth. CNF produced by thermal and plasma enhanced CVD have shown “whisker-like” growth morphologies and bi-directional growth on the nickel catalyst. The diameters of CNF are in the range of 10 to 100 nm, and length range from 0.5 to 5 µm. CNF grown by CVD have catalyst particles at the tip that are enveloped by a thin layer of carbon. After purification treatment by nitric acid the remaining nickel powder was removed and CNF were found in the form of the macroscopic ropes.

Thermal CVD has been used at low pressures from $10^{-3}$ mbar to 2 mbar, and CNF growth was obtained at relatively low temperatures from 350 °C upwards. Optimum growth conditions with best yield and minimum disorder in the graphitic structure were found to be in the temperature range from 450 to 550 °C. When acetylene was used as the carbon containing gas instead of methane temperature ranged from 500 °C to 800 °C and process pressure was $10^{-2}$ mbar. Typically, experiments were run for 30 min.

A novel method for the synthesis of carbon nanofibres using radio-frequency plasma enhanced chemical vapour deposition (r.f.-PECVD) at room temperature and temperatures below 250 °C has been developed and described in this thesis. Previously, the lowest reported temperature for growth of carbon nanofibres by catalytic
decomposition of hydrocarbons or carbon monoxide has been above 450 °C. This is the first evidence of growth of carbon nanofibres at room temperatures by any method. These low temperature growth conditions will allow the growth of carbon nanofibres on temperature sensitive substrates, such as plastics and glass over large areas, and this would be useful in many applications such as flat panel displays. It will also open the possibility of using organic materials for electronic applications.

Growth of CNF was obtained at room temperature using radio frequency PECVD and radio frequency assisted microwave PECVD. Carbon nanofibres were synthesised using an industry standard parallel plate radio frequency PECVD system, where samples were placed on the bottom electrode where substrate temperature could be controlled in the range from around 30 °C to 250 °C. We have achieved the room temperature (around 24 °C) synthesis of CNF in a radio frequency assisted microwave PECVD system using nickel powder as a catalyst, at 100 W radio frequency power and microwave power ranging from 250 to 850 W. Room temperature CNF growth conditions were obtained by placing the nickel powder catalyst on a water-cooled sample holder. It was demonstrated that this new technique offers the possibility of forming “Y”-shaped CNF junctions. This might well open up the possibility of creating interconnections for electronic devices on a nanometer scale and assembling new classes of materials from carbon nanofibres.

Ropes of roughly-aligned carbon nanotubes (CNT) have been synthesised using nickel catalysed thermal and plasma-enhanced chemical vapor decomposition (CVD). Mixtures of remaining nickel powder and synthesised CNT and CNF have been treated in 35% nitric acid from 3 minutes to 2 hours and CNT ropes have been observed in dried sediment. Rope diameters obtained are from 20 μm up to 80 μm, and lengths up to few millimeters were observed. The size of these ropes can offer easy manipulation with special opportunities for their characterization and applications.

The characterisation and structural analysis of the nanofibres was conducted using conventional scanning electron microscopy (SEM) and transmission electron microscopy (TEM) described in details in Chapter 3.
4. Results

4.2. THERMAL CHEMICAL VAPOUR DEPOSITION OF CARBON NANOFIBRES AT LOW PRESSURE

4.2.1. Growth characteristics

Carbon nanofibres (CNF) have been grown by thermal chemical vapour deposition (CVD) of methane and acetylene at low pressures ranging from \(10^{-3}\) mbar to 2 mbar allowing relatively low growth temperatures ranging from 350 °C to 800 °C. It was found that the optimum temperature is around 550 °C, and it was found that pressure plays a secondary role when compared to temperature. Carbon nanofibres were grown on a Ni catalyst supported on graphite and silicon wafer plates, and no difference between carbon nanofibres grown on either support substrates was observed.

Nickel powder particles of diameter 4-7 μm were used in all experiments. Experiments with nickel powder particles of 2 μm diameter were not successful, and no evidence for carbon nanofibre growth was observed in TEM studies. Using SEM it was found that the 2 μm diameter nickel powder catalyst particles have relatively smooth surface when compared to 4-7 μm nickel powder particles obtained from same supplier (Goodfellow Cambridge Ltd.). Surface roughness observed more frequently on particles in the range 4-7 μm could be a major factor that determines formation of carbon nanofibres nucleation sites. It is not possible to give a definitive opinion at this stage as to whether better CNF growth will result from use of smaller or larger Ni particles. We were not able to commercially obtain nickel powder with particle size smaller than 2 μm during this study. SEM micrographs in Fig. 4.1 have shown carbon nanofibres obtained in experiments with methane/nitrogen (1:2) mixtures and pure methane for three different pressures from \(2\times10^{-3}\) mbar, \(10^{-2}\) mbar and 1 Torr. From these micrographs it can be seen that carbon nanofibre lengths vary from half micron to few microns and that diameters are 1/10 of micron or less. The majority of the carbon nanofibres have particles on their tip, seen as a white spots. The nanofibres grow in random paths forming loops, spirals and interconnected networks.
Figure 4.1. SEM micrographs of carbon nanofibres produced for one hour with Ni catalyst: (a) CH₄, T=650 °C, p=1 Torr, (b) CH₄/N₂ (1:2) mixture, T=700 °C, p=2x10⁻³ mbar (c) CH₄/N₂ (1:2) mixture, T=650 °C, p=10⁻² mbar.
Carbon nanofibres have been produced by thermal CVD using acetylene and Ni powder at temperature of 600 °C and at pressures of the order $10^2$ mbar are show in Fig. 4.2. SEM and TEM examination have shown that the diameter of the carbon nanofibres is distributed in the range of 20 to 100 nm with lengths from 1 to 5 μm, with no major difference compared to the distribution when methane was used as the carbon source. Nickel catalyst particles have been observed at the end as well as in the middle of the carbon nanofibres (Fig. 4.2). Bi-directional growth from a diamond shaped particle in the middle of the carbon nanofibre has been observed more frequently when acetylene was used, compared to the carbon nanofibres grown under similar conditions using methane as a carbon source gas. Gas impurities in very small concentrations could play a major role in bi-directional carbon nanofibre growth (Prof. Motojima, personal communication). Both methane and acetylene gas are same purity (99%) and obtained from the same supplier (BOC Special Gases), however simple fact that very small concentration of impurity present in acetylene gas and not present in methane gas could be explanation for more frequently observed bi-directional growth conformation when acetylene was used.

Figure 4.2. SEM micrograph of carbon nanofibres grown by thermal CVD process using acetylene. Large bi-directional carbon nanofibre with a diamond shaped catalyst particle can be seen in the center.
In Fig. 4.3 an area where CNF growth has occurred is shown, and this area is surrounded by other Ni powder particles that have not catalysed the growth of CNFs. This type of growth was observed in experiments at all temperatures and all pressures.

**Figure 4.3** SEM micrographs showing area covered by carbon nanofibre deposits and surrounding Ni particles.

Carbon nanofibres have been grown on commercial carbon fibres used as a substrate. Downs and Baker [4.1, 4.2] proposed that the presence of carbon nanofibres on the carbon fibre surface will enhance the surface area and consequently increase the interfacial bonding between the fibre in the matrix of carbon-fibre reinforced composites (CFRC). The diameter of T650/35 carbon fibres obtained from Goodfellow was 7 µm. Commercial carbon fibres before deposition are shown in Figure 4.4a, and after deposition in Figure 4.4b. The surface of the fibre after deposition is covered with tiny carbon nanofibres compared to the smooth surface prior to CNF growth. In order to obtain a uniform growth of carbon nanofibres on carbon fibres a surface pre-treatment of the catalytic species could be a key step in the process to increase attraction of catalyst powder on the carbon fibre surface. At the same time it is important to maintain the structural integrity of the carbon-fibre.
4. Results

Figure 4.4. SEM micrographs of (a) commercial carbon fibre, diameter 7 μm; (b) carbon nanofibres grown on carbon fibre surface, CH₄, T=650 °C, p=1 Torr.

4.2.2. Morphology characteristics

The identity and structural features of individual carbon nanofibres were established from TEM examination. The TEM studies have shown that the average length of the carbon nanofibres lie between 0.5 and 5 μm with a thickness from 30 to 100 nm. Nickel catalyst particles have been observed at the end of the carbon nanofibres, as shown in Fig. 4.5. TEM studies have shown that the carbon nanofibres consist of a mixture of configurations. In general, the carbon nanofibres produced tend to adopt a "whisker-like" form where the catalyst particle is carried away from the support during the growth process and remains at the tip of the nanofibre. Bi-directional growth where the diamond shaped catalyst particle is located within the structure was observed in typical samples. Coiled carbon nanofibres were observed very rarely. It is significant that in all the structures found, the active catalyst particles were considerably smaller than those of the original metal powders (estimated to be 4 to 7 μm in diameter) indicating that fragmentation of the starting catalyst and formation of nanodomains on the surface occurs prior to carbon nanofibre growth.
4. Results

Figure 4.5. Carbon nanofibres grown by CVD of methane at T=500 °C, showing Ni catalyst particle at tips.

TEM studies have shown that a majority of carbon nanofibre produced have conventional single-whisker structure with the catalytic particle at the tip of the nanofibre (Fig. 4.6a and 4.7a). Some of nanofibres had bi-directional growth from diamond shaped catalyst particles in the middle of the filament (Fig. 4.6b and 4.7b).

Regardless of the type of hydrocarbon gas used both unidirectional and bi-directional growth morphologies were observed. In Fig. 4.6, carbon nanofibres produced using methane as the carbon source are shown. In Fig. 4.7 unidirectional and bi-directional growth morphologies obtained when acetylene was used as the carbon source are presented.
The typical lengths of carbon nanofibre produced vary from 0.5 to 5 μm and diameters range from 40 to 100 nm. Spaghetti-like bi-directional carbon nanofibres with diamond shaped catalyst particle in the middle, and length of few microns are shown in Fig. 4.8.
Bi-directional growth presented in Figs 4.6-4.8 have not led to formation of coiled carbon nanofibre morphology characteristic of carbon microsprings grown by Motojima [4.3]. Coiled carbon nanofibres could be grown when carbon diffusion through metal catalyst particle have non-uniform character. That could lead to the conclusion of uniform character of carbon diffusion through the nickel catalyst particle which could be result of nickel carbide formation.

Helical or coiled structures have not been observed often in SEM and TEM examination of the deposits. A TEM image of the coiled CNF is presented in Fig. 4.9. They have properties of a spring (i.e. extension and compression without fracture or fatigue of the material) [4.3]. From the enlarged images shown in Fig. 4.9b, it can be concluded that coiled carbon nanofibre appear to have a hollow central core.
4. Results

Filled carbon nanotubes or nanofibres were not observed in carbon deposits following the chemical vapour deposition process used in this study. Instead of filled carbon nanotubes and nanofibres, deposits containing a significant number of filled nanoparticles, shown in Fig. 4.10 are seen. A TEM micrograph of nickel catalyst particle embedded in a graphite deposit and with a carbon nanofibre growing out of the structure is shown in Figure 4.10b. Encapsulated nickel nanocrystals found in carbon nanofibre deposits are shown in Fig 4.11. Catalyst particle embedded or at the tip of the nanofibres are always enveloped by graphene layers (Fig. 4.12).
4. Results

Figure 4.10. A SEM image of (a) nickel particle embedded in carbon deposits, CVD of methane at T=500 °C (b) nickel particle embedded in carbon deposits with a carbon nanofibre growing out of the structure, CVD methane at T=500 °C.

Figure 4.11. Encapsulated nickel nanocrystals found in soot following chemical vapour decomposition of methane at T= 500 °C.
Figure 4.12. Encapsulated nickel particle with surrounded carbon. Graphene layers could be seen on the surface of the nickel particle. CVD of methane at $T=500$ °C.

The deposited carbon nanofibres appear to have a amorphous or hollow core and well-crystallised graphite layers usually covered with amorphous carbon on their outer most layers. Detailed TEM analysis shows that the nickel catalyst particle at the tip of the nanofibre is completely enveloped by a layer of carbon (Fig. 4.12). A layer of carbon always envelops catalyst particle at the tip of the nanofibre after their growth has ended. The lattice fringes of the deposit were oriented in a direction parallel to the face of the catalyst particle associated with these platelet structures and had a spacing of 0.34 nm, indicative of a highly ordered graphitic material. As a result of the TEM analysis it was concluded that the relative amount of well-graphitised nanofibre was highest in the temperature range from 450 to 550 °C. The inner diameter of poorly-graphitised nanofibres was not constant along the longitudinal axis. However, long-range lattice symmetry may not form due to relatively low growth temperatures.
4. Results

4.2.3. Structural characteristics

4.2.3.1. Electron microscopy

TEM studies have shown that nanofibres have a duplex structure, an outer graphitic sheet surrounding an amorphous core, as was proposed for the first time by Baker and co-workers [4.4]. From TEM micrographs in Figure 4.13, it can be seen that both "whisker like" and bi-directional carbon nanofibres have hollow or less dense core surrounded by a graphitic skin.

![TEM micrographs of carbon nanofibres grown by CVD of methane, graphitic skin and hollow or amorphous core can be seen: (a) "whisker-like" with pear shaped catalyst particle, at the growing end of the nanofibre, T=650 °C, and (b) bi-directional with diamond shaped catalyst particle in the middle of the fibre, T=450 °C.](image)

The diameter of the filament was always the same as that of the nickel particle at their head. Moreover, each active nickel particle was responsible for the growth of only a single nanofibre either unidirectional or bi-directional. Almost all nanofibres have a "heart-shaped" particle at their growing end. Nanofibres, which had ceased to grow,
showed that the catalyst particle at the growing end was completely enveloped by a layer of deposit.

Depending on the conditions of the reaction, various morphologies and different degrees of crystallinity of carbon nanofibres were produced. The highest degree of crystallinity of the graphitic skin in the temperatures range studied was observed with reactions at temperatures of around 450-550 °C. For lower growth temperatures nanofibres have a more amorphous structure.

In Figure 4.13a a Ni crystal particle surrounded by a "heart-shaped" shell which could be attributed to nickel carbide. The role of carbides was first reported by Lobo and Trimm [4.5]. Renshaw and co-workers [4.6] concluded that Ni$_3$C or another nickel carbide in an intermediate product formed on the nickel surfaces.

From TEM and SEM micrograph analysis it can be concluded that some of the carbon nanofibres have hollow cores. In Figure 4.14, a SEM micrograph of a surface covered in carbon nanofibre deposit is shown. It can be seen that some of the nanofibres are hollow, where arrow identifies hollow nanofibres. TEM micrograph of carbon nanofibre with a missing catalyst particle is shown at Figure 4.15. The catalyst particle was probably lost during sample preparation in the ultrasonic bath.

**Figure 4.14.** SEM micrograph of the surface of carbon nanofibre growth area taken using a HITACHI S-4000 SEM. Hollow nanofibres are identified by an arrow. CVD of methane at T=550 °C.
4. Results

Figure 4.15. TEM micrograph of carbon nanofibre with missing catalyst particle at the tip of the fibre, CVD of methane at T=650 °C.

A Ni catalyst particle completely enveloped by a layer of carbon deposit is shown in the TEM micrograph in Figure 4.16a. This is a result of poisoning effects, which cease the growth of the catalytic carbon nanofibre. An enlarged interface between the Ni particle surface and carbon nanofibre from the same micrograph is shown in Figure 4.16b. Detailed investigation of carbon nanofibre structure by high-resolution electron microscopy (HRTEM) has revealed interlayer spacing of graphite of a 0.34 nm. It can be seen that graphite platelets are parallel with the Ni catalyst particle surface. Baird, Fryer and Grant [4.7] reported graphite layer planes that were parallel with the surface of the metal particle for the first time in 1971.
Layer of carbon deposit

Ni

Carbon nanofibre

20 nm

Ni

5 nm

(a) (b)

Figure 4.16. TEM micrographs of (a) Ni particle completely enveloped by a layer of carbon deposit, (b) enlarged interface between Ni particle surface and carbon nanofibre, shows graphite layer planes with 0.34 nm distance.

TEM studies have shown that nanofibres grown by CVD have a duplex structure with an outer graphitic sheet surrounding an amorphous core (Fig. 4.17). Graphitic sheets of the carbon nanofibre form a “herring-bone” or “cap-stacked” type of structure, with an interlayer spacing of 0.34 nm. Angles of graphene sheets with respect to the nanofibre axes could be so small that these layers could be almost parallel to the axes (Fig. 4.18).
Figure 4.17. Carbon nanofibre, grown by thermal CVD of acetylene, showing duplex structure with an outer graphitic sheet with a "herring-bone" type of structure, surrounding an amorphous core. (b), (c), (d) enlarged parts of the image. Distance between graphene layers (black fringes) is 0.34 nm.
Figure 4.18. Enlarged part of the carbon nanofibre, grown by thermal CVD of acetylene, showing carbon lattice fringe images with 0.34 nm distance, almost parallel to the surface of the nanofibre.

4.2.3.2. Raman spectroscopy

Raman spectroscopy analysis of carbon nanofibres synthesised using methane and acetylene as the carbon source was conducted in order to obtain additional information on nanofibre structure. A Lorentzian fitting routine was used to determine the peaks and the main frequencies in the spectra (see Appendix 2).

Figure 4.19. An optical micrograph showing areas with carbon nanofibres (black areas) and remaining nickel powder (yellow areas). A Raman spectrum was taken from the biggest black area in the center.
A Raman spectra for two different areas of carbon nanofibres grown using methane CVD synthesis at a pressure of $10^{-2}$ mbar and temperature of 550 °C is shown in Fig. 4.20. An optical micrograph of the one of the areas where Raman spectra was taken is shown in Fig. 4.19 (central black area). Optical microscope investigation has shown that carbon nanofibres containing areas (black areas in the Fig. 4.19) can be easily distinguished in comparison to remaining nickel catalyst (yellow areas in the Fig. 4.19). This could be useful technique for rough determination of the relative yield by using ratio between carbon area and area covered by remaining nickel powder.

**Figure 4.20.** Raman spectrum of carbon nanofibres grown using CVD of CH$_4$ at 550 °C at two different areas: (a) $I_G/I_D = 1.44$ ($I_D/I_G = 0.694$), and (b) $I_G/I_D = 1.097$ ($I_D/I_G = 0.912$).
4. Results

The spectrum shown in Fig. 4.20a has a high frequency G-peak at about 1564 cm\(^{-1}\) and additional disorder D-peak at about 1343 cm\(^{-1}\), with ratio of intensities of these two peaks of \(I_G/I_D = 1.44\). A sharp G peak is an indicator of a higher degree of crystalline perfection of the carbon nanofibres in this area of the sample. The position of the G-peak and the D-peak for spectrum shown in Fig. 4.20b is 1347 cm\(^{-1}\) and 1585 cm\(^{-1}\), respectively, with their intensities ratio of \(I_G/I_D = 1.097\). Position of G peak is shifted to higher wave numbers in Raman spectra presented in Fig. 4.20a compared to spectra in Fig. 4.20b; this is a reflection of the higher activation energy of vibration mode. The ratio of intensities of the G and D bands are a measure of the degree of order of graphite clusters, \(I_G/I_D\) increases with a higher degree of graphitisation. The significant difference between \(I_G/I_D\) ratios for these two areas confirms the TEM observation that carbon nanofibres with various degree of structural perfection were produced in the same experimental conditions.

Structural analysis using Raman spectroscopy of carbon nanofibres synthesised using acetylene as the carbon source conducted for three different temperatures (500, 600 and 700 °C) is shown in Figures 4.21. The G-peak and the D-peak for all three spectra is almost at the same position around. The positions of the G peak are around 1594 cm\(^{-1}\) for 500 °C, around 1592 cm\(^{-1}\) for 600 °C and around 1599 cm\(^{-1}\) for 700 °C. The D-peak characteristic of small graphite crystallite is around 1354 cm\(^{-1}\) for 500 °C, around 1357 cm\(^{-1}\) for 600 °C and around 1360 cm\(^{-1}\) for 700 °C. All three curves have very broad overlapping peaks indicating more amorphous-like structure with very similar \(I_G/I_D\) ratios (1.13 for 500 °C, 1.11 for 600 °C, and 1.17 for 700 °C). For discussion of growth temperature influence on carbon nanofibre structure based on these results please see Chapter 5, where these three curves are presented on the same diagram (Figure 5.8).
4. Results

Figure 4.21. Raman spectrum of carbon nanofibres grown using CVD of $\text{C}_2\text{H}_2$ at (a) $T=700$ °C, $I_D/I_G=1.13$ ($I_D/I_G = 0.88$), (b) $T=600$ °C $I_D/I_G=1.11$ ($I_D/I_G = 0.90$), and (c) $T=500$ °C, $I_D/I_G=1.17$ ($I_D/I_G = 0.85$).
4.3. SYNTHESIS OF CARBON NANOTUBES AND NANOFIBRES BY RADIO FREQUENCY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

4.3.1. Growth Characteristics

SEM and TEM micrographs showing CNF obtained at room temperature using r.f. PECVD are shown in Figs. 4.22-4.25. From SEM and TEM studies it can be concluded that the majority of the CNT and CNF have catalyst particles at their tips. This suggests the "tip" growth model in which the catalyst particle was located at the tip of the structure and during growth was transported away from the initial powder surface. The typical lengths of nanofibres and nanotubes vary from 0.5 to 5 \( \mu \text{m} \) and diameters from 20 to 100 nm. The observed CNF have a number of configurations resulting in the formation of loops and interconnected networks.

Figure 4.22. A scanning electron micrograph of carbon nanofibres produced at room temperature in a r.f. PECVD of methane on Ni catalyst.
Deposited carbon nanofibres found in certain areas are entangled together and are surrounded by nickel powder particles. In Fig. 4.23 one area of carbon nanofibre growth between nickel powder particles is shown. Another carbon nanofibre growth area is shown in Fig. 4.24 and Fig. 4.25. In Fig. 4.24, a closer image of the area helps distinguish the difference between nickel powder particles and carbon nanofibre material. This difference can be seen in Fig. 4.25 where lower resolution images have shown that carbon nanofibres appear much darker in comparison to surrounding nickel powder. This could be explained with larger secondary electron emission from metal particles in comparison to carbon nanofibres, which should possess higher resistivity.

Figure 4.23. A scanning electron micrograph of carbon nanofibre growth area at room temperature in a r.f. methane plasma on Ni catalyst, 1 Torr.
Figure 4.24. A scanning electron micrograph of carbon nanofibre growth area and nickel powder surface at room temperature in a r.f. methane plasma on Ni catalyst.

Figure 4.25. A SEM micrograph showing area of carbon nanofibre growth between nickel powder particles.
4.3.2. Morphological characteristics

TEM studies on the majority of nanofibres have shown existence of a duplex structure, with a graphitic sheet surrounding an amorphous or hollow core, as observed for the first time by Baker and co-workers [4.8]. TEM micrographs of grown carbon nanofibres grown at room temperature from the surface of nickel powder particle are shown in Fig. 4.26. Nickel catalyst particles at the tip of the nanofibres could be seen. CNF diameter distribution analysis has shown that average diameter is about 50 nm (see Discussion section, Fig. 5.1).

Figure 4.26. Transmission electron micrograph of carbon nanofibres grown from nickel powder particle surface at room temperature in a r.f. methane plasma on Ni catalyst.
TEM micrographs of carbon nanotubes grown at room temperature from nickel powder catalyst particles are shown in Fig. 4.27a. The catalyst particle at the growing end of the nanotube is usually “ice-cream” cone or hearth or diamond shaped, and completely enveloped by a layer of carbon. Bi-directional growth with diamond shaped catalyst particles in the middle of CNF was also observed (Fig. 4.27b).

![TEM micrographs of carbon nanotubes](image)

**Figure 4.27.** Transmission electron micrographs showing carbon nanofibres grown at room temperature using r.f.-PECVD: (a) nickel catalyst particle at the end of the carbon nanofibre, (b) bi-directional carbon nanofibre with catalyst particle in the middle.

### 4.3.3. Structural characteristics

#### 4.3.3.1. Electron microscopy

The TEM micrographs of carbon a nanofibre grown at room temperature are shown in Fig. 4.28. The central part of the carbon nanofibre is hollow or less dense (more electron-transparent) than the outer region, which contains extremely ordered regions of individual graphite platelets usually aligned parallel (Fig. 4.28a) or at some angle to carbon nanofibre longitudinal axis. Studies of individual nanofibres have also shown the
existence of a "herringbone" stacking or "cup-stacked" arrangement, whose characteristics are normally associated with a well-ordered crystalline structure (Fig. 4.28b). At the end of nanotube not containing a catalyst particle characteristic spherically curved graphene layers were observed (Fig. 4.28c, and Fig. 4.30). More detailed analysis of carbon nanofibre structure along a cross section is shown in Fig. 4.29 and this reveals, a "herringbone" stacking arrangement, with two different angles with respect to the fibre axes. Distance between graphene layers is 0.34 nm.

![Figure 4.28. TEM micrographs showing graphene layers with distance of 0.34 nm: (a) parallel to the nanofibre axes, (b) in "herringbone" stacking, and (c) end of the nanofibre with spherically curved graphene layers.](image-url)
Figure 4.29. A TEM carbon nanofibre cross-section structural analysis.
Figure 4.30. End of the nanofibre with spherically curved graphene layers.
A carbon nanofibre with a nickel catalyst particle at the tip of the structure is shown in Fig. 4.31, where compositional maps have been produced using electron energy loss spectroscopy. A bright field TEM image is shown in Fig. 4.31a; a carbon map showing carbon in white is shown in Fig. 4.31b; and the corresponding nickel map is shown in Fig. 4.31c showing nickel as white contrast in shape of the catalyst particle at the tip. Figures 4.31b and 4.31c are energy-filtered TEM (EFTEM) images formed with electrons that have passed through the sample and have lost energy characteristic for the carbon K-edge (1s-2p transition, 285 eV) and Ni L-edge (2p-3d transitions, 855 eV). EFTEM reveals that the surface layer of the Ni particle is carbon-rich, indicating that the carbon atoms have acquired the thermal energy needed to form the nanofibre by flowing within the r.f- superheated surface similar to a supersaturated fluid drop.

**Figure 4.31.** Carbon nanofibre synthesised by r.f. - PECVD at room temperature with nickel catalyst particle at the tip: (a) bright field TEM image, (b) Carbon map, (c) Nickel map.
4. Results

4.3.3.2. Raman spectroscopy

Structural analysis of carbon nanofibres synthesised using radio frequency PECVD was conducted using Raman spectroscopy analysis. Peaks in the spectra were determined using fitting with three or four Lorentzian curves (see Appendix 2). Optical micrographs with carbon nanofibres containing areas where Raman spectra was taken are shown in Fig. 4.32 (central black areas) for two substrate temperatures room temperature (30 °C) and 250 °C.

Raman spectrum of carbon nanofibres synthesised on nickel powder catalyst using methane as the carbon source at 250 °C substrate temperature is shown in Figure 4.33a. The position of the G peak is around 1590 cm\(^{-1}\) and the disorder induced D peak is around 1358 cm\(^{-1}\) with the ratio of intensities of \(I_G/I_D = 1.154\). Raman spectrum of carbon nanofibres synthesised at room temperature (30 °C) is shown in Figure 4.33b. G peak is slightly shifted down up to to around 1584 cm\(^{-1}\), and the D peak is also shifted down towards lower wave numbers at around 1350 cm\(^{-1}\). The ratio of intensities of the G and D peak (\(I_G/I_D = 1.041\)) is slightly lower than for 250 °C indicating the expected influence of the growth temperature on the structural perfection of graphene layers.

![Image](image1.png)

**Figure 4.32.** Optical micrographs showing areas with r.f. grown carbon nanofibres (black areas) where Raman spectrum was taken and remaining nickel powder (yellow areas); substrate temperatures: (a) 30 °C, (b) 250 °C.
A shift to higher wave numbers is reflection of higher activation energy of the vibrational mode and could be caused by internal stress in the material, and indicates the very complex influence of the plasma growth process on carbon nanofibre structure. Broad overlapping peaks are characteristic of both spectra indicating imperfectly crystalline graphene layers are characteristic for CVD grown carbon nanofibres. For further discussion of carbon nanofibre structure and the influence of substrate temperature in this structure, please see Chapter 5.
4.4. CARBON NANOFIBRES SYNTHESIS BY RADIO FREQUENCY SUPPORTED MICROWAVE PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

4.4.1. Growth characteristics

Carbon nanofibres were synthesised at room temperature in a radio frequency assisted microwave PECVD system using nickel powder as a catalyst, at 100 W radio frequency power and microwave power ranging from 250 to 850 W. Radio frequency power was kept constant at 100 W radio frequency power and process pressure, flow rate, growth time and other parameters were constant. Three experiments were performed with nickel powder as a catalyst and methane as carbon source at microwave power of 250 W, 500 W and 850 W. No difference in CNF produced at these three microwave powers was observed after electron microscopy investigation.

![SEM micrograph of CNF grown by radio frequency assisted microwave PECVD at P=240 W and SEM micrograph showing Ni particles on the top end of CNF.](image)

**Figure 4.34.** (a) SEM micrograph of CNF grown by radio frequency assisted microwave PECVD at P=240 W and (b) SEM micrograph showing Ni particles on the top end of CNF.

SEM analysis has shown that the average length of the CNF is between 0.5 and 5 μm with a thickness from 30 to 80 nm for CNF (Fig. 4.34). From SEM it can be
concluded that the majority of the CNF have catalyst particles at their tips. Nickel catalyst particles that appear as white spots have been observed at the end of the CNF, as shown in Fig 4.4.1b. The diameters of the CNF are the same as that of the nickel particles at their tips. SEM micrographs showing CNF obtained at room temperature using a microwave power of 500 W, are shown at Fig. 4.35-4.37.

Deposited carbon nanofibres were found in certain areas entangled together and surrounded by remaining nickel powder particles (4-7 μm in diameter). In Fig. 4.35 one area of carbon nanofibre growth between nickel powder particles is shown. The difference between nickel powder particle and carbon nanofibre growth areas can be seen in Fig. 4.36, where a lower resolution image shows the carbon nanofibres to appear much darker than surrounding nickel powder particles space.

**Figure 4.35.** Scanning electron micrograph of carbon nanofibres growth area at room temperature in a radio frequency assisted microwave methane plasma on Ni powder (4-7 μm in diameter) catalyst at P=500W.

CNF grown by the radio frequency supported microwave PECVD method have shown the remarkable characteristic of branching during the growth and “Y”-shaped junctions have been formed (Fig. 4.37). The synthesis of connections between two or
more CNF is an important step in the development of carbon nanofibres network by creating interconnections for nanometer scale.

![SEM micrograph showing area of carbon nanofibre growth between nickel powder particles at room temperature in a radio frequency assisted microwave methane plasma on Ni powder (4-7 μm in diameter) catalyst at P=500W.](image)

**Figure 4.36.** SEM micrograph showing area of carbon nanofibre growth between nickel powder particles at room temperature in a radio frequency assisted microwave methane plasma on Ni powder (4-7 μm in diameter) catalyst at P=500W.

Variations in carbon nanofibres produced by radio frequency supported microwave PECVD (Fig. 4.38) are much greater compared to carbon nanofibres grown by radio frequency PECVD in terms of diameter and shape. A histogram showing diameter distribution of carbon nanofibres grown using r.f. PECVD is presented in Discussion section (Fig. 5.1).

The formation of small domains that act as nucleation seeds for CNF growth is captured in Fig. 4.39. In Fig. 4.39a, conglomerates of nickel catalyst particles in an area where CNF growth just started or is just about to start are shown. Magnification of the area in Fig. 4.39a in Fig 4.39b shows small domain formation. In Fig 4.39c, a few CNF that have just started growth and Fig. 4.39d shows nickel catalyst particles outside of CNF growth areas.
Figure 4.37. (a) A SEM micrograph showing area where "Y"-shaped junctions and interconnections between carbon nanofibres grown at room temperature in a radio frequency assisted microwave methane plasma on Ni powder at P=850W, (b) A SEM micrograph with enlarged image of carbon nanofibre junctions.
4. Results

Figure 4.38. A scanning electron micrograph of carbon nanofibres produced at room temperature in a radio frequency assisted microwave methane plasma on Ni catalyst at $P=850\text{W}$.

Figure 4.39. Formation of small domains acting as nucleation seeds for the CNF growth: (a) conglomerate of nickel catalyst particles forming the growth area, (b) small domains formation, (c) CNF just started growth, and (d) nickel catalyst particles outside of CNF growth area ($P_{\text{mw}}=500\text{W}$, $P_{\text{rf}}=200\text{W}$).
4. Results

4.4.2. Morphological characteristics

The TEM studies revealed that average diameter of carbon nanofibres (CNF) is about 50 nm varying approximately from 10 to 100 nm. Variety of carbon nanofibre diameters is shown in Fig. 4.40. Length of CNF lies between 0.5 and 5 μm.

![Figure 4.40. TEM images illustrating variety of carbon nanofibre diameters synthesised using r.f. MW PECVD at $P_{MW}=850$ W with average diameter approximately about 50 nm.](image)

The catalyst particle at the top end of the nanotube is usually "heart-shaped", and completely enveloped by a layer of carbon (Fig. 4.41a). Bi-directional growth with a diamond-shaped catalyst particle in the middle of CNF was also observed (Fig. 4.41b). Moreover, each nickel particle was responsible for the growth of a single CNF, either unidirectional or bi-directional.

In addition to the well known whisker-like and bi-directional morphologies CNF grown by the radio frequency supported microwave PECVD method have shown branching during the growth, which results the formation of "Y"-shaped junctions (Fig. 4.41 - 4.43).

Two CNF “welded” together forming “Y” junction are shown in Figs. 4.43a-c. Image shown is slightly under focused in order to show better contrast between carbon
nanofibre edges and channel. Joint between CNF could be clearly seen from the image shown in Fig 4.43b, which is tilted image from Fig 4.43a for 26°, and 36° tilted image at Fig. 4.43c.

Figure 4.41. TEM micrographs of (a) whisker-like CNT with "pear-shaped" Ni catalyst particle, (b) bi-directional morphology of CNF with diamond shaped Ni catalyst particle.

Figure 4.42. Branching of carbon nanofibre in "Y" shape during growth in radio frequency assisted microwave plasma.
Figure 4.43. "Y" junction of welded CNF produced using r.f. supported MW PECVD at $P_{MW}=840$ W: (a) under focus image, (b) under focus image with 26° tilt, and (c) under focus image, tilt 36°.
4. Results

4.4.3. Structural characteristics

4.4.3.1. Electron microscopy

The structural analysis of “Y”-shaped junction of two CNFs is shown in Fig. 4.44a. Figure 4.44b is a magnification of the rectangular area marked in Fig. 4.44a, and shows carbon layers with the characteristic 0.34 nm interlayer spacing of graphene sheets. The synthesis of connections between two or more different CNT and CNF is an important step in the development of carbon nanotube-based electronic devices and conducting polymer composite structures [4.9-4.13], by creating interconnections for electronic devices on a nanometer scale.

![Figure 4.44. TEM micrographs of “Y”-shaped CNF grown by radio-frequency supported microwave PECVD method; (a) “Y-shaped” morphology, (b) enlarged part of image (a), showing 0.34nm distance graphene sheets.](image)

Carbon nanofibres grown using radio frequency microwave PECVD are often missing a catalyst particle at their tip. These open-end carbon nanofibres could be very good candidates for effective hydrogen storage material. The open tip could be used as an access route for hydrogen molecule or intercalation of other molecules. The image of nickel catalyst particle missing on the tip of CNF is shown in Figure 4.45.
Figure 4.45. Missing catalyst particle on the tip of carbon nanofibre grown by radio frequency supported microwave PECVD at $P_{MW}=250W$.

A TEM image of carbon nanofibre with a nickel catalyst particle at the tip is shown in Fig. 4.46. Poorly ordered graphene layers are characteristics of CVD grown
CNT and CNF. In a majority of observed CNF graphene layers are parallel to the surface of catalyst particle at the tip (Fig. 4.46b).

Figure 4.46. TEM micrographs showing: (a) CNF with catalyst particle at the tip, and (b) magnification of the rectangular areas marked in Fig. 4.46a showing disordered graphene layers parallel to the surface of catalyst particle and nickel catalyst particle surface interface.
Compositional maps produced using electron energy loss spectroscopy of the carbon nanofibre with a nickel catalyst particle at the tip shown in Figure 4.46 are shown in Figure 4.47. A carbon map showing carbon in white is shown in Fig. 4.47a, and corresponding nickel map is shown in Fig. 4.47b showing white contrast in shape of the catalyst particle at the tip. Figures 4.47a and 4.47b are energy-filtered TEM (EFTEM) images formed with electrons that have passed through the sample and have lost energy characteristic for the carbon K-edge (1s-2p transition, 285 eV) and Ni L-edge (2p-3d transitions, 855 eV).

Figure 4.47. Carbon nanofibre synthetised by r.f. – MW PECVD at room temperature with nickel catalyst particle at the tip with bright field image shown in Fig. 4.46: (a) Carbon map, (b) Nickel map.

Thickness map structured image using EELS of the carbon nanofibre shown in Figs 4.46 and 4.47 have shown uniform thickness along the nanofibre and cup shape of the catalyst particle at the tip is shown in Figure 4.48.
Figure 4.48. Thickness map of the carbon nanofibre shown in Figs 4.46 and 4.47.

4.4.3.2. Raman spectroscopy

Raman spectroscopy was used for structural analysis of carbon nanofibres synthesised using r.f. combined microwave PECVD. The carbon nanofibres studied were synthesised using pure methane as the carbon source and nickel powder as the catalyst placed on a water-cooled substrate holder. The wave numbers of the main characteristic peaks in the spectra were determined by fitting with two, three or four Lorentzian curves (see Appendix 2). The Raman spectrum of carbon nanofibres synthesised at 240W of microwave power is shown in Figure 4.49. The position of the G peak is 1573 cm\(^{-1}\) and the very broad D peak overlapping with the G peak is positioned at around 1373 cm\(^{-1}\). Broad and overlapping G and D peaks are characteristic of poorly graphitised material. The ration of peak intensities is however very high \(I_G/I_D=2.5\), which could lead to the opposite conclusion.
4. Results

Figure 4.49. Raman spectra of carbon nanofibres synthesised using RF combined MW PECVD. 

- For P$_{MW}$=240 W, T=24 °C, CH$_4$, 70 sccm at (a) P$_{MW}$= 240 W, I$_D$/I$_G$= 2.531 (I$_D$/I$_G$= 0.395), (b) P$_{MW}$= 500 W, I$_D$/I$_G$= 0.847 (I$_D$/I$_G$= 1.182), and (c) P$_{MW}$= 840 W, I$_D$/I$_G$= 1.232 (I$_D$/I$_G$= 0.812).
4. Results

The Raman spectrum of carbon nanofibres synthesised at 500 W of microwave power shown in Figure 4.49b is contrary to the spectrum of 240W nanofibres shown in Figure 4.49a. The 240 W nanofibres exhibit much sharper G and D peaks indicating possibly greater structural perfection. The position of the G peak is around 1577 cm\(^{-1}\) with a shoulder at around 1611 cm\(^{-1}\) or separate D' peak. Position of D peak, representing disorder of the perfect graphite structure, is around 1346 cm\(^{-1}\), with higher intensity that the G peak \((I_G/I_D = 0.84)\). Carbon nanofibres synthesised at a higher microwave power of 840 W have shown again broader overlapping G and D peaks at around 1592 cm\(^{-1}\) and 1356 cm\(^{-1}\), respectively with \(I_G/I_D = 1.23\) (Fig. 4.49c).

4.5. CARBON NANOROPES

Ropes of roughly-aligned carbon nanotubes have been synthesised after nickel catalysed chemical vapour decomposition (CVD) of methane. After exposing the nickel powder catalyst to hydrocarbon gas (methane or acetylene) in thermal CVD or plasma enhanced CVD, the carbon nanofibres and nanotubes containing powder was treated in 35% nitric acid for 3 min to 2 hours with the intention of removing the remaining nickel powder particles. Filtration, washing, and drying followed the nitric acid treatment. In their study Niu et al. [4.14] found that more than 90% of the catalyst residue was removed by nitric acid treatment. After removing the residue nickel powder, we observed that the nanotubes were adhered to each other to and had formed ropes. CNT were self-organised into ropes after nitric acid action, and these ropes were bundled together by van der Waals forces.

4.5.1. Electron microscopy

CNF ropes were observed in the dried sediment by scanning electron microscopy (SEM). Rope diameters ranging from 20 \(\mu\)m up to 80 \(\mu\)m, and lengths up to few
millimeters were observed (Fig. 4.50). The dimensions of these ropes offer easy manipulation by hand using only a low magnification optical microscope. The possibility of using these macroscopic CNT ropes as a structural material on its own or as composite fillers cannot be overstated.

Figure 4.50. SEM images of ropes of carbon nanotubes observed in dry sediment after nitric acid treatment, showing ropes length of few milimetres,

Nanotubes tend to adhere to one another or to other surfaces like a glass plate. Ropes of carbon nanotubes were often covered with amorphous carbon (Fig. 4.51a and Fig. 4.51b). During SEM investigation using energy dispersive x-ray spectroscopy (EDX) analysis the carbon contents of these ropes have been verified (Fig. 4.52).
Dry sediments mainly consist of many ropes and can be clearly distinguished as they have lengths of several millimeters and are about 30 μm in diameter. Some particles or particle clusters, such as carbon nanoparticles, remaining catalyst particles and carbon
4. Results

blacks, exist on the surface or among carbon nanotube ropes. These ropes can be isolated from one another under the optical microscope using tweezers. A closer SEM image showing the surface texture of a carbon nanorope is shown in Figs. 4.53 and Fig. 4.54.

Figure 4.52. A SEM-EDX spectrum of sample after nitric acid purification showing high carbon and low nickel content.

Figure 4.53. A SEM image of carbon nanorope.
Figure 4.54. (a) A SEM image of the left hand side section of the rope in Fig. 4.53, showing surface texture of carbon nanorope, (b) a SEM image of the right hand side section of the rope in Fig. 4.53, showing surface texture of carbon nanorope.
Figure 4.55. A SEM image of the cross-section of a rope of carbon nanotubes, with bundles of carbon nanotubes roughly aligned to each other, (b) enlarged image of section in Fig. 4.55a.

The PECVD synthetised carbon deposits were also acid treated in the same way as for the thermal CVD material. Nitric acid (35%) was used as a standard nickel-etch for
4 min and after filtration and drying, rope-like carbon deposits were observed in the sediment (Fig. 4.56).

Figure 4.56. Ropes of carbon nanotubes in dry sediment after nitric acid treatment of as-synthesised mixture of carbon nanotubes and remaining nickel powder after radio frequency assisted microwave PECVD.
4. Results

Figure 4.57. TEM images of dry sediment after nitric acid treatment: (a) mats of CNTs, (b) enlarged central part from the Fig. 4.57a (180° rotated).

It can be seen from Fig 4.50 and Figs. 4.51-54 that individual ropes in these sediments have a round fibre-like shape with some small bundles of nanotubes split off from the larger rope, at the surface. Small particles or clusters of remaining catalyst particles exist on the surface of the rope. SEM examination of the cross-section of a rope of carbon nanotubes (Fig. 4.55) revealed that the carbon nanotubes in the ropes are arranged semiparallel to each other. It can be seen from Fig 4.53 that ropes are composed of hundreds of roughly-aligned whisker-like filaments, which might be individual carbon nanofibres, nanotubes or bundles of nanotubes. Evidence of SWCNT bundles was not found after TEM examination. TEM examination of dry sediments has shown carbon nanofibres and nanotubes clumped together, but not in the form of ropes (Fig. 4.57). Mats of randomly oriented nanotubes similar to these reported to be synthesised by both laser vaporization and electric arc methods [4.15, 4.16] were also observed. Ultrasonic preparation of samples might destroy ropes in solution prepared for TEM examination.
Several researchers have investigated electrical characteristics of catalytically grown carbon nanotubes or carbon nanotube ropes. Collins and co-workers [4.17] used a scanning tunneling microscope (STM) to explore the local electrical characteristics of single-wall carbon nanotubes which were components of CNT ropes. The adhesion of the nanotubes to a metal STM tip was not observed for tubes that do not bind together into ropes. It can be postulated that the same van der Waals forces that so effectively bind the SWNTs together into ropes also bind the nanotubes to the STM tip, even as the tip is withdrawn from the film. Dai and co-workers [4.18] have used catalytically grown carbon nanotubes for their electrical conductance probing experiments because the material produced by the catalytic process is in the form of isolated nanotubes, not bundles, and these can be probed individually. The catalytic growth process also yields curved nanotubes that have a much greater density of structural defects; these curved nanotubes can be exploited to investigate how defects affect electrical transport.

Investigation of electrical and mechanical properties of the ropes described in this thesis is suggested for the future work. Since the long and wide ropes of aligned carbon nanofibres can be easily handled and manipulated by hand, the availability of such nanofibres will be of importance for many applications.

### 4.5.2. Raman spectroscopy

Raman spectroscopy was employed to identify whether the carbon nanoropes are bundles of single-walled nanotubes because the Raman spectra of SWCNT have fingerprint features, quite different from those of graphite, multi-walled nanotubes or amorphous carbon. Raman scattering measurements can indicate the vibrational and electronic states that were modified from graphite by the zone-folding effect arising from a change in the symmetry from a layer to a cylinder.

The Raman spectra for carbon nanoropes are typical for single-walled nanotubes indicating that carbon nanoropes indeed consist mainly of SWCNT. The double peak in the high frequency region consists of lines at 1582 and 1601 cm\(^{-1}\), so-called tangential modes, which are related to the \(E_{2g}\) graphite mode, split due to the curvature of the rolled-up graphite sheet. The existence of such a group is a fingerprint for SWCNT since
MWCNT and graphite exhibit only a single peak at 1580 cm$^{-1}$. This Raman doublet can be assigned to the tangential C-C stretching modes of SWCNT [4.19]. In the low-frequency region, a broad peak near 180 cm$^{-1}$ was identified, which is characteristically associated with the radial breathing mode (RMB) of SWCNT [4.19]. The unique resonant behaviour of the Raman spectra in SWCNT was first reported by Rao and co-workers [4.19], who showed that the shape and position of the Raman bands associated with RBM, around 180 cm$^{-1}$ were strongly dependent on the energy of the exiting laser. This is also a fingerprint mode, since MWCNT do not show any low frequency mode and the low frequency mode of graphite is at 42 cm$^{-1}$. Bandow and co-workers [4.20] have shown that SWCNT symmetry types RBM frequencies versus the inverse tube diameter ($1/d$) all fall on a straight “universal” line well fit by the function

$$\omega = \frac{223.75}{d},$$

where $d$ is the diameter of the tube in nanometers and $\omega$ the mode frequency of the RBM in cm$^{-1}$. The smaller the SWCNT diameter, the higher is the Raman frequency. From the relation between diameter and frequency given above, the calculated diameters of SWCNT are 1.09 and 1.2 nm for 206 and 186 cm$^{-1}$, respectively. In order to confirm diameter distribution a high resolution TEM analysis is needed.

After assignments of the peaks in the Raman spectrum given in Figure 4.58 and 4.59 to specific vibrational modes of (n,n) SWCNT it was concluded possible presence of (8,8), (9,9) and (10,10) armchair nanotubes in the studied sample (Table 4.1). The peaks are in the spectral position predicted by theory calculations [4.19] with the deviation not greater than ±1%. Armchair tubes for n = 8 to 12 are the most stable SWCNT species in this diameter range [4.19]. The notation (n,m) defines the atomic coordinates for the 1D unit cell of the nanotube [4.21]. For $n \neq m \neq 0$ the tube has a chiral symmetry. Achiral tubes exist for $m = 0$ (zigzag) or $n = m$ (armchair) (see Fig. 2.2 in Chapter 2).

The low frequency region of the Raman spectrum of SWCNT is displayed in Fig. 4.60, where the resonantly enhanced lines associated with the RBM of various diameter SWCNT are expected. This band was decomposed using Lorentzian fitting routine explained in Appendix 2, and it was concluded that it can be fit by at least five Lorentzian peaks at 165, 182, 208, 224 and 280 cm$^{-1}$ (Fig. 4.60). These peaks coincide with the $A_{1g}$ vibrational modes of armchair SWCNT (n,n) [4.19]. The peak maximum of the $A_{1g}$ mode
on the lower-energy side are at 206, 183, 165 for \( n = 8, 9, \) and 10 respectively. Raman peaks at 405, 756, 1154 and 1370 cm\(^{-1}\) were assigned to the armchair SWCNT (9,9), (8,8), (10,10) and (9,9) respectively (Table 4.1), using the study published by Rao et al [4.19]. The high frequency band were decomposed using Lorentzian fitting routine (Fig. 4.61) into two peaks at 1582 cm\(^{-1}\) assigned to \( E_{1g} \) mode of graphite, and 1601 cm\(^{-1}\) peak to \( E_{2g} \) mode [4.19]. For the peak around 1340 cm\(^{-1}\) there are two contributions, mainly from disordered carbon but with a weak contribution from SWCNT.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>166</th>
<th>182</th>
<th>208</th>
<th>405</th>
<th>756</th>
<th>1154</th>
<th>1370</th>
<th>1582</th>
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<tr>
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<td>183</td>
<td>206</td>
<td>408</td>
<td>762</td>
<td>1152</td>
<td>1369</td>
<td>1582</td>
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<td>((n,n))</td>
<td>(10,10)</td>
<td>(9,9)</td>
<td>(8,8)</td>
<td>(9,9)</td>
<td>(8,8)</td>
<td>(10,10)</td>
<td>(9,9)</td>
<td>(9,9)</td>
</tr>
<tr>
<td>Symmetry</td>
<td>( A_{1g} )</td>
<td>( A_{1g} )</td>
<td>( A_{1g} )</td>
<td>( E_{2g} )</td>
<td>( E_{1g} )</td>
<td>( E_{2g} )</td>
<td>( A_{1g} )</td>
<td>( E_{1g} )</td>
</tr>
</tbody>
</table>

Table 4.1. Experimental Raman spectra peak frequencies (in cm\(^{-1}\)) compared to the first order Raman vibrational mode frequencies (in cm\(^{-1}\)) and assigned SWCNT mode symmetry according to the ref. [4.19].

![Raman spectra](image)

**Figure 4.58.** Raman spectra of the carbon nanorope (Fig. 4.55) obtained using 514.6 nm \( \text{Ar}^+ \) laser with optical power at the source of 20 mW.
Figure 4.59. Raman spectra of the carbon nanorope presented in Fig. 4.58 in more detail (a) low frequency part of the spectra and (b) high frequency part of the spectra.
4. Results

Figure 4.60. Five Lorentzian fit to the peak in the low frequency Raman spectra characteristic for SWCNT.

![Low frequency Raman spectra](image)

- $y_0 = -6 \pm 20$
- $x_1 = 166 \pm 1$
- $w_1 = 20 \pm 5$
- $A_1 = 20000 \pm 10000$
- $x_2 = 182.2 \pm 0.9$
- $w_2 = 31 \pm 7$
- $A_2 = 90000 \pm 40000$
- $x_3 = 208 \pm 2$
- $w_3 = 39 \pm 9$
- $A_3 = 170000 \pm 80000$
- $x_4 = 224.8 \pm 0.6$
- $w_4 = 26 \pm 2$
- $A_4 = 150000 \pm 40000$
- $x_5 = 280 \pm 1$
- $w_5 = 77 \pm 7$
- $A_5 = 140000 \pm 10000$

Figure 4.61. Two Lorentzian fit to the double peak in the high frequency Raman spectra characteristic for SWCNT.

![High frequency Raman spectra](image)

- $y_0 = 4000 \pm 30$
- $x_1 = 1582.38 \pm 0.08$
- $w_1 = 5.7 \pm 0.2$
- $A_1 = 50000 \pm 1000$
- $x_2 = 1601.79 \pm 0.04$
- $w_2 = 9.1 \pm 0.1$
- $A_2 = 220000 \pm 2000$
4. Results

References

Chapter 5

DISCUSSION

5.1. CATALYTIC CVD SYNTHESIS

The existence of catalytically grown carbon nanofibres (also known as carbon filaments) has been known since the early 1950's [5.1]. However, lijima's observation of carbon nanotubes (CNT) in the carbon arc deposits in 1991 has attracted huge interest from the scientific community [5.2]. Since then, arc-discharge was the only method used among researchers for the synthesis of carbon nanotubes [5.3, 5.4], and not long after other carbon nanotubes growth methods were developed. Carbon nanotubes have also been produced by a vaporisation process using a laser [5.5, 5.6], electron beam [5.7], and solar energy [5.8]. Carbon nanotubes can be grown by catalytic chemical vapour deposition (CVD) of hydrocarbons over a metal catalyst using thermal CVD [5.9, 5.10] or plasma-enhanced CVD [5.11]. Catalytically grown carbon nanotubes are very similar in microstructure to much longer known carbon nanofibres.

At present two main methods for carbon nanotubes production in academic and industrial communities are: arc-discharge evaporation [5.2] and catalysed decomposition of hydrocarbons in a CVD [5.24]. Yacaman and co-workers [5.10] concluded that the catalytic CVD method can produce tubes with fullerene structure with similar characteristics to those produced by the carbon-arc method described by ijima [5.2]. Catalytic cracking of hydrocarbon gas is able to generate large volumes of nanotubes, comparatively cheaply, without the presence of contaminating nanoparticles [5.12]. Catalytic carbon nanotubes have more structural defects when compared to those synthesised by arc-discharge graphite evaporation.

Nanotubes grown by arc discharge and laser ablation aggregates into tangled bunches, which makes them difficult to purify, manipulate and sort. With these materials, selecting individual nanotube wires is challenging. Nanotubes can be grown catalytically...
on surfaces using CVD with a degree of control that is unmatched by arc-discharge or laser-ablation techniques. The nanotubes grow so that they are aligned with each other and are perpendicular to the surface of the substrate. This "self-orientation" is due to strong van der Waals interactions between the tubes, which cause the nanotubes to bundle together and form rigid structures. Controlled growth of carbon nanotubes by CVD, on the other hand, has opened up new routes to forming "addressable" structures that can be used to measure the properties of nanotubes and to build nanoscale devices with ease. Electrical circuits that incorporate individual nanotubes can be fabricated by growing nanotubes on specific sites on a substrate patterned with catalyst islands.

Carbon nanofibres (CNF) can be grown by using catalytic decomposition of hydrocarbons over transition metal particles such as iron, cobalt, nickel, and their alloys at temperatures ranging from 700 to 1000 °C [5.12]. They are often thicker and have more structural defects than nanotubes obtained by arc-discharge, yet they are an attractive material for potential use in electrochemical capacitors (also known as super capacitors) [5.13], flat panel displays [5.14], and as a hydrogen storage material [5.15]. The CVD of hydrocarbons in the presence of a metal catalyst as a CNT and CNF growth method is simple and efficient. Moreover, the catalytic CVD method offers a route to control the diameter, length, and alignment of CNT and CNF. The growth of CNT and CNF by thermal CVD method can be achieved with high purity and high yield at relatively low temperatures (from 450 °C to 1000 °C) when compared to arc-discharge and laser vapourisation techniques. Low growth temperatures are especially useful for any applications, which use carbon nanotube as an electron emitter for flat panel displays. For example, if glass substrates are to be used it is important to lower the growth temperature to at least 650 °C (for soda-lime glass) [5.16]. Ren and his co-workers [5.11] reported the growth of carbon nanotubes using hot filament plasma-enhanced CVD method, at 666 °C. However, the growth temperature of thermal CVD is normally as high as 700-1000 °C, and many researchers have tried to lower the temperature of the growth process. For example, Lee and co-workers [5.16] have used palladium (Pd), chromium (Cr) and Platinum (Pt) as co-catalysts in order to lower the growth temperature of carbon nanotubes to 500-550 °C. Microwave PECVD, used for the preparation of diamond and diamond-like carbon films, has been recently developed for successful growth of CNT
and CNF at low temperatures [5.17-5.21, 5.22]. However, all these methods require substantial temperatures for CNT and CNF synthesis and none of them can be used for CNT or CNF growth at temperatures close to room temperature. In order to use polymers and organic substrates for CNT and CNF growth, which cannot tolerate higher process temperatures, new methods have to be developed.

A perfect nanotube may be thought of as a cylindrical graphene sheet composed only of hexagons with a few pentagon rings needed to close the tip. In the study by Bulusheva et al. [5.23] x-ray emission and photoelectron spectroscopy were applied to obtain information about the electron structure of multiwalled carbon nanotubes prepared by catalysed CVD and arc-evaporation. The methods used detected notable distinctions in the distribution of \( \pi \) valence electrons and the binding energy of core electrons for two kinds of carbon nanotubes. From the similarity between x-ray spectra of arc-produced nanotubes and graphite it may be assumed that these two carbon materials have approximately the similar portion of defects, which could mainly be concentrated close to the tips of nanotubes, due to pentagon defects, and at the boundaries of graphite crystallites. The alternative production method of multiwalled carbon nanotubes based on the catalytic decomposition of hydrocarbons resulted in the appearance of a large amount of curved, bent and coiled nanotubes. The bending and coiling of the tubes is suspected to be caused by occurrences of pentagon-heptagon pairs in the honeycomb structure.

Structural defects, which might occur in multiwalled carbon nanotubes and carbon nanofibres, are more likely to appear in the low-temperature growth conditions [5.23]. Ivanov and co-workers [5.24] found that a decrease in the temperature from 700 to 600 °C leads to a strong decrease in the amorphous carbon production. However, a decrease in temperature also has an influence on the process of graphitisation. After SEM and TEM study it was found that the relative amount of well-graphitised nanofibres with minimal amorphous carbon production was reached an optimum level in the temperature range from 450 to 550 °C. Lower growth temperatures in thermal CVD have resulted in the production of CNF with much more structural defects and with a much smaller yield.

As a source of carbon in CVD synthesis of CNF, methane was chosen in this study because it is the most stable of all hydrocarbon molecules with respect to self-decomposition at high temperatures, which is a crucial property that prevents the
formation of amorphous carbon that can poison the catalyst and overcoat the nanotubes. The key element in the growth of carbon nanofibres and nanotubes is the catalyst, which is typically in the form of a fine powder, which can be sprayed in the form of an aerosol. The catalyst consists of nanometer-sized particles dispersed on a support material. The support is needed so that there are large numbers of sites to place and fix the metal catalyst particles from which the nanotubes can grow. Interaction between the metal species and the support could prevent catalyst particles from aggregating and producing large particles that are not capable of forming nanotubes.

Carbon nanotubes and nanofibres with different structures and morphologies can be fabricated by several methods mentioned previously. Work described in this thesis has introduced a new method for catalytic CNF growth at room temperature using radio frequency PECVD and radio frequency supported microwave PECVD methods. Instead of using high temperatures (> 500 °C) to provide the correct growth environment for the CNF, hydrocarbon plasmas were utilised in this study to provide the energy dynamics necessary for a dissociation of the carbon and the subsequent catalytic growth on transition metal particles at room temperature. It is envisaged that a variant of the proposed catalytic effect could be used to grow aligned nanofibres as well as carbon nanotubes. The room temperature synthesis of CNF have been also achieved in a radio frequency assisted microwave PECVD system using nickel powder as a catalyst. Microwave plasma-assisted CVD has already been established as an efficient technique for preparing carbon nanotubes [5.17-5.22]. The room temperature CNF growth is possible by carefully controlling the microwave and radio frequency power level and monitoring the temperature of the substrate. Both of these methods allow the growth of carbon nanotubes on different technologically important substrates, such as plastics and other polymers, which is suitable for flat panel display [5.22] and fuel cells [5.15] applications. During the growth process in our system branching of nanofibres has occurred which has resulted in the formation of "Y"-shaped junctions. This might well open the possibility of creating interconnections for electronic devices on a nanometer scale and assembling new classes of materials from nanotubes.

The results of CNF diameters distribution study have shown remarkable characteristic of radio frequency PECVD not found in any other CVD method. The
diameter distribution for different substrate temperatures is largely independent of substrate temperature with average diameter of approximately 50 nm.

![Histogram of CNF diameters](image)

**Figure 5.1.** A histogram displays the distribution of nanofibre diameters as a function of substrate temperature, showing that the average diameter of the CNFs is 50nm, largely independent of the temperature.

### 5.2. CARBON NANOROPES

Acid treatment is usually used to remove remaining catalyst after CNT synthesis. In their study Niu *et al.* [5.25] have found that more than 90% of the catalyst residue was removed by nitric acid treatment. In the work described in this thesis in an attempt to remove nickel catalyst, carbon nanofibres prepared by thermal and plasma enhanced CVD, were treated with nitric acid, followed by filtration, washing, and drying. After removing the residue nickel powder, it was observed that nanotubes are adhered to each other to form ropes. The macroscopic ropes consist of aligned carbon nanotubes, in comparison to the mats of randomly oriented nanotubes reported by both laser vaporization and electric arc methods [5.26, 5.27]. Synthesized ropes of aligned carbon nanotubes are long and wide can be easily handled and manipulated by hand or with the aid of a low-magnification optical microscope.

Ropes of single-wall carbon nanotubes (SWNT) have been produced for the first time using condensation of laser-vaporized carbon-nickel-cobalt mixture at 1200 °C, by Thess *et al.* [5.26]. Their high-purity samples of SWNT consist of a mats of randomly
oriented ropes or fibres, 10 to 20 nm in diameter and many micrometers long, which can consist of 100 to 500 SWNT. CNF ropes diameters produced in this study ranging from 20 μm up to 80 μm, and lengths up to few millimetres, and they are more comparable in size to ropes of SWCNT reported by H. M. Cheng and co-workers [5.28]. Using floating catalyst method they synthesized ropes of carbon nanotubes at temperatures ranging from 1100 to 1200 °C, which were 10 to 20 nm in diameter and up to 3 cm long. After TEM study of the dry sediment, presented in the Results section of this thesis (Fig. 4.55), no evidence of SWCNT was found, and it was concluded that ropes were consisted of carbon nanofibres.

In the joint study between researchers from Tsinghua University in Beijing and researchers from Rensselaer Polytechnic Institute in Troy long ropes of SWCNTs of up to several centimetres in length were reported [5.29]. They have used n-hexane in combination with thiophene and hydrogen in their study. The n-hexane solution with a given composition of ferrocene and thiophene was introduced into a vertical reactor after heating to the pyrolysis temperature of 1150 °C, with hydrogen as carrier gas. Remaining catalyst particles were removed by high temperature vacuum annealing or reflux the ropes in nitric acid for several minutes. This was the first time that nitric acid treatment was mentioned in the literature in the process that resulted synthesis of carbon nanoropes. In the study described in this thesis nitric acid treatment used for removal of residual nickel catalyst could result in functionalisation of carbon nanofibres surface that could be necessary step in carbon nanoropes formation.

Investigation of electrical and mechanical properties of carbon nanotube ropes of catalytically grown carbon nanotubes is very important since the long and wide ropes of aligned carbon nanotubes can be easily handled and manipulated compared to single carbon nanotubes which will be of importance for many applications. Tensile strength measurements done by three different research groups have shown very good results for mechanical properties of carbon nanotube ropes [5.28, 5.30, 5.31]. Collins et al. [5.32] used a scanning tunneling microscope (STM) to explore the local electrical characteristics of single-wall carbon nanotubes, which were components of the CNT ropes. The adhesion of the nanotubes to a metal STM tip was not observed for tubes that do not bind together into ropes. It can be postulated that the same van der Waals forces that so
effectively bind the SWNTs together into ropes also bind the nanotubes to the STM tip, even as the tip is withdrawn from the film.

5.3. GROWTH MODEL

It is likely that a variety of mechanisms play a role in the catalytic growth of CNT and CNF. Two growth-models a base growth model and a tip growth model, have been proposed for the catalytic growth of carbon filaments by Terry Baker [5.33, 5.34]. These growth models have been frequently adopted to explain the growth mechanism of CNT and CNF. It is believed that nanotubes grow as carbon precipitates from a supersaturated metal catalyst that resides at either the base (i.e. "base growth") or the tip of a growing nanotube (i.e. "tip growth"). Catalyst-substrate interactions and temperature gradients across the catalyst particle are considered to be important factors that determine the growth mechanism. In our experiments the encapsulated catalytic particle was found close to the tip of the CNF grown by thermal and plasma enhanced CVD of methane, and we adopt a tip growth model to explain such a process. However, despite the large number of studies in CVD growth of CNT and CNF, there are many unanswered questions about the growth mechanism. On the basis of the experimental results, a growth models based on a carbon-metal eutectic synthesis process that gives rise to CNF growth at low temperature is proposed.

The growth model proposed for the low temperature thermal CVD growth of CNF, illustrated in Fig. 5.2, is based on carbon filaments growth model proposed by Baker and Harris [5.34]. Prior to the carbon nanofibre growth, nickel powder particles increase in surface roughness and form small domains inside each of the metal clusters. These domains act as nucleation seeds for the carbon nanofibre growth (Fig 5.2a). The size of small domains within the metal corresponds to the diameter of the CNF. 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 further supplied, a carbon-metal eutectic alloy can be formed, decreasing the melting temperature of the alloy. Role of the carbides in the initial and steady state growth of carbon nanofibre, was first pointed
in the study done by Lobo and Trimm [5.35]. The formation of carbon-metal eutectic alloys promotes the diffusion of carbon in the metal alloy by decreasing the melting its point, initiating carbon aggregation followed by the nanofibre formation (Fig 5.2b). Carbon diffused at the rear faces precipitate at the interface to form carbon nanofibre structure. The carbon diffusion is limited to the domain size within the metal particle and the diameter of 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, as shown in Fig 5.2c. 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 carbon (Fig. 5.2d). Encapsulation of catalytic particles indicates an occurrence of melting of the catalytic particles. It was suggested that the existence of the quasi-liquid state at the temperature below melting point of the bulk phase could be attributed to the size of metal at nanometre level [5.36] and/or the interfacial effect between metal and carbon [5.37].

In this study a TEM analysis on the majority of carbon nanofibres have shown a duplex structure with a graphitic sheet surrounding an amorphous core, as observed for the first time by Baker and co-workers [5.38]. Baker explained the growth of this type of nanofibres using mechanism in which exothermic reactions are required. Their experiments were conducted at temperatures above 500 °C. The mechanism for the growth of carbon nanofibres proposed by Baker excluded pure methane as the source of carbon, which we have used. In a separate study, carbon nanofibres obtained from reactions at elevated temperatures with methane were explained in terms of the presence of higher hydrocarbons as impurity [5.39]. Studies of the thermal decomposition of methane, however, have shown that the formation of carbon is the end result of a sequence of reactions forming a variety of other hydrocarbons [5.40]. Small amounts of other hydrocarbons are therefore always present during the formation of carbon nanofibres from methane. Although, Robertson [5.41] reported a variant to the accepted theory when he postulated that nanofibre growth in the endothermic decomposition methane should be ascribed to an exothermic decomposition of impurities of higher hydrocarbons. The energy released would be small compared to that imported by radio frequency plasma.
The particle size of the metal catalyst particle used is a further variable that affects the growth of carbon nanotubes. Particles with diameters less than 25 nm will tend to produce nanotube growth whereas, larger particles usually generate solid nanofibres [5.42]. Yudasaka and co-workers [5.43] have obtained carbon nanotubes by catalytic pyrolysis at 700 °C when the diameter of the Ni particles was about 20-30 nm.

The SEM and TEM analysis of material synthesised in r.f. PECVD and r.f. assisted microwave PECVD confirmed the presence of Ni particles at the growing end of nanofibres, which is strong evidence for a “tip growth” mechanism, where the catalyst particle is carried away from the support during the growth process and remains at the tip of the nanofibre. Therefore, the “tip growth” mechanism can be proposed for the growth of carbon nanofibres by radio frequency supported microwave PECVD method presented in this thesis. Figure 5.3 shows the proposed growth mechanism of the carbon nanofibre by radio frequency supported microwave PECVD method on Ni powder catalyst similar to that reported by Baker and Harris for CVD grown carbon filaments [5.34]. Branching
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Formation of small domains acting as nucleation seeds for the CNF growth in radio frequency assisted microwave PECVD is captured in Fig. 4.39. In Fig. 4.39a conglomerate of nickel catalyst particles are observed forming an area where CNF have just started or about to start growth. Magnification of the growth area in Fig. 4.39a in Fig 4.39b shows small domains formation. In Fig 4.39c a few CNF have just started to grow and in Fig. 4.39d, nickel catalyst particles outside of CNF growth area are shown.

There are number of reports of growth models for microwave PECVD grown CNT and CNF [5.44, 5.45, 5.46]. The growth model for microwave grown CNT proposed by Bower et al. [5.48] essentially adopts the established concepts of CVD carbon nanofibre growth developed by Baker and Harris in the 1970s [5.34, 5.48]. Instead of a thermal energy source for carbon filament CVD growth described by Baker and Harris, radio frequency plasma is the energy source for carbon nanofibres grown using r.f. PECVD. This model could be adopted to explain carbon nanofibres growth in r.f. assisted microwave PECVD and r.f. PECVD.

Within radio frequency produced plasma, due to the nature of the sheath space, above the substrate, any surface features, such as micron sized nickel catalyst particles, would create small but sufficient field enhancement inside the r.f. plasma. Recently, Chhowalla [5.49] reported that the activation energy for carbon diffusion through the Ni catalyst particle, in the presence of plasma, is much lower (0.54eV) than in the thermal deposition in the absence of plasma (1.5eV). Taking that into account it is clear that once suitable conditions are present the energy requirements are not significant. Langmuir probe studies on the rf PECVD chamber, under similar growth conditions, show an average plasma energy of 2.0-3.0 eV, with a dc self-bias of —70V on the driven electrode. The difference between the plasma potential and the floating potential of the methane plasma was measured to be 2-3eV, equating to an average energy gain of 2-3eV for ionised carbon and hydrocarbons in a 1 Torr plasma. In the tip growth process, radio frequency heating of supersaturated nickel catalyst particle helps in the diffusion of the carbon. Formation of the CNF initiates on the cooler bottom of the catalyst particle, due to the precipitation of diffused carbon.
The melting point of Ni is 1455°C, whilst the temperature range for the growth of CNF and CNT is between 450-1250°C. However, the growth of the CNF can be explained by noting that the melting temperature of the Ni-C eutectic is 1311°C [5.50], and is reached through the radio frequency or radio frequency assisted microwave heating of the supersaturated nickel particle.

The radio frequency and microwave energy create heating within the material through the 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 or microwave electromagnetic field. The molecular mechanism involved is complex and it is beyond the scope of this thesis. Only brief overview of the important basic relationship and principles is discussed in Appendix 3. Characteristic of microwave and radio frequency heating is volumetric heating rather then the surface absorption and thermal diffusion of conventional heating. Potentially ‘uniform’ heat distribution, and quick on and off the heating source without thermal lag are also characteristics of microwave and radio frequency heating.

Figure 5.3 (a-d) shows the proposed growth mechanism of the carbon nanofibre by r.f. PECVD or r.f. assisted microwave PECVD method on Ni powder catalyst, adapted from the process proposed by Baker and Harris for CVD-grown carbon filaments [5.38]. The thermal energy source necessary for CVD growth of the carbon filaments is replaced here by the catalytic radio frequency or radio frequency assisted microwave plasma process. Upon radio frequency or radio frequency assisted microwave heating, the number of nucleation sites in the Ni particles increases through the formation of small domains, whose sizes correspond to the diameters of the CNF, and appears to be independent of low substrate temperatures. As more carbon atoms arrive, the particle melting temperature is lowered by the formation of a Ni-C eutectic alloy; the eutectic alloy promotes further the diffusion of carbon, leading to the formation of carbon precipitates and CNF formation [5.50]. Carbon diffusion is limited by domain size within the metal particle. As the CNF grow further, part of the metal domain is pushed upward, forming a metal cap, which stabilises the dangling bonds of the nanofibre at the edge by saturating them. The growth of the nanofibre is significantly reduced when the metal particle is completely enveloped by graphene layers (Fig. 5.3d). A temperature
dependence on the critical radius for nucleation [5.50] was not observed, but the substrate temperatures considered here are much lower.

**Figure 5.3.** Detailed TEM bright field image of the carbon nanofibre tip region revealing graphene planes parallel to the facets of the Ni particle in a herring-bone or stacked cup structure. The black lines are guides to the eye for the orientation of the graphitic planes. Figures (a), (b), (c) and (d). Schematics of the proposed growth mechanism for the CNF growth in radio frequency PECVD (after Baker and Harris [5.34]).
5.4. STRUCTURE

Before 1985 it was assumed that carbon has the only two stable forms: graphite (with threefold-coordination symmetry) and diamond (with fourfold-coordination symmetry). The discovery of new types of stable carbon structures namely fullerenes in 1985 [5.51] and carbon nanotubes in 1991 [5.2], in which a finite curvature is imposed to the atomic threefold coordination has widened and revived the interest in studying carbon structures.

5.4.1. Structure models

During their work at Pennsylvania State University Nelly Rodriguez and Terry Baker performed a very comprehensive evaluation of the potential of a number of metals and bimetallic as catalyst for production of carbon nanofibres. They come to the conclusion that the structure of carbon nanofibres ("herringbone", "perpendicular" and "parallel") is tailored by the selection of metal catalyst. They concluded that nickel and iron based alloys are among most effective catalysts [5.52]. In this study a nickel powder catalyst was used in all experiments and the structure of graphitic platelets in carbon nanofibres was "herringbone", "perpendicular" and "parallel" to the nanofibre axes (Fig. 5.2). Graphitic platelets are usually parallel to the metal catalyst particle surface and shape, as well as, the nature of the catalyst particle at the nanofibre tips influences structure and orientation of graphitic layers in respect to the nanofibre axis. The most common case is an "ice-cream cone" or "heart" shape catalyst particle, as shown in Fig 5.4, which will result "herringbone" or "cap stacked" structure. The shape of the catalyst particle will depend on how fast the metal particle is detached from support surface (see growth model in Fig 5.2b). If this process is slow the catalyst particle might have very flat shape (Fig. 5.4) and graphitic layers could be very "perpendicular" to the nanofibre axis. In the case of very fast detachment from the support, the catalyst particle cone could
be very sharp (Fig. 5.4) and graphitic layers could be very “parallel” to the nanofibre axis.

An illustration of “perpendicular” graphitic platelets structure can be found in the carbon nanofibre structure shown in Fig. 4.15, an illustration for “herringbone” structure is shown in Figs 4.17 and 4.28b, and “parallel” graphitic platelet structure can be found in the carbon nanofibre structure shown in Fig. 4.18 and 4.28a.

Baker and Rodriguez have also investigated the influence of the catalyst and process parameters to the morphology of carbon nanofibres. Pre-adsorption of sulfur on nickel induced some major perturbations in morphological characteristics of the filamentous carbon deposits, which are generated in the form of coiled structures [5.53].

### 5.4.2. Electron energy-loss spectroscopy studies

Electron energy-loss spectroscopy (EELS) is a valuable technique for light element analysis in the transmission electron microscope, and can provide useful information on chemical states and bonding [5.68]. For graphite related carbon specimens, information can be obtained from two energy ranges. In the approximate range from 280 eV to 300 eV, energy loss is associated with the excitation of an electron from 1s carbon shell (K shell) to Fermi level. The nature of the 1s core level spectra can
enable estimates to be made of relative amounts of sp² and sp³ bonding. In the region from 0 to 40 eV, energy loss is due to excitation of plasmons, arising from π electrons and π and σ states of the carbon L shell. Highly ordered graphite gives a broad peak in this region, centered about 28 eV.

Core-edge features in EELS occur when a core electron is excited to the unoccupied states above the Fermi level. In this work excitation of 1s electrons (K edge) was investigated. EELS on the core K level probes the distribution of available unoccupied states in the conduction band. Two bands are observed, which are attributed to the transitions to the π* and σ* conduction bands.

Electron energy-loss spectra from an individual carbon nanofibre (Fig. 5.5) grown at room temperature using r.f. PECVD are presented in Fig. 5.6. The carbon K edge shows similar energy loss features as graphite (see Fig. 3.6). Similarities with graphite spectra indicate presence of carbon in a graphite phase. The energy-loss peaks from the nanofibres are seen to be broader compared to the one from graphite and this could be due to the orientation-related energy-loss dispersion in graphite.

The EELS spectra presented in Figure 5.6 shows characteristics similar to those of graphite spectra with spectra exhibiting a peak at around 285 eV corresponding to the 1s π* transition and a peak at about 290 eV and a broader peak at around at 305 eV that corresponds to the K transitions to the σ* orbital [5.55]. Peak at about 292 eV is much sharper than in graphite spectrum, and no shift was observed at the two probed positions. The fine structure present in these peaks is difficult to compare due to the limiting energy resolution. In the C₆₀ spectrum two humps could be seen in the K-shell p-electron energy loss, one at 285 eV (same as graphite) and one at the 288 eV (from a second, due to the cage-strained π electrons) [5.56]. In our carbon nanofibres spectrum the 288 eV peak was not observed.
Figure 5.5. A bright field STEM image of large diameter carbon nanofibre synthesised at room temperature, using r.f. plasma with marked two positions where EELS spectra presented in Fig 5.6 was probed, Position 1 is near the carbon nanofibre edge and Position 2 was in the middle.

Figure 5.6. Electron energy loss spectra from individual carbon nanofibre synthesised at room temperature using r.f. PECVD.

Electron energy-loss spectra from individual carbon nanofibre (Fig. 5.7) grown at room temperature using r.f. supported MW PECVD is presented in Fig. 5.8. The carbon K edge shows similar energy loss features as graphite (see Fig. 3.6) and EELS spectra of carbon nanofibre synthesised using r.f. PECVD shown in Figure 5.6. Similarities with graphite spectra indicate presence of amorphous carbon in carbon nanofibre structure. The energy-loss peaks from the carbon nanofibre produced using r.f. PECVD is broader
compared to the one from carbon nanofibre produced using r.f. MW PECVD, which could indicate more ordered and oriented structure of the graphene layers.

**Figure 5.7.** A bright field TEM image of large diameter carbon nanofibre synthesized at room temperature, using r.f. MW PECVD with marked two positions where EELS spectra presented in Fig 5.8 was probed, Position 1 is near the carbon nanofibre edge and Position 2 was in the middle.

**Figure 5.8.** Electron energy loss spectra from individual carbon nanofibre synthetised at room temperature using r.f. MW PECVD.

The EELS spectra presented in Figure 5.8 shows characteristics similar to those of graphite spectra with spectra exhibits the peak at around 285 eV corresponding to the 1s
\[ \pi^* \] transition and a peak about 290 eV and a broader peak at around 305 eV that corresponding to the K transitions to the \( \sigma^* \) orbital [5.55]. Peak at about 292 eV is much sharper than in graphite spectrum and compared to r.f. PECVD nanofibre spectrum at Fig. 5.6. No spectrum shift was observed at two probed positions. The fine structure present in these peaks is difficult to compare due to the limiting energy resolution.

5.4.3. Raman spectra studies

Raman spectroscopy is one of the most sensitive methods for studying carbon materials, providing very important information on the microstructure and crystalline ordering of carbon materials [5.57]. Crystalline perfection can be characterised using Raman spectroscopy, as Raman scattering from perfect crystals is limited to contributions from Raman active zone-centre modes. Raman spectra are very sensitive to changes in translational symmetry and thus are useful for the study of disorder and crystallite formation in carbon films.

The Raman spectrum of carbon nanofibres shows features common to the spectra of any graphite-like material with characteristic G and D peaks or bands at about 1580 cm\(^{-1}\) and 1355 cm\(^{-1}\) respectively [5.58]. The G and D peaks are attributed 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 [5.59]. The bonding in graphite exhibits one of the largest anisotropies of any solid. Moreover the nearest-neighbour C-C bonding in graphite is considerably stronger than C-C bonding in diamond. In contrast, the bonding between the planes is very weak and exhibits a van der Waals character. The very weak and very strong bonding in graphite will yield both unusually low and high frequency contributions to the lattice vibration spectrum. A complete theory explaining why double resonance in graphite and dominant Raman intensities of the breathing modes of clusters of six fold rings, both give rise to the D peak in graphite and in amorphous carbon does not yet exist [5.60].

All samples studied exhibit mainly G and D Raman bands. G-bands at about 1580 cm\(^{-1}\), correspond to the Raman-allowed E\(_{2g}\) mode called graphite mode. D-band, at about 1355 cm\(^{-1}\), represents the contribution of disordered graphitic material. Amorphous
carbon deposits on the surface of as-grown carbon nanofibres induce the large intensity of the D-band. The $D'$-band, at about 1620 cm$^{-1}$, is due to the maximum in the phonon density of states. The G-band is sensitive to the degree of two-dimensional graphite ordering, whereas non-planar microstructural distortions contribute to the D-band [5.57].

Raman spectra of the room temperature CNF synthesised using r.f. PECVD (Fig 5.7) shows two broad band peaks centred at 1321 cm$^{-1}$ and 1599 cm$^{-1}$ respectively, these are not observed in spectra obtained from CNT grown by hot filament CVD at 450°C or from purified MWCNT obtained commercially. In general, it is expected that the $I_D/I_G$ ratio will be much smaller for purified MWCNT. For r.f. PECVD and hot filament CVD samples, a large amorphous carbon background signal is expected, but the position and the well defined shape of the D and G peaks point to a well-structured graphitic morphology in the films. In the CNF sample, it is unclear if the high D peak is only due to the amorphous carbon component or if the structural disorder also has an effect. The observed CNF spectrum is typical of vapour grown CNF and CNF grown using a graphite resistance furnace, at temperatures between 1100 and 1500°C [5.58].

![Figure 5.7. Raman characterization of room temperature produced CNF using r.f.-PECVD at 200W power and 30 sccm methane flow rate. Comparison of the Raman spectra obtained from room temperature CNF, CNT grown by hot filament PECVD at 450°C [5.61].](image-url)
The influence of growth temperature on carbon nanofibre structure was studied for samples synthesised using thermal CVD and r.f. PECVD. Raman spectra for carbon nanofibres grown at 500, 600 and 700 °C using thermal CVD of acetylene at process pressures of $10^{-2}$ mbar are shown in Figure 5.8. Broad overlapping peaks characteristic of all three growth temperatures are indication of limited structural perfection of carbon nanofibres grown in the range of studied temperatures. The ratio of G and D peak intensities with growth temperature did not increase as expected result contrary to the well known fact that degree of structural perfection of graphite-like materials increase with synthesis temperature indicating a possibly more complex CNF growth mechanism at low pressures.

![Figure 5.8](image.png)

**Figure 5.8.** Comparison of Raman spectra from carbon nanofibres grown using acetylene at three different temperatures 500 °C ($I_G/I_D=1.13$), 600 °C ($I_G/I_D=1.11$), and 700 °C ($I_G/I_D=1.17$).

An increase of the ratio of G and D peak intensities at higher growth temperature was observed at very low substrate temperatures when r.f. PECVD was used. Comparison of Raman spectra for carbon nanofibres grown at room temperature (30 °C) and at 250 °C using r.f. PECVD under otherwise identical conditions is shown in Figure 5.9. The influence of growth temperature on crystalline perfection of synthesised carbon nanofibres, represented by the $I_G/I_D$ ratio, was confirmed even in this case for extremely
5. Discussion

low substrate temperatures, and growth conditions where energy generated using the heating source was replaced by plasma energy.

The influence of microwave power on carbon nanofibre structure in r.f. combined microwave PECVD could not be established from analysis of Raman spectra. Comparison of Raman spectra shown in Fig. 5.10 for two different microwave powers of 500 W and 840 W could lead to two different conclusions. The higher ratio of G and D peak intensities for higher microwave power \( \frac{I_G}{I_D} = 1.232 \) for \( P_{MW} = 840 \) W compared to \( \frac{I_G}{I_D} = 0.847 \) for \( P_{MW} = 500 \) W could be an indication of the higher degree of crystalline perfection of carbon nanofibres synthesised at higher microwave power. Opposite conclusion could be drawn from half width Lorentzian peak comparison, where Raman spectra of carbon nanofibres synthesised at lower microwave power exhibit sharper corresponding D and G peaks \( \omega_G = 20 \) for \( P_{MW} = 500 \) W and \( \omega_G = 84 \) for \( P_{MW} = 840 \) W, see fitting data in Fig. 4.49).

![Raman spectra comparison](image)

**Figure 5.9.** Comparison of Raman spectra for carbon nanofibres grown using r.f. PECVD of methane on nickel powder catalyst at two substrate temperatures, room temperature (30 °C) with \( \frac{I_G}{I_D} = 1.154 \) and 250 °C with \( \frac{I_G}{I_D} = 1.041 \).

Existence of the shoulder peak at 1611 cm\(^{-1}\) in \( P_{MW} = 500 \) W spectra (Fig. 5.10 and Fig. 4.49b) was revealed after Lorentzian peak fitting routine. This peak could be
compared to MWCNT characteristic peak at 1620 cm\(^{-1}\) (Fig. 3.8), and could be further argument that is sometimes very hard to draw solid line of difference between catalytic MWCNT and CNF.

![Figure 5.10. Comparison of Raman spectra for carbon nanofibres synthesised by r.f. combined microwave PECVD at two different microwave powers of 840 W (I\(_g/I_d=1.232\)) and 500 W (I\(_g/I_d=0.847\)).](image)

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Chapter 6

CONCLUSIONS

6.1. CONCLUSIONS

Progress in understanding the basic physics and chemistry of carbon nanotubes (CNT) and carbon nanofibres (CNF) has advanced at a phenomenal rate and shows no signs of slowing. Researchers are developing a host of new technologies that creatively combine lithography, chemistry and nanoscale manipulation. Carbon nanotubes can behave like metals or semiconductors, can conduct electricity better than copper, can transmit heat better than diamond, and they rank among the strongest materials known. Catalytic CVD of hydrocarbon gases is able to generate large volumes of carbon nanotubes and nanofibres, comparatively cheaply, without the presence of contaminating nanoparticles.

A new catalytic method developed for the growth of carbon nanofibres at room temperature using radio frequency and radio frequency assisted microwave plasma-enhanced chemical vapour deposition (PECVD) has been described in this thesis. Radio-frequency plasma can produce structural changes and chemical reactions at room temperature to enable the growth of carbon nanofibres. To the best of my knowledge, this is the first evidence of the growth of carbon nanofibres at room temperature by any method. The use of a transition metal catalyst and carbon containing gas is required for the carbon nanofibre growth in radio frequency PECVD system at room temperature. Nickel powder was used as a catalyst in both systems and methane gas as the carbon source. In order to obtain room temperature (24-25 °C) CNF growth conditions in radio frequency assisted microwave PECVD system nickel powder was placed on a water-cooled sample holder. In radio frequency PECVD growth of CNF was at temperatures between 29 and 31 °C when additional heating source in the bottom electrode was not used. Room and low temperature growth conditions will allow the growth of carbon nanofibres on thermo-sensitive substrates, such as plastics and glass over relatively large
areas, which is a specially useful technique for the development of flat panel display applications. Radio frequency PECVD is a well established technique within the semiconductor industry and could be very suitable for the growth of carbon nanotubes for various electronic and photonic devices applications. Carbon nanofibres grown by radio frequency assisted microwave PECVD have characteristics of branching during growth, formation of “Y”-shaped junctions and their interconnecting networks. Using lower loading of branched carbon nanofibres in polymer composites compared to whisker-like nanofibres will further enhance conductivity of the matrix due to the lower percolation threshold. It might open up the possibility of creating interconnections for electronic devices on a nanometric scale and assembling new classes of materials from nanofibres. It is envisaged that a variant of the proposed catalytic effect could be used to grow aligned nanofibres as well as carbon nanotubes.

Carbon nanofibres were produced using thermal CVD by the decomposition of methane, and acetylene in temperatures ranging from 350 °C to 750 °C and pressures ranging from $10^{-3}$ to 2 mbar on nickel powder catalyst particles. It was found that optimum yield with a minimum of structural defects was obtained at temperatures between 450 and 550 °C. Furthermore, it was found that within the range examined pressure plays a secondary role when compared to temperature. Carbon nanofibres were grown on Ni catalyst supported on graphite and silicon wafer plates, and no difference between nanofibres grown on different support substrates was found. It was expected that thickness and/or length of produced carbon nanofibres would increase with deposition time, but results gave no indication of this pattern when deposition time was varied from 15 min to 3 hours. The length of entangled carbon nanofibres is very difficult to determine. Bi-directional growth from a diamond shaped particle in the middle of the carbon nanofibre has been observed more frequently when acetylene was used, compared to the carbon nanofibres grown under similar conditions using methane as a carbon source gas.

Ropes of roughly-aligned carbon nanofibres have been synthesised after nickel catalysed thermal CVD and plasma enhanced CVD. After deposition the carbon nanofibres containing powder was treated in 35% nitric acid from 3 to 10 minutes, and ropes have been observed in dried sediments. Rope diameters from 20 μm up to 80 μm,
and lengths up to few millimeters have been observed. CNF are self-organised into ropes by adhesion after functionalisation of the nanofibre surface by nitric acid action, and bundled together by van der Waals forces. These ropes could be ideal in composites where it is essential that a strong bond can be formed between the nanotubes and the host material. The dimensions of these ropes offer easy manipulation with opportunities for novel applications. These macroscopic CNF ropes could be used as a structural material on their own or as composite fillers.

The characterisation and structural analysis of the nanofibres were conducted using conventional scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with electron energy-loss study (EELS) and with Raman spectroscopy. It was observed “whisker-like” growth morphologies and bi-directional growth on the nickel catalyst. The diameter of CNF is in the range of 30 to 100 nm, and the length is from 0.5 to 5 μm. The CNF growth by CVD has the catalyst particle at the tip enveloped by a thin layer of carbon. TEM analysis shows well-ordered graphene sheets with the characteristic distance of 0.34 nm between planes. No structural or morphological differences between carbon nanofibres grown when carbon source was acetylene and methane were observed using SEM, TEM and Raman analysis. Energy-loss spectroscopy of the atomic core (K-edge) has shown similar characteristics as graphite. The sharp peak at 285 eV is due to transitions from 1s core level to the π* band and the band starting at 291 eV corresponds to the transitions to the π-orbital projected part of broad σ* band. The near-edge structure with sharply defined π* and σ* band features, confirms sp² hybridisation states of carbon (as in graphite). Raman spectroscopy studies have shown broad G and D peaks characteristic of fully graphitised and disordered carbon nanofibre structure. Some spectra have shown similarities with carbon nanotube Raman spectra indicating existence of more ordered structure.

On the basis of the experimental results, a growth model based on a carbon-metal eutectic synthesis process that gives rise to CNF growth at low temperature is proposed. Branching of carbon nanotubes involves more a complex growth mechanism that is yet to be determined.

The study presented in this thesis has proven that choosing a different catalyst is not a route to lower growth temperature such as room temperature. Using plasma energy
instead of thermal energy for chemical vapour deposition is a route to follow in order to achieve this goal. Carbon nanofibres and nanotubes produced by various methods used in this study have showed very similar morphological and structural characteristics. This can lead to the conclusion that neither different CVD synthesis method or gas mixture and pressure change within the operation range did not affect diameter or length of nanofibres and these factors do not play major role in tailoring carbon nanofibres properties. Baker and Rodriguez [6.1] concluded that the type of catalyst plays a major role in the resulting properties of carbon nanofibres, and the choice of metal catalyst particles is an effective way of controlling the structure of carbon nanofibres [6.1, 6.2]. In this study, nickel catalyst particles were used for all three synthesis methods and similar structures were obtained for all three CVD methods. Therefore, the results of this study support the theory that choice of catalyst is more important than variation of the CVD synthesis method in controlling the CNF structure.

6.2. SUGGESTIONS FOR FUTURE WORK

Catalytic radio frequency plasma enhanced CVD has possibility for the generation of large volumes of nanofibres on different substrates, such as plastics and organic substrates, which can only tolerate temperatures close to room temperature. This opens the door for future bulk production of these materials for the improvement of existing applications (like flat panel screens on plastic substrates) and development of novel applications, which could be only possible using the room temperature growth conditions. Further optimisation of growth method and conditions for bulk production is proposed. Catalytic carbon nanofibres grown using this method will have more structural defects comparing to those synthesised by arc-discharge graphite evaporation, however this might not be important for the majority of applications.

The plasma-enhanced CVD methods, described in this thesis, are the most promising candidates for the growth of well-aligned carbon nanotubes selectively on patterned substrate using the metal catalytic effect, where the growth temperature is not an obstacle (see Section 2.4.2). However, the conditions for the production of long,
aligned and well-graphitised nanotubes have yet to be optimised. Optimisation of growth conditions and use of different patterned and ion implanted catalyst is suggested for the future work. After full optimization of the area controlled carbon nanofibres growth on plastic substrates detailed study of the field emission properties, as described in Section 2.3.2, is suggested. Construction of the field emission display prototype (see Section 2.6.2) should be the final goal of this research. Optical properties of the CNF synthesised using r.f. PECVD could be promising for investigation and further work is recommended (see Section 2.3.5).

Further work is needed for full structural identification and characterisation of nanoropes. Investigation of the electrical and mechanical properties of nanoropes is also suggested. Especially it would be important to determine electrical conductivity following experiments described in Section 2.3.1, and determine stress-strain curve (see Section 2.3.3) in order to prove potentially fascinating mechanical properties. Since the long and wide ropes of aligned carbon nanotubes can be easily handled and manipulated it will be of importance for many applications.

Branched carbon nanofibres could be used in forming “Y”-shaped junctions in creating carbon nanofibres interconnections for electronic devices on a nanometar scale using nanomanipulation tools like AFM or nanotweezers described in Section 2.6.7. The first step is suggested to be investigation of the mechanical and electrical properties of these CNF junctions. Using AFM tip investigation of the mechanical properties of branched carbon nanofibres could be carried out in same manner like it was described in Section 2.3.3. Electrical properties of “Y” carbon nanofibre junctions could be investigated using techniques described in Section 2.3.1.

Further theoretical and experimental work is required to fully understand the mechanism of room temperature carbon nanofibres growth in r.f. PECVD. Computer modeling, like suggested in Appendix 3, is proposed and spectroscopy analysis of r.f. plasma during the CNF growth is recommended.

Realisation of the most fascinating idea of the carbon nanofibres growth in controlled manner on bio-substrates is opened after high temperature growth requirement was removed with work described in this thesis. Future work is recommended to fully explore this opportunity.
6. Conclusions

References

APPENDIX 1

Carbon nanotubes contaminants on TEM grids

In his book "Carbon Nanotubes and Related Structure" [al.1] Peter J. F. Harris has written a word of warning in the chapter 2.4 entitled “Nanotubes on TEM support grids: a word of warning”:

“When carrying out TEM studies of carbon nanotubes it is essential to be aware that nanotubes and nanoparticles can sometimes be present as contaminants on evaporated carbon support film. Needless to say, this is particularly important in studies aimed at exploring new methods for nanotube synthesis, and there are examples in the literature where these contaminants have almost certainly been mistaken for sample material. As result, several papers claiming new methods for nanotube synthesis should be treated with caution.”

In his study Peter J. F. Harris [a1.2] has examined ten unused evaporated carbon films supported on copper grids, obtained from two different suppliers. In his later study [a1.3], he has examined carbon films from four different suppliers: two from UK (Agar Scientific and Taab), one in the USA (SPI) and one in Japan (Oken Shoji; type B grids). The films were continuous, “holey” or “lacey”, and were supported on copper or nickel grids. Carbon nanotubes, nanoparticles and other graphic carbon structures were found to be present as contaminants on all of the grids examined.

Carbon contaminants often found on evaporated carbon support films for TEM include poorly graphitised carbon, fragments of graphite, and fullerene-like structures such as carbon nanotubes and nanoparticles [a1.1-a1.3]. In order to avoid the possibility that these contaminants could be mistaken for sample material, TEM characterisation of unused “holey” carbon films on copper grids was carried out.
A1.1 TEM characterisation of unused support grid

Carbon nanotube clusters, nanoparticles and other graphitic structures were found on unused “holey” carbon films obtained from Agar Scientific Ltd (Fig. A1.1-A1.4). These grids were later used for TEM characterisation of all material examined in this study.

Within the unused “holey” carbon grids, carbon nanotubes occurred in clusters with carbon nanoparticles (Fig. A1.1). The carbon nanotubes found on the grids were multiwalled carbon nanotubes coated with amorphous carbon (Fig. A1.2). Poorly graphitised carbon (Fig. A1.3) and smaller sheet-like partially graphitised particles in tube-like or globular form were also observed (Fig. A1.4).

![Image](a) (b)

**Figure A1.1.** (a) Cluster of carbon nanotubes and nanoparticles on unused “holey” carbon film supported on copper grids from Agar Scientific Ltd. (300 mesh), (b) enlarged central part of Fig A1.1a.
Figure A1.2. Carbon nanotubes coated with amorphous carbon found in unused "holey" carbon film supported on copper grid from Agar Scientific Ltd. (300 mesh).

Figure A1.3. Poorly graphitised carbon observed on unused "holey" carbon films supported on copper grids from Agar Scientific Ltd. (300 mesh).
As result of finding carbon nanotubes and nanoparticles on the unused “holey” carbon grids, very cautious TEM analysis of our samples was undertaken. Any structures similar to those shown in Fig. A1.1 to Fig. A1.4 were attributed to the “contaminants” on the “holey” carbon grid, not to our samples. It was generally easy to distinguish these forms of “contaminants” as a significant amorphous carbon normally surrounding them.

A1.2 TEM sample analysis

The conclusions of studies done by Peter J. F. Harris on unused TEM support grids resulted in greater caution when conduction TEM analysis of this type. In Fig. A1.5 a carbon nanofibre together with a cluster of carbon nanotubes is shown. Highly graphitised carbon nanotubes in clusters with carbon nanoparticles very similar to carbon nanotubes synthesised by carbon arc evaporation were observed during TEM examination of almost all samples produced using CVD methods of this study (Fig. A1.6). From studies of unused “holey” carbon films explained previously, it can be
concluded that only carbon nanofibre and not clusters of carbon nanotubes results of CVD experiment in this work.

![Figure A1.5](image_url)

**Figure A1.5.** Carbon nanofibre together with cluster of carbon nanotubes. The cluster of carbon nanotubes is a contaminant on the TEM grid, and was not synthesised in using CVD in this study.
Figure A1.6. (a) Cluster of carbon nanotubes together with nanoparticles, and (b) multiwalled carbon nanotube from this cluster. The cluster of carbon nanotubes with nanoparticles is highly likely to be a contaminant on TEM grid, and not synthesised in CVD in this study.

Using the conclusions study conducted by Peter J. F. Harris, it is concluded the structures observed in Fig. A1.5 and Fig. A1.6 are more likely to be product of arc discharge process rather than a low temperature CVD process. Throughout this study, extra caution has been used to distinguish between TEM support grid contaminants and this study samples. It is concluded that the results presented as low temperature grown PECVD CNF definitively arise from the growth in our chamber rather than as a result of contamination of the grids. The fact that CNF are observed in SEM analysis proves that synthesis was achieved.
References


APPENDIX 2

Raman Spectra Fit

The aim of the fitting procedure is to find those values of the parameters which best describe the data. The standard way of defining the best fit is to choose the parameters so that the sum of the squares of the deviation of the theoretical curve from the experimental points for a range of independent variables is at its minimum. This procedure is called the Chi$^2$ ($\chi^2$) test. Two functions Lorentzian and Gaussian were used for Raman spectra fitting. It was found that Lorentzian function fitting much better represents Raman spectroscopy data for carbon nanofibres. Peak frequencies of the Raman spectra were determined using two, three or four Lorentzian fittings.

Lorentzian peak function is defined by equation

$$y = y_o + \frac{2A}{\pi} \frac{w}{4(x-x_c)^2 + w^2},$$  \hspace{1cm} (a2.1)

where

$y_o$ is baseline offset,
$A$ is total area under the curve from the baseline
$x_c$ is centre of the peak
$w$ is full width of the peak at the half height.

Area version of Gaussian function

$$y = y_o + \frac{A}{w\sqrt{\pi}/2} e^{-\frac{(x-x_c)^2}{w^2}},$$  \hspace{1cm} (a2.1)

where $w \approx 2\sigma$ is approximately 0.849 the width of the peak at the half height.

The Raman spectra fittings for carbon nanofibres synthesised using acetylene at $T=500$ °C are presented in Fig. A2. Comparison of two peak Lorentzian and Gaussian fitting routine is shown in Fig. A2.1a and Fig. A2.1b.
Figure A2.1. Raman spectra fitting: (a) two Gaussian, (b) two Lorentzian, (c) three Lorentzian, and (d) four Lorentzian.
Two peak Lorentzian fitting (Fig. A2.1b) has shown a much smaller Chi$^2$ value ($\text{Chi}^2 = 16439$) compared to two peak Gaussian fitting ($\text{Chi}^2 = 27727$). Three Lorentzian fitting routine (Fig. A2.1c) has shown a significantly smaller Chi$^2$ value ($\text{Chi}^2 = 7871$) indicating a much better curve fit. Four Lorentzian fitting (Fig. A2.1d) has shown a much smaller improvement in Chi$^2$ value ($\text{Chi}^2 = 6792$) for Raman spectra of carbon nanofibres synthesised using acetylene at 500 °C.
Molecules can absorb and emit energy by alternating the state of motion of their constituent atoms, where they can vibrate or rotate. The energy associated with either motion is quantised, and molecules possess rotational and vibrational energy levels in addition to those due to their electrons. Only polar molecules will experience forces via the electric field of an incident electromagnetic wave that will cause them to rotate into an alignment, and only they can absorb photon and make rotational transition to an exited state. Since massive molecules cannot easily rotate it can be anticipated that they will have low rotational resonance. Water molecules are polar and when exposed to an electromagnetic wave, they will rotate, trying to stay in line with the alternating electric field. This effect will be extremely intensified at any of its rotational resonance frequencies. Consequently water molecules efficiently and dissipatively absorb microwave radiation at or near such frequencies. In the microwave oven (2.45 GHz, 12.2 cm) electromagnetic radiation will be efficiently transformed into rotation of water molecules and this will result in heating of water. Non polar molecules, such as carbon dioxide, hydrogen, nitrogen and methane cannot make rotation transitions by absorbing of photons. The weak attractive forces between neighboring molecules contribute to the mechanism responsible for dielectric heating.

The interaction of electromagnetic wave with materials is determined by the electrical and magnetic properties of a material, most importantly permittivity $\varepsilon$ and permeability $\mu$. Permittivity and permeability are defined as:

$$\varepsilon = \varepsilon' - j\varepsilon'' = \varepsilon_0 (\varepsilon'_r - j\varepsilon''_r), \quad (a3.1)$$
$$\mu = \mu' - j\mu'' = \mu_0 (\mu'_r - j\mu''_r), \quad (a3.2)$$

where

- $\varepsilon'$ is dielectric constant,
- $\varepsilon''$ is loss factor,
- $\varepsilon'_r$ is relative dielectric constant,
Appendix 3 – Electromagnetic heating

\[ \varepsilon''_{\text{eff}} \] is effective relative loss factor, \( \varepsilon''_{\text{eff}} = \varepsilon''_r + \frac{\sigma}{\varepsilon_0 \omega} \)

\[ \varepsilon'_r \] is relative loss factor,

\[ \sigma \] is conductivity,

\[ \mu' \] is permeability,

\[ \mu'' \] is magnetic loss factor

\[ \mu'_r \] is relative permeability, and

\[ \mu''_{\text{eff}} \] is effective relative magnetic loss factor.

From Maxwell’s equations it can be shown [a3.1], that power absorbed in a volume \( V \), where \( E \) is internal electric field is

\[
P_a = \int_{V} 2\pi f \varepsilon'' |E|^2 \, dv,
\]

where \( f \) is frequency of electromagnetic irradiation and \( \varepsilon'' = \varepsilon_0 \varepsilon''_{\text{eff}} \) is effective dielectric loss factor. The magnitude of the internal field is the attenuated magnitude of the incident electric field

\[
E = E_0 e^{-\alpha z},
\]

where \( \alpha \) is the attenuation constant defined as:

\[
\alpha = \frac{\sigma}{2} \left( \frac{\mu}{\varepsilon} \right)^{1/2}, \quad \frac{\sigma}{\omega \varepsilon} < 1.
\]

Attenuation of electric field is a result of the transfer of the electromagnetic energy into thermal energy within a material, i.e. heating. As a result of electromagnetic wave propagation into the material the wavelength changes according to the following relationship:

\[
\lambda = \frac{\lambda}{\sqrt{\varepsilon'_r}}, \quad \text{for} \quad \varepsilon''_{\text{eff}} \ll \varepsilon'_r.
\]

By measuring the change in the wavelength and attenuation of the wave, the properties of the material can be determined.

When \( E \) is replaced by Eq. (a3.4), Eq. (a3.3) for homogeneous and isotropic material becomes:

\[
P_a = 2\pi f \varepsilon_0 \varepsilon''_{\text{eff}} E^2_0 \int_{V} e^{-2\alpha z} \, dv.
\]

For a cylinder of unit cross section and height \( d \) equation (a3.7) becomes
\[ P_s(z) = 2nf \varepsilon_0 \varepsilon_{\text{eff}}^n E_0^2 \int_0^d e^{-2a_z} dz, \quad (a3.8) \]

\[ P_s(d) = 2nf \varepsilon_0 \varepsilon_{\text{eff}}^n E_0^2 \frac{1}{2a} (1 - e^{-2a_d}). \quad (a3.9) \]

The heat generated in the medium is transmitted in the material by conduction, convection, and radiation \[ [a3.2] \]. The heat flux transmitted in the \( x \) direction is given by

\[ q_x = -\Lambda s \frac{dT}{dx}, \quad (a3.10) \]

where \( \Lambda \) is thermal conductivity and \( s \) the flux cross section area.

Radiation occurs only at the surface of the material. From the Stefan-Boltzmann law, the radiated heat flux is

\[ q_r = \sigma_s e S T^4, \quad (a3.11) \]

where Stefan-Boltzmann constant is \( \sigma_s = 5.67 \times 10^{-8} \text{Wm}^{-2}\text{K}^{-4} \), \( S \) is radiating area, and \( e \) is emissivity coefficient.

Convection occurs only in liquids and the corresponding heat flux is

\[ q_c = \alpha_c s \Delta T, \quad (a3.12) \]

where \( \Delta T \) is temperature differential, \( s \) is cross section area, and \( \alpha_c \) is the heat transfer coefficient.

Consider a medium in which heat transfer occurs by conduction alone. Microwave and radio frequency heating of the medium can be described by standard equation for heat transfer, including a term for internal heat release. For a slab

\[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} + \frac{q(x,y,z)}{\Lambda} = \frac{1}{a} \frac{\partial T}{\partial t}, \quad (a3.13) \]

where \( a \) is the thermal diffusivity

\[ a = \frac{\Lambda}{\rho C_p}, \quad (a3.14) \]
where \( \rho \) is density, \( C_p \) the specific heat at constant pressure, and \( q(x,y,z) \) is the power per unit volume (in Wm\(^{-3}\)) generated by microwaves or radio frequency at \((x,y,z)\):

\[
q = \frac{P}{V}.
\]  

(a3.15)

For cylindrical or spherical object Eq. (a3.13) is

\[
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{q(z,r)}{\Lambda} = \frac{1}{a} \frac{\partial T}{\partial t},
\]

(a3.16)

\[
\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} + \frac{q(r)}{\Lambda} = \frac{1}{a} \frac{\partial T}{\partial t}.
\]

(a3.17)

For a slab of thickness \( d \) in which \( T(x_0, 0) \) is the temperature at time \( t=0 \), the temperature at \( x \) at time \( t \) is

\[
T(x,t) = \frac{1}{2\pi} \int_0^d T(x_0,0) \sqrt{\frac{\pi}{at}} e^{-\frac{(x-x_0)^2}{4at}} dx_0.
\]

(a3.18)

Radio frequency and microwave heating could be computer modeled using the above equation. The time could be discretised in successive intervals of \( \Delta t \) and the material in slices of \( \Delta x \) to simulate \( T(x) \) curve by series of segments [a3.3].

References


